Ground state energy and low-energy excitations

The sum over the filled states

$$E_0 = N\alpha + 4\beta \sum_{|k| \le \frac{\pi}{2}} \cos(k)$$

$$E_0 = N\alpha + \frac{2\beta N}{\pi} \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \cos(k)\, dk = N\left(\alpha + \frac{4\beta}{\pi}\right)$$

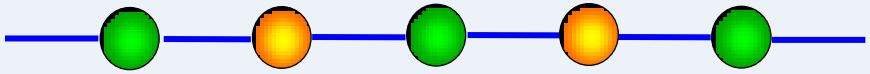
The energy of an electron moving in the field of an ion chain: the quasi-particle nature of low-energy excitations

$$\lambda = \alpha + 2\beta\cos(k) = \alpha + 2\beta - \beta\left(\frac{2\pi a}{L} l\right)^2, \quad l = 0, 1, 2 \ldots << N$$

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi(x)}{(dx)^2} = \lambda\Psi(x) \rightarrow \lambda = \frac{h^2 l^2}{2mL^2}$$

$$m = \frac{\hbar^2}{2|\beta|\, a^2}$$

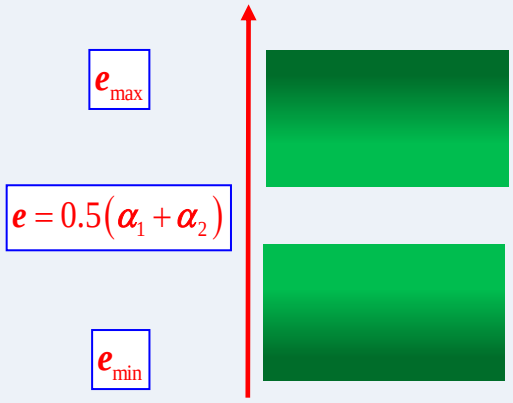
Polynitrile chain



$$\varphi_l = \sum_{m=1}^{N}\left(a_{m,l} f_m + b_{m,l} g_m\right),\ k_l = \frac{2\pi}{N} l$$

$$a_{m,l} = x\exp\left(ik_l m\right),\ b_{m,l} = y\exp\left(ik_l m\right)$$

$$\begin{cases}\left(\alpha_1 - e_k\right)x + \left(1+\exp(-ik)\right)\beta y = 0\\ \left(\alpha_2 - e_k\right)y + \left(1+\exp(ik)\right)\beta x = 0\end{cases}$$

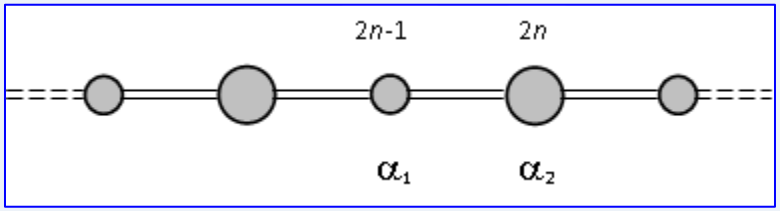


$$e_k = \frac{\alpha_1 + \alpha_2}{2} \pm \left[\left(\frac{\alpha_1 - \alpha_2}{2}\right)^2 + 4\beta^2 \cos^2\left(\frac{k}{2}\right)\right]^{1/2}$$

$$\lim_{N\to\infty}\left(\Delta E\right) = \left|\alpha_1 - \alpha_2\right|$$

$$e_{max,(min)} = 0.5\left\{\alpha_1 + \alpha_2 \pm \left[\left(\alpha_1 - \alpha_2\right)^2 + 16\beta^2\right]^{1/2}\right\}$$

Elementary excitations in a semiconductor as quasiparticles



$$\lambda_k = \frac{\alpha_1 + \alpha_2}{2} + \left[\left(\frac{\alpha_1 - \alpha_2}{2} \right)^2 + 4\beta^2 \cos^2 \left(\frac{k}{2} \right) \right]^{1/2}$$

Near the Fermi level:

$$k = \pi + \frac{4\pi}{N} l, \quad l = 0, 1, 2 \ldots$$

$$\Delta\lambda_k = |\alpha_1 - \alpha_2| \left(\frac{2\beta}{\alpha_1 - \alpha_2} \right)^2 \sin^2 \left(\frac{\pi}{N} l \right)$$

$$m = \frac{\hbar^2 |\alpha_1 - \alpha_2|}{8(\beta a)^2}$$

Electrical conductivity of solids

Electrical conductivity is the property of a body to conduct an electric current.

Voltage-current characteristic: $J = f(E)$,

Specific electrical conductivity : $\sigma = dJ/dE$

Specific resistivity: $\rho = \sigma^{-1} = R * S/l$

Linear voltage-current characteristic (Ohm's law): $J = \sigma E$

According to the value of electrical conductivity σ (in units of ohm^{-1} cm^{-1}), all solids are divided into three groups:

1) conductors ($\sigma > 10^4$); (various metals)
2) semiconductors ($10^{-10} < \sigma < 10^4$); (graphite, boron, germanium)
3) dielectrics ($\sigma < 10^{-10}$) (diamond).

Organic metals (OM)

Organic or synthetic metals are organic compounds with metallic conductivity.
Specific electrical conductivity OM – 10-10^5 ohm^{-1} *cm^{-1}

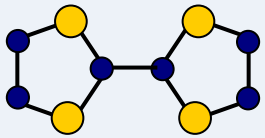
OM can be divided by structure into two types:

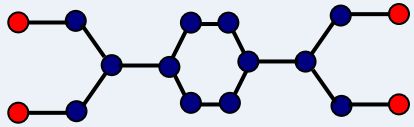
1. Polymers (polyacetylene, polypyrrole, polyaniline)
2. Crystals with charge transfer, for example, salts of tetracyanoquinodimethane (TCNQ)

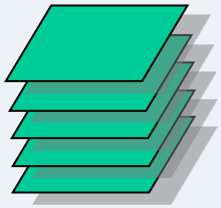
Conducting polymers based on hydrocarbons (polyacetylene, polypyrrole, polyparaphenylene, polythiophene, etc.) have conjugated bonds along their entire length, which gives the delocalization of π-electrons along the polymer molecule.

Charge transfer polymer complexes

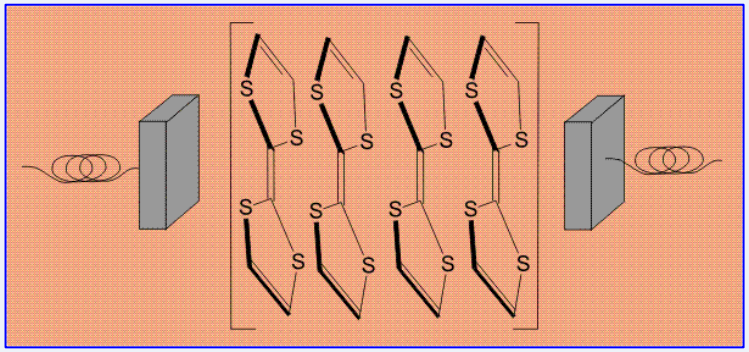
TTF·TCNQ:







$$Д + A \leftrightarrow Д^{+} + A^{-}$$



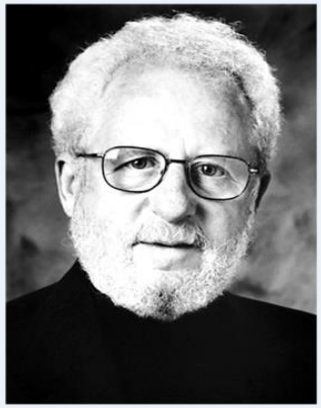
Conducting polymers (CP)

CP can combine the mechanical properties of plastics (flexibility, strength, elasticity, etc.) with high electrical conductivity. Their properties can be precisely adjusted using methods of organic synthesis.

Application:
Antistatic coatings
Corrosion inhibitors
Electromagnetic protection for computers
Solar panels
Displays of mobile phones
LEDs and transistors

Polyacetylene

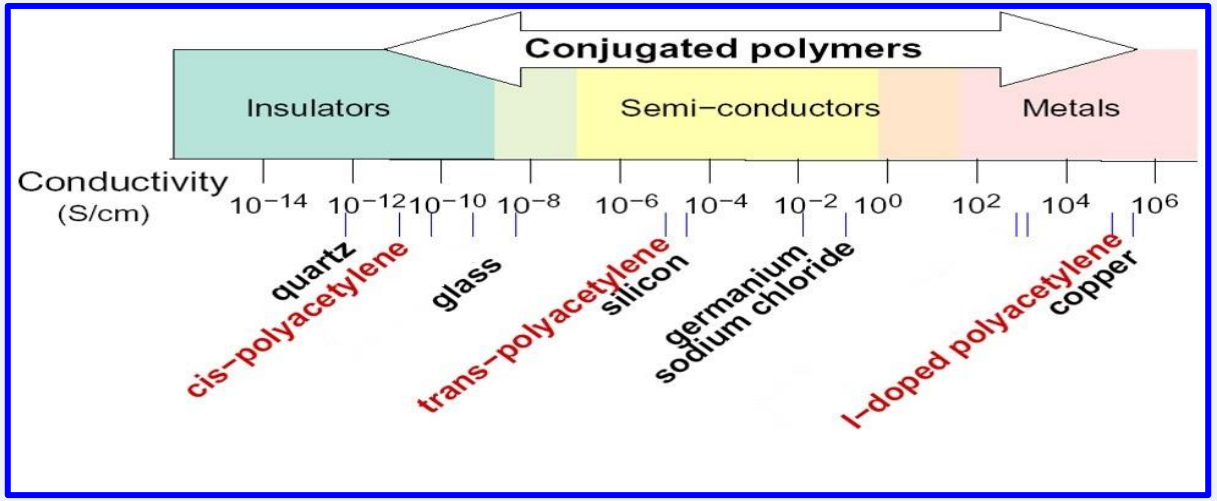
Nobel Prize in Chemistry 2000： for the discovery and development of conductive polymers



Alan J. Heeger

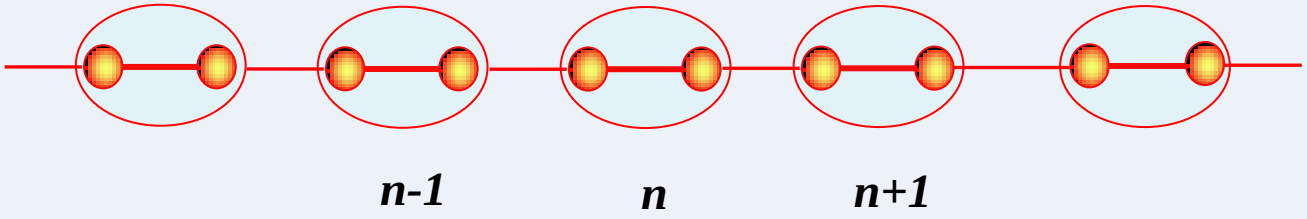
Alan G. MacDiarmid

Hideki Shirakawa



Peierls instability

The ground state of the dimerized chain



$$\beta(r) = \beta(0) + \left(\frac{d\beta}{dr}\right)_{r=0} r = \beta_0 + Ar = (1+x)\,\beta_0$$

$$(1-x)\,b_{n-1} + (1+x)\,b_n = \varepsilon\, a_n$$

$$(1+x)\,a_n + (1-x)\,a_{n+1} = \varepsilon\, b_n$$

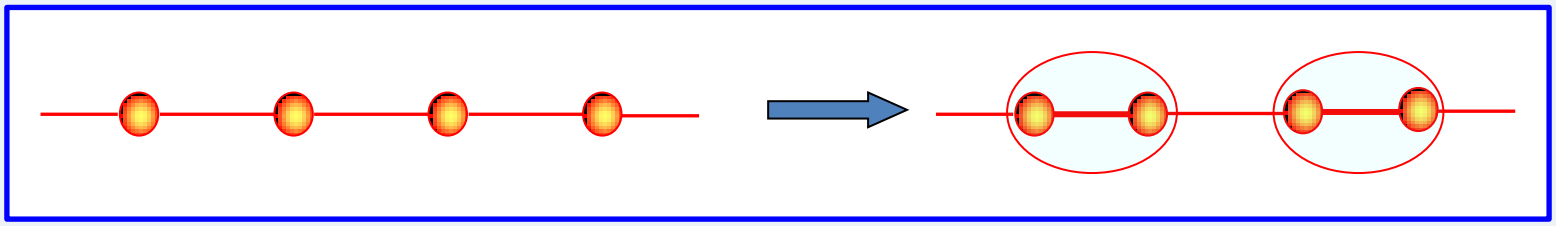
$$\varepsilon_k = \pm 2(\cos^2(k/2) + x^2\sin^2(k/2))^{1/2}$$

$$E_0/N = -4/\pi E(p),\ p^2 = 1-x^2$$

$$E_0/N = -4/\pi(1 + x^2 ln(4/x)/2)$$

Peierls instability

Stabilization of the structure due to the symmetry reduction



$$\mathbf{H}\left(R_0+\delta R\right)=\mathbf{H}\left(R_0-\delta R\right),\quad 0<x=\delta R/R_0<<1$$

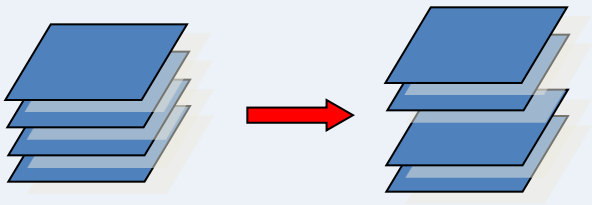
$$E_0\left(x\right)=E_0\left(-x\right)\rightarrow \Delta E_1=0,\ \Delta E_2<0\ \rightarrow\ \Delta E_\pi<0$$

$$\Delta E_\pi\sim x^2\ln x<0,\quad \Delta E_v=\frac{Kx^2}{2}>0$$

Peierls transition in crystals TTF·TCNQ

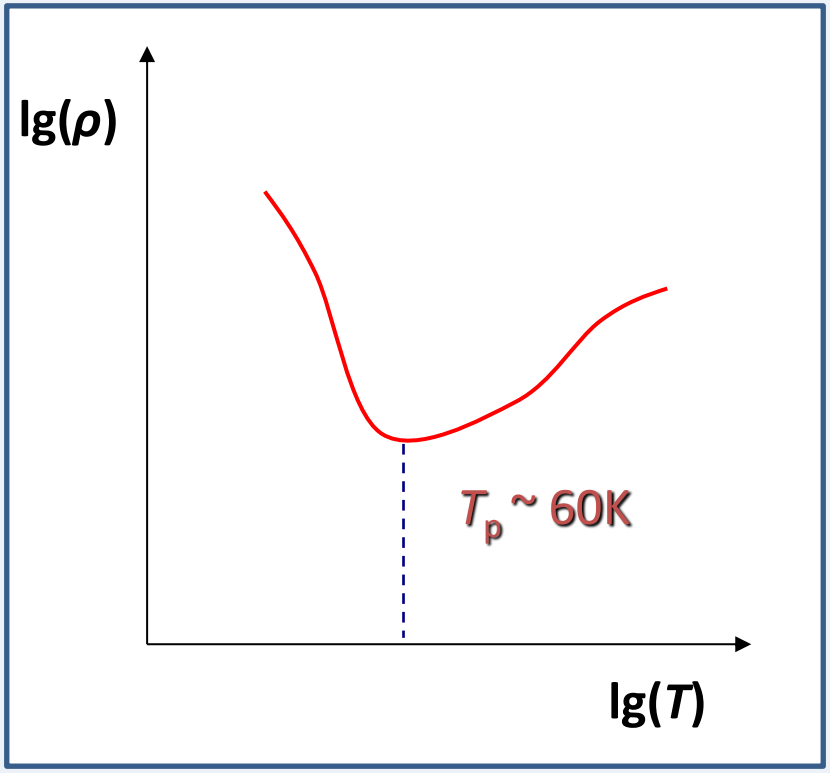
(taking into account the three-dimensional electron-phonon interaction)

TTF·TCNQ:



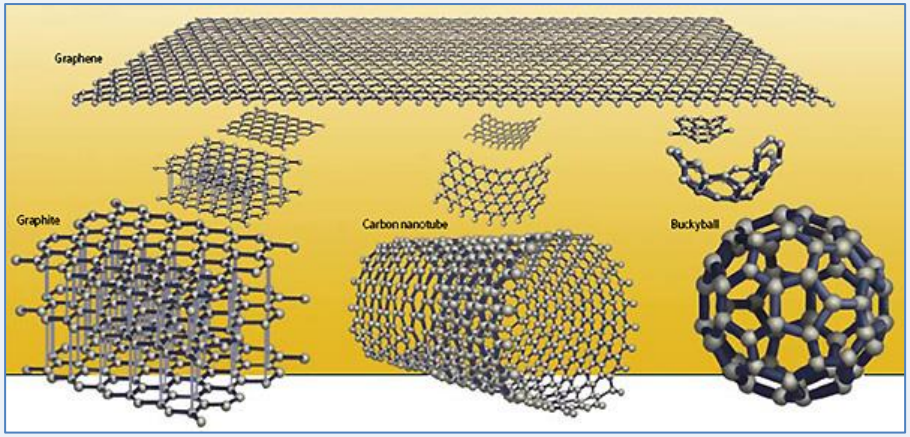
(doubling of the crystal lattice period)

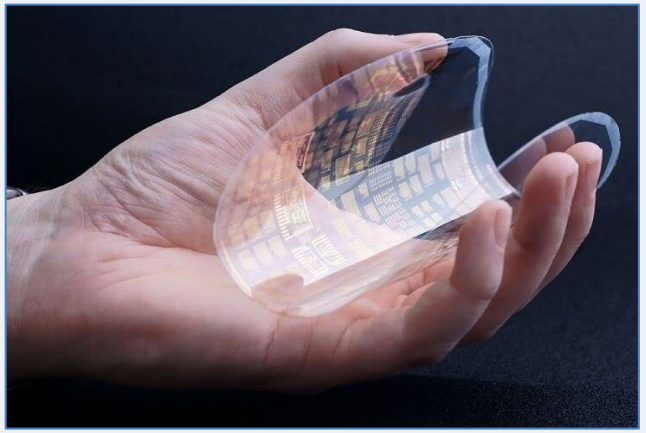
$(TSeT)_2Cl$: T_p~24K



Graphene

Graphene is a crystalline two-dimensional surface one or two atomic layers thick.
A. Heim and K. Novosyolov: formation of a two-dimensional crystalline surface on a silicon oxide substrate.





Several billion dollars have been allocated for graphene research, and scientists predict that this material will be able to replace silicon in the semiconductor industry.

Graphene and its properties

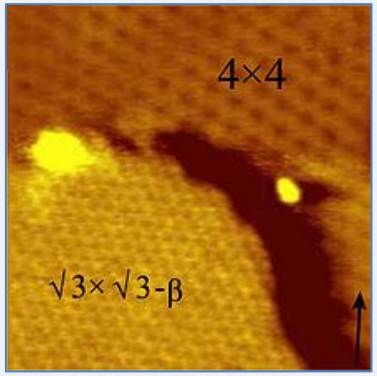
Graphene is a two-dimensional allotropic modification of carbon, formed by a layer of carbon atoms one atom thick. Carbon atoms are sp^2-hybridized and connected by σ- and π-bonds in a hexagonal two-dimensional crystal lattice. It can be imagined as one plane of layered graphite separated from the bulk crystal.

The high mobility of charge carriers, which is the maximum among all known materials (at the same thickness), makes it a promising material for use in various fields, in particular, as the future basis of nanoelectronics and a possible replacement of silicon in integrated circuits. Due to strong carbon non-covalent bonds, graphene is inert to acids and alkalis at room temperature. However, the presence of certain chemical compounds in the atmosphere can lead to doping of graphene, which has found application in record-sensitive sensors - detectors of individual molecules.

Graphene batteries

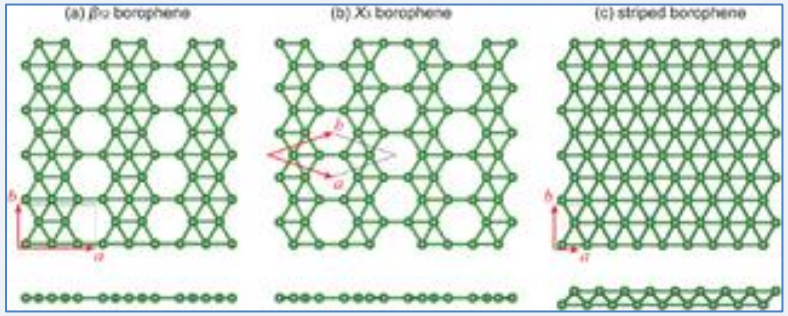
On the basis of graphene, a rechargeable battery was developed in Spain, which is 77% cheaper than lithium analogues, is twice as light in weight and can be fully charged in just 8 minutes. This charge is enough for 1,000 kilometers of electric vehicle mileage, while the most modern mass-produced electric vehicles with lithium batteries require several hours to charge, and the charge is only enough for 300 kilometers.

Analogues of graphene



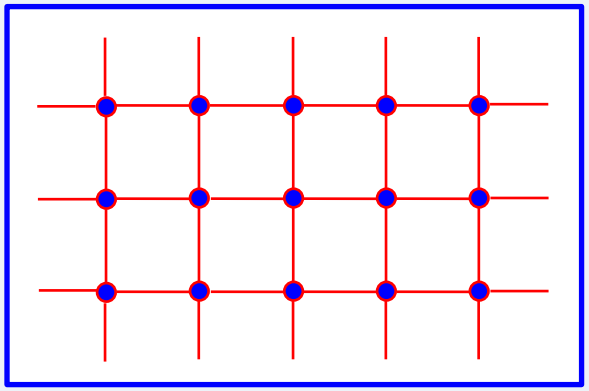
Silicene is a two-dimensional allotropic compound of silicon, similar to graphene, in which at least part of the atoms are in sp^2-hybridization

Silicene was grown on a ZrB_2 substrate in 2012



Borophene is a two-dimensional crystal consisting only of boron atoms. Several forms of borophene are obtained experimentally, many others are predicted theoretically.
Borographene - graphene doped with boron.

The energy spectrum of a square lattice in the Huckel method



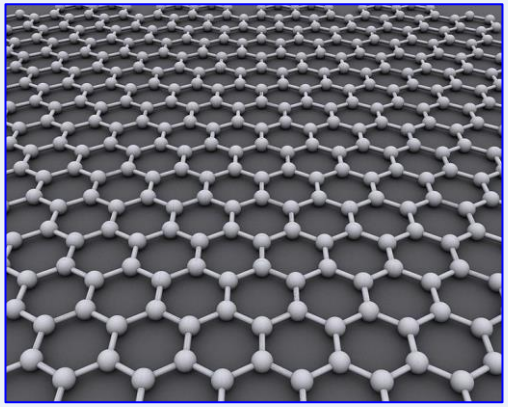
$$\begin{cases} (\alpha-\lambda)a_{1,1}+\beta a_{1,2}+\beta a_{1,N}+\beta a_{2,1}+\beta a_{M,1}=0 \\ \beta a_{1,1}+(\alpha-\lambda)a_{1,2}+\beta a_{1,3}+\beta a_{2,2}+\beta a_{M,2}=0 \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ \beta a_{M,N-1}+\beta a_{M,1}+\beta a_{1,N}+\beta a_{M-1,N}+(\alpha-\lambda)a_{M,N}=0 \end{cases}$$

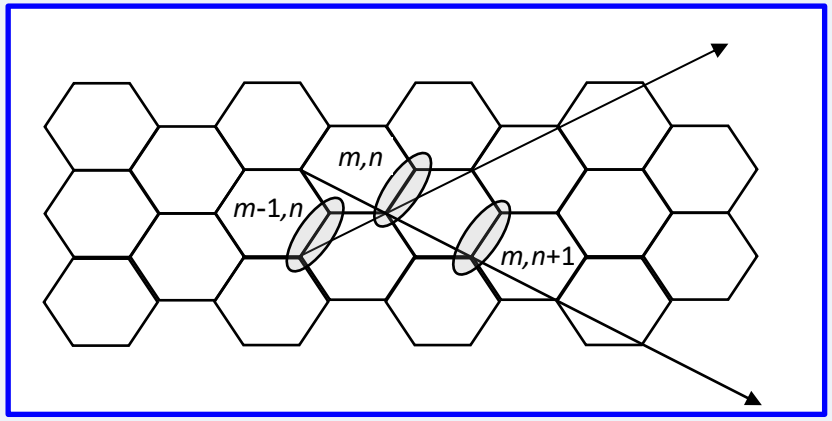
$$\begin{cases} a_{m,n}=a_{m,n+N} \\ a_{m,n}=a_{m+M,n} \end{cases} \qquad a_{m,n}=A\exp(ik_1m+ik_2n) \qquad \lambda=\alpha+2\beta\left[\cos(k_1)+\cos(k_2)\right]$$

$$k_1=\frac{2\pi}{M}l_1, \quad l_1=0,1,2\ldots M-1, \qquad k_2=\frac{2\pi}{N}l_2, \quad l_2=0,1,2\ldots N-1$$

$$\lambda=\alpha+4\beta\cos\left(\frac{k_1+k_2}{2}\right)\cos\left(\frac{k_1-k_2}{2}\right) \qquad \varepsilon_0=\alpha+\frac{4\beta}{\pi^2}\int_{-\frac{\pi}{2}}^{\frac{\pi}{2}}\int_{-\frac{\pi}{2}}^{\frac{\pi}{2}}\cos(x)\cos(y)dxdy=\alpha+\frac{16\beta}{\pi^2}$$

Graphene in the Huckel method





$$\begin{cases} (\lambda-\alpha)a_1(m,n)=\beta\left[a_2(m,n)+a_2(m-1,n+1)+a_2(m-1,n)\right] \\ (\lambda-\alpha)a_2(m,n)=\beta\left[a_1(m,n)+a_1(m+1,n-1)+a_1(m+1,n)\right] \end{cases}, \quad \begin{matrix} m=1,2\cdots M, \\ n=1,2\cdots N \end{matrix}$$

$$\begin{cases} a_i(m,n)=a_i(m+M,n) \\ a_i(m,n)=a_i(m_1,n+N) \end{cases}, \quad i=1,2 \qquad \begin{cases} a_1(m,n)=x\exp(ik_1m+ik_2n) \\ a_2(m,n)=y\exp(ik_1m+ik_2n) \end{cases} \qquad \begin{matrix} k_1=\dfrac{2\pi}{M}l_1, & l_1=0,1,2\ldots M-1, \\ k_2=\dfrac{2\pi}{N}l_2, & l_2=0,1,2\ldots N-1 \end{matrix}$$

The energy spectrum of graphene

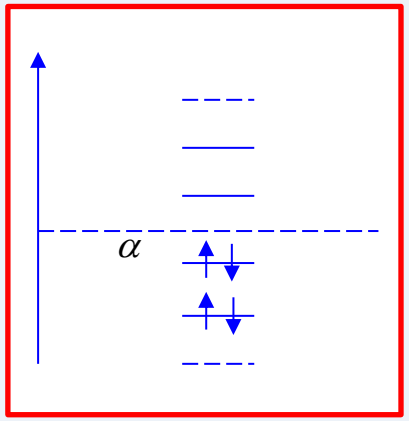
One-electron states in Huckel method

$$\begin{cases} (\lambda-\alpha)x = \beta y\left[1+\exp(-ik_1)+\exp\left(i(k_2-k_1)\right)\right] \\ (\lambda-\alpha)y = \beta x\left[1+\exp(ik_1)+\exp\left(i(k_1-k_2)\right)\right] \end{cases}$$

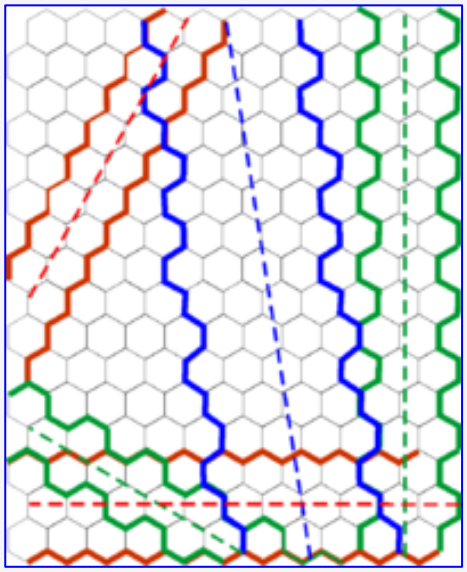
The absence of the energy gap

$$\lambda = \alpha \pm \beta\left[3+2\cos(k_1)+2\cos(k_2)+2\cos(k_1-k_2)\right]^{1/2}$$

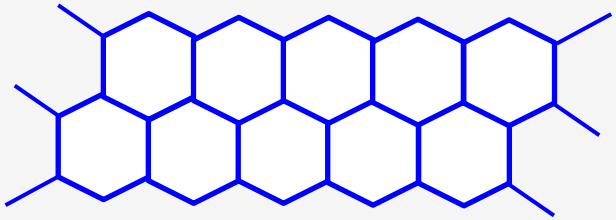
$$\left(k_1=\frac{2\pi}{3}, k_2=\frac{4\pi}{3}\right) \qquad \left(k_1=\frac{4\pi}{3}, k_2=\frac{2\pi}{3}\right)$$

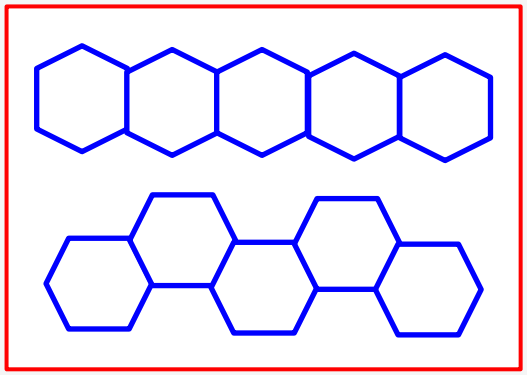


Graphene nanoribbons

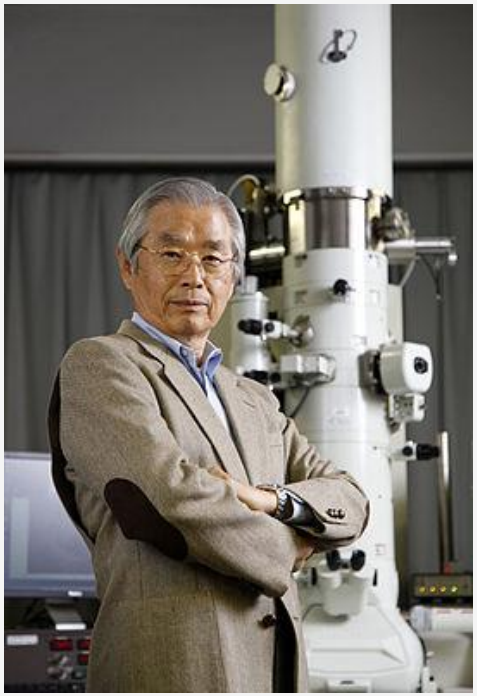


Methods of cutting the graphene plane into nanoribbons. The dotted lines correspond to the centers of the nanoribbons. Red lines correspond to nanoribbons with zigzag edges (acene edge), and green lines to armchair edges (phenanthrene edge). The blue nanoribbon has a mixed boundary type.

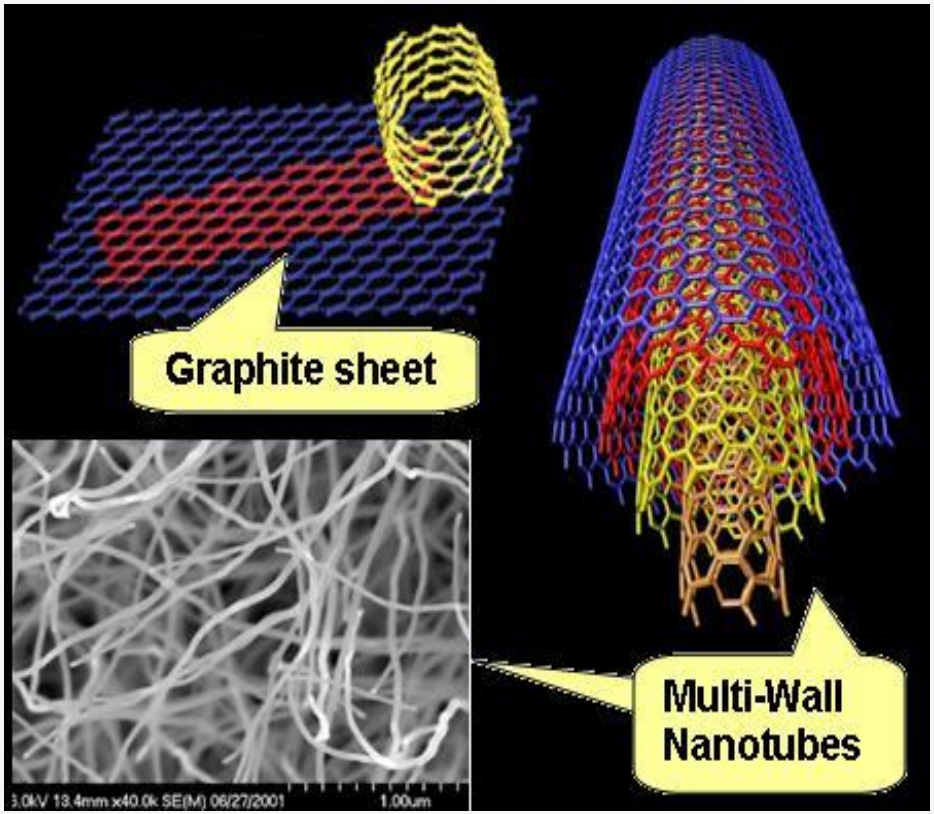




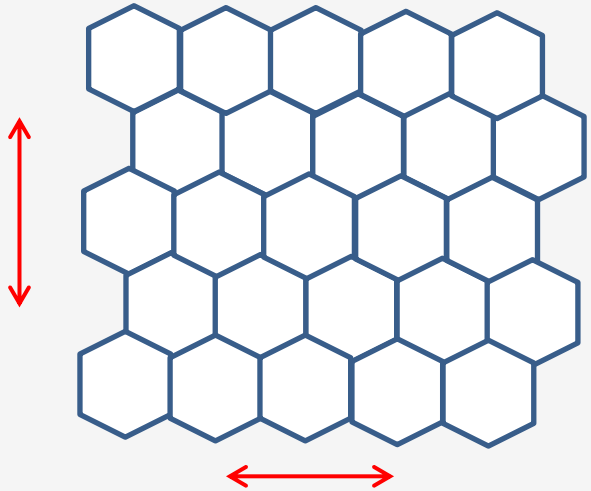
Carbon nanotubes (CNT)

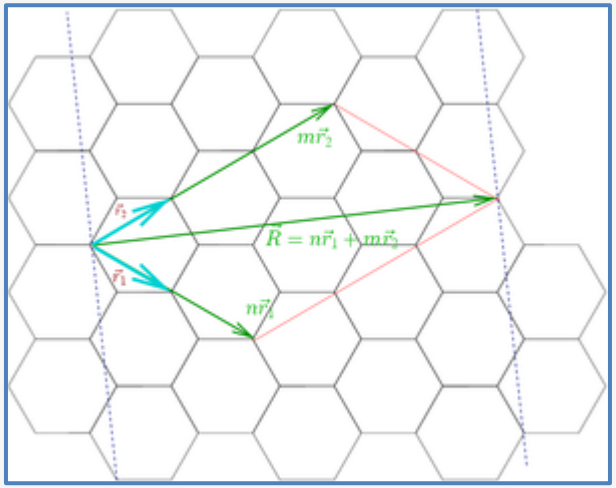


Sumio Iijima 1991.



The structure of single-layer nanotubes





Types of nanotubes

1. Armchair: $m=n$
2. Zigzag $m=0$
3. Chiral $m \neq n$

$$c = \sqrt{a^2 + b^2 - 2ab\cos\varphi}$$

$$D = \frac{r\sqrt{3}}{\pi}\sqrt{n^2 + m^2 + nm}, \quad r = 1.42A$$

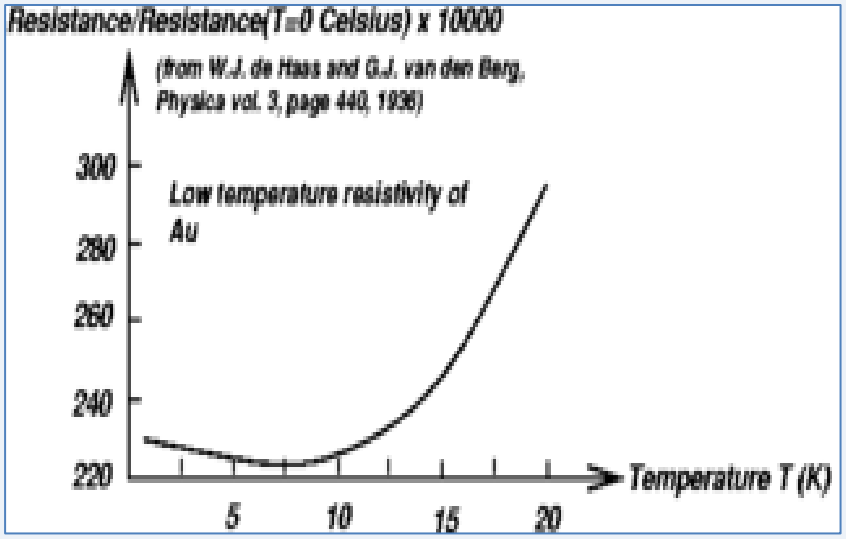
Electrical conductivity of nanotubes

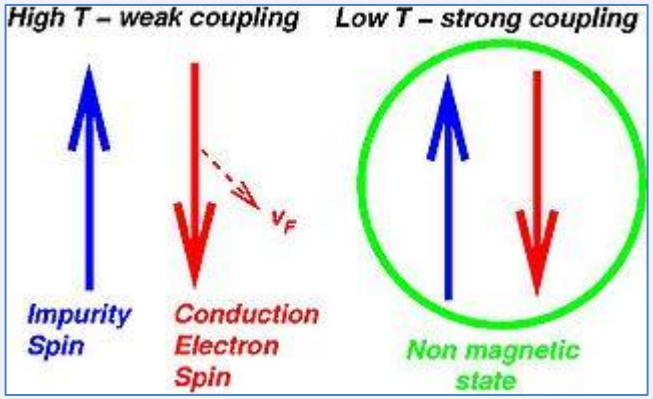
Calculations showed that the metallic type of zone structure has those for which the difference n - m is a multiple of three, i.e. a third of the nanotubes. The rest of the nanotubes must be semiconductors. It took six years for the quantum-chemical prediction to be confirmed experimentally.

Conductivity in single-layer carbon nanotubes is quantized due to their one-dimensionality. Nanotubes behave like quantum wires, and charge carriers are transferred through discrete conduction channels. This conduction mechanism can be ballistic or diffusive in nature or based on tunneling. In the ballistic mechanism, electrons pass through the nanotube channel without experiencing scattering due to impurities, local defects, or lattice oscillations. As a result, electrons do not encounter resistance, and energy dissipation does not occur in the conduction channel.

Kondo effect

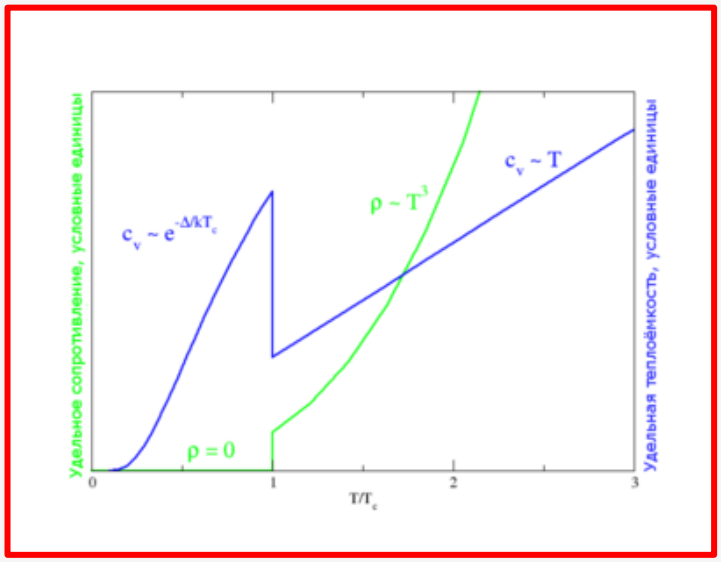
The Kondo effect is the effect of increasing the electrical resistance of non-magnetic metal alloys weakly doped with magnetic impurities at temperatures close to absolute zero. The temperature at which the minimum resistance is observed is called the Kondo temperature.

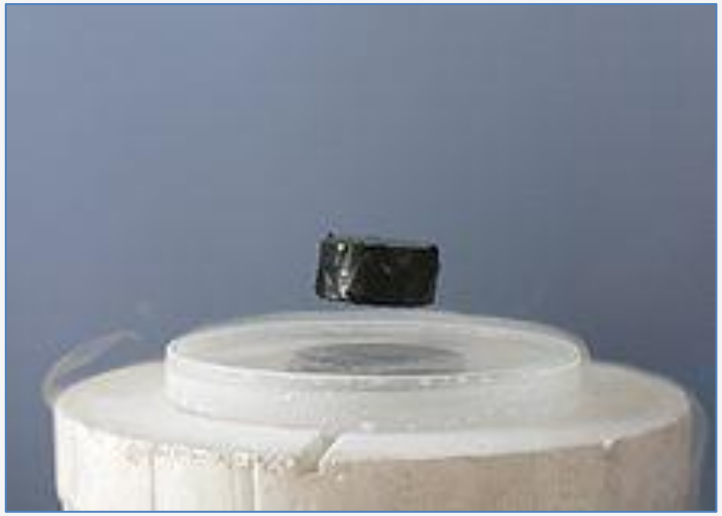




Superconductivity

Superconductivity is the property of some materials to have strictly zero electrical resistance when they reach a temperature below a certain value (critical temperature). Several hundreds of compounds, pure elements, alloys, and ceramics are known that transition into a superconducting state.



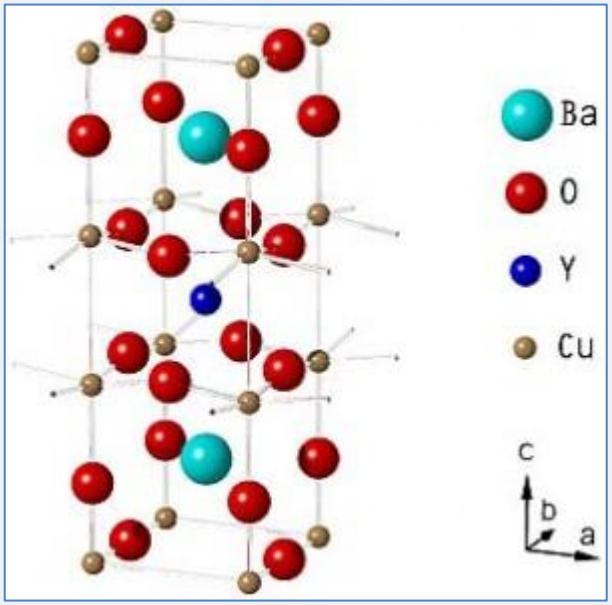


Bardin-Cooper-Schriefer theory (BCS)

Electrons near the Fermi surface can undergo effective attraction, via the interactions with phonons. These electrons are combined into pairs, called Cooper pairs. Cooper pairs, unlike individual electrons, have a number of properties characteristic of bosons, which, upon cooling, can enter one quantum state.

This feature allows the pairs to move without collision with the lattice and other electrons, that is, without energy loss (superfluidity of Cooper pairs).

High-temperature superconductivity



BCS theory: the maximum value of the critical temperature cannot exceed 40K. HTSC - superconductors with a critical temperature higher than the boiling point of nitrogen (77 K or -196 ° C). The first compound from the class of high-temperature superconducting cuprates $La_{2-x}Ba_xCuO_4$ was discovered by Karl Müller and Georg Bednorz in 1986. The substance $HgBa_2Ca_2Cu_3O_{8+x}$ has a record critical temperature value of T_c = 135 K x. Hydrogen sulfide under a pressure of ~ 1400000 atm. has T_c = 203 K.