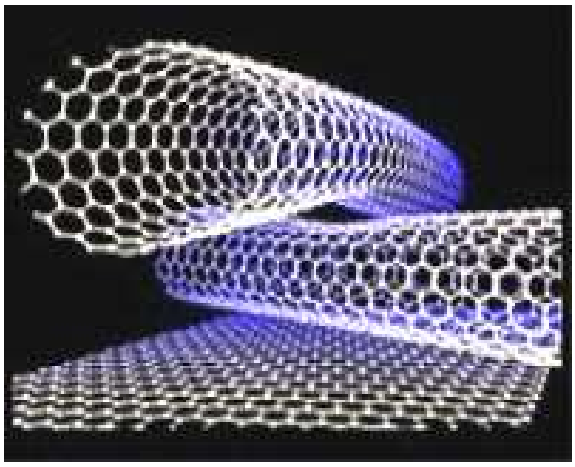
ELECTRONIC INSTABILITIES AND SUPERCONDUCTIVITY OF CARBON NANOTUBES

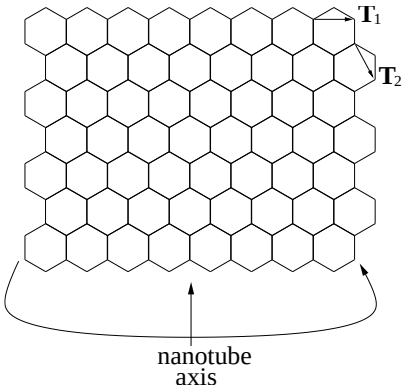


— Carbon nanotubes as strongly correlated electron systems

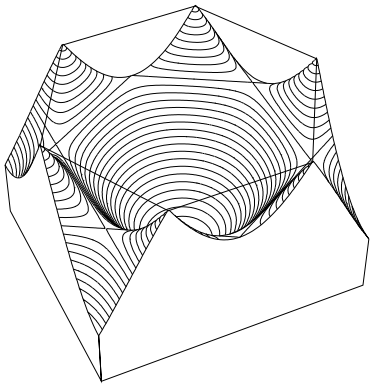
— Superconductivity of carbon nanotube ropes

— Strong-coupling phases in small-diameter carbon nanotubes

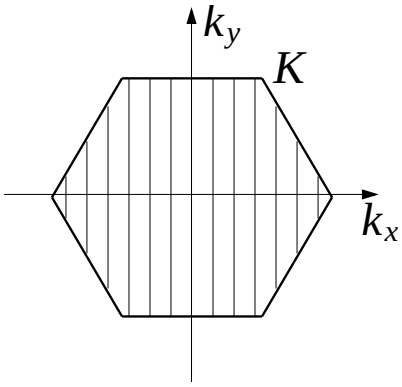
The band structure of the carbon nanotubes can be understood by applying periodic boundary conditions to a graphite sheet:



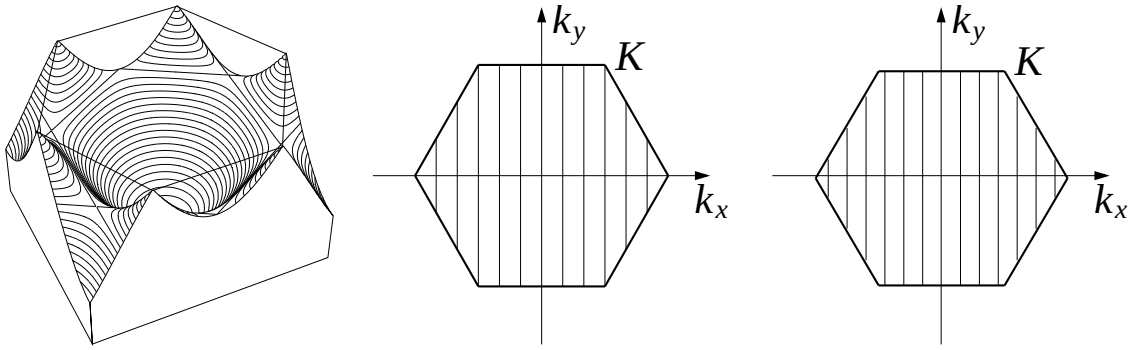
The graphene sheet has Fermi points at the corners of the Brillouin zone:



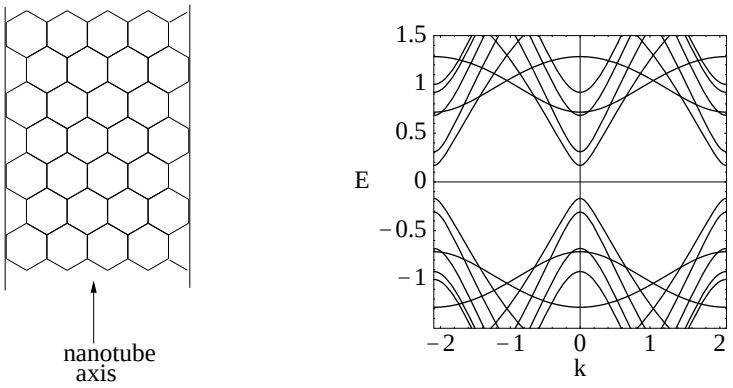
The different subbands of the nanotube appear after quantizing the momentum in the direction transverse to the nanotube axis. For a zigzag nanotube, we may have for instance:



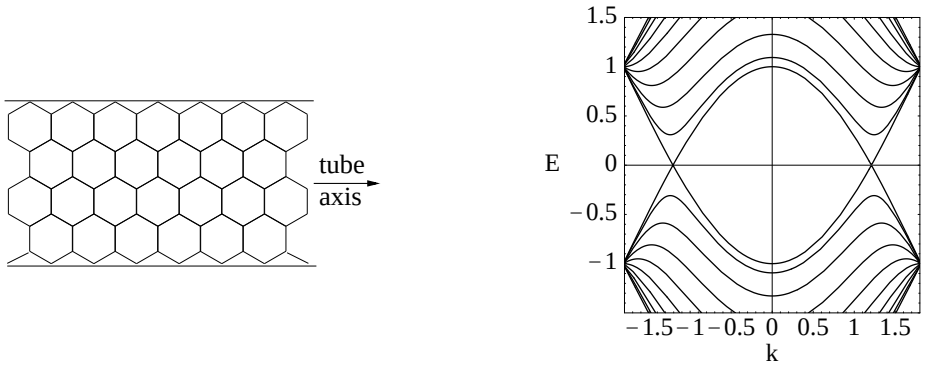
In the case of zigzag nanotubes, there may be some subband containing the K point of the Brillouin zone, depending on the number N of hexagonal carbon rings encircling the nanotube:



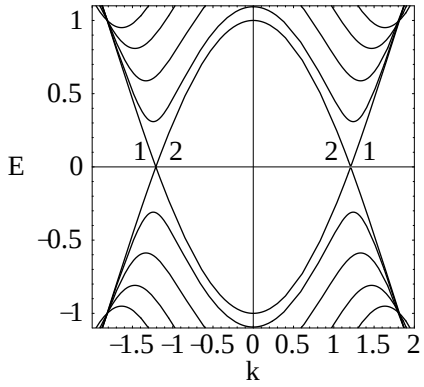
For a zigzag nanotube with a number N of carbon rings which is not a multiple of 3, a gap is always found in the spectrum:



In the case of armchair nanotubes, the allowed momenta correspond to horizontal lines and the points where the valence and the conduction band meet are always in the spectrum:



At low enough energies such that all the higher subbands decouple, the metallic nanotubes behave as genuine 1D electronic systems:



(the energy is measured in units of the overlap integral $t \approx 2.5$ eV and the momentum in units of the inverse of the C-C distance $a \approx 1.4$ Å)

But only about 1/3 of the tubes have this metallic character. The rest are semiconducting with a gap

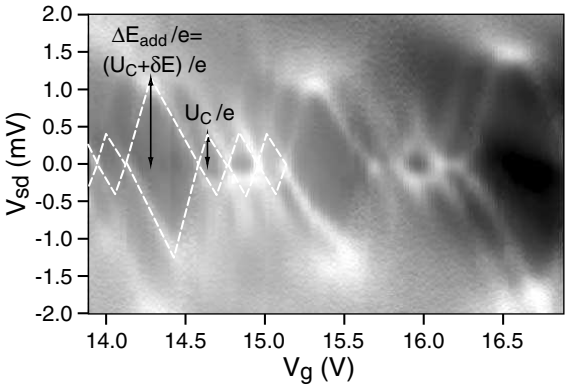
$$\Delta = 2ta/d$$

where d is the diameter of the nanotube.

This theoretical prediction has been confirmed by
J. W. G. Wildöer *et al.*, Nature **391**, 59 (1998)
T. W. Odom *et al.*, Nature **391**, 62 (1998)

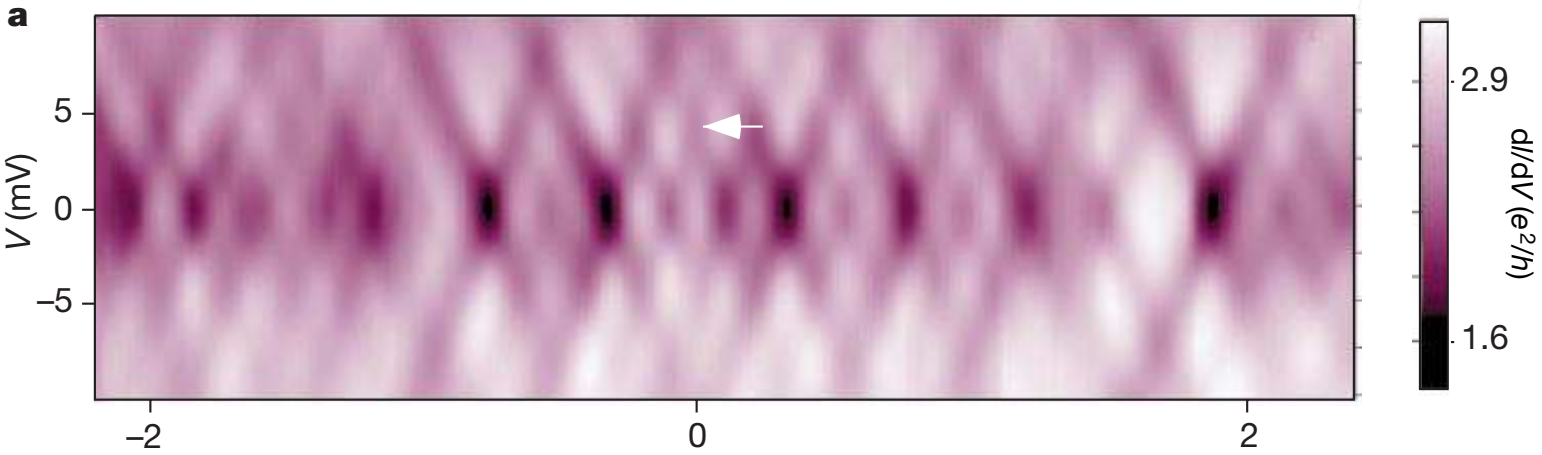
CARBON NANOTUBES AT LOW TEMPERATURES:

— transport through tunnel junctions



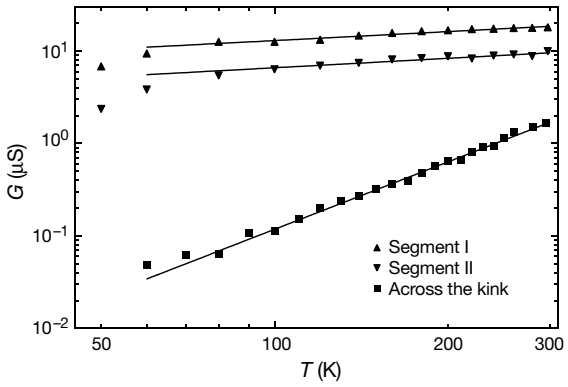
M. R. Buitelaar *et al.*, Phys. Rev. Lett. **88**, 156801 (2002)

— transport through highly transparent contacts



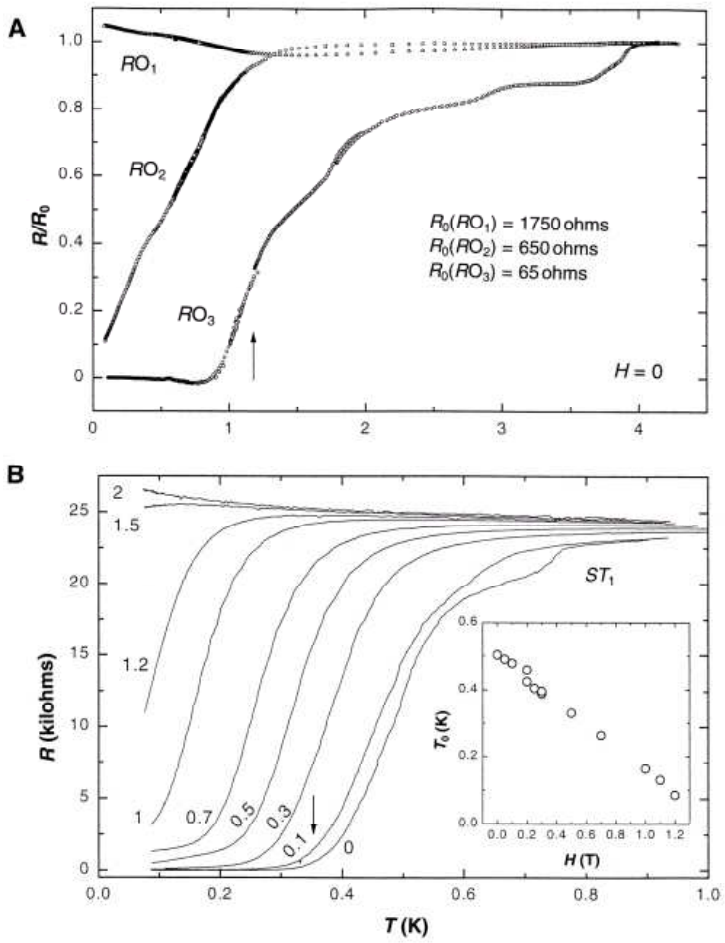
W. Liang *et al.*, Nature **411**, 665 (2001)

CARBON NANOTUBES AT ROOM TEMPERATURES:



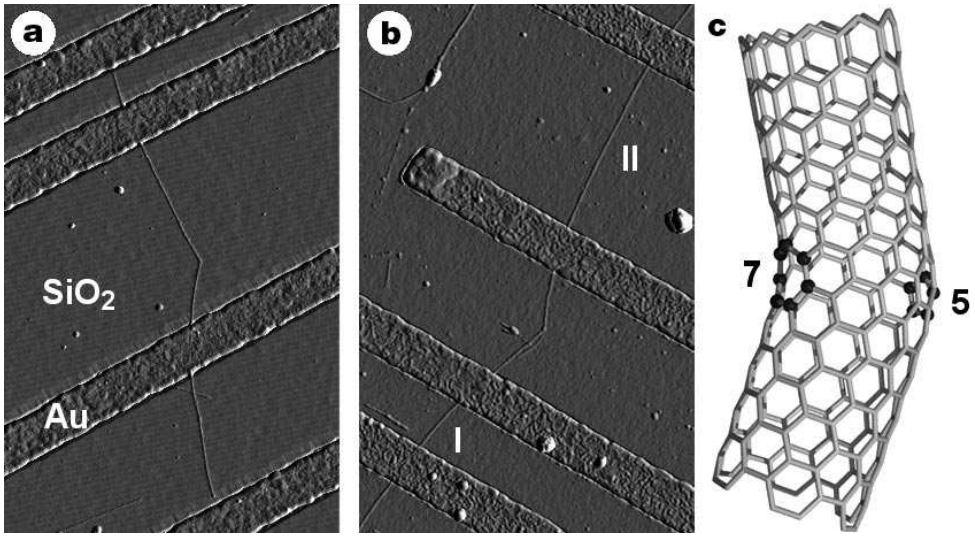
Z. Yao *et al.*, Nature **402**, 273 (1999)

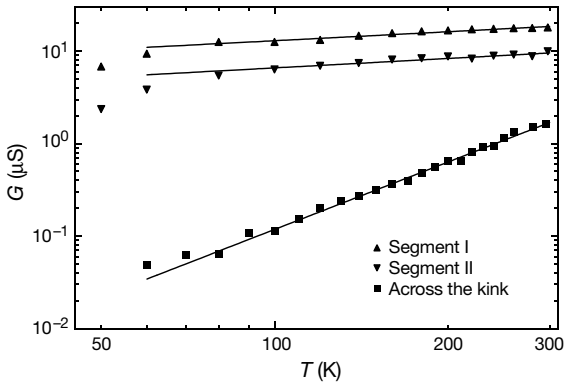
CARBON NANOTUBE ROPES:



A. Yu. Kasumov *et al.*, Science **284**, 1509 (1999)

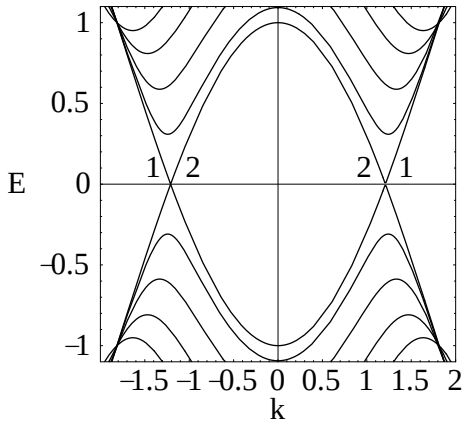
In the long nanotubes, there is the signature of a new kind of electronic state where the electron quasiparticles are suppressed at the Fermi level





Z. Yao *et al.*, Nature **402**, 273 (1999)

The metallic carbon nanotubes are strongly correlated electron systems, since in D = 1 the slightest interaction destroys the conventional Fermi liquid picture.



Focusing on a given subband, the density operators satisfy

$$[\rho_R(-q), \rho_R(p)] = \delta_{pq} pL/2\pi \quad , \quad [\rho_L(-q), \rho_L(p)] = -\delta_{pq} pL/2\pi$$

The noninteracting hamiltonian becomes

$$H_0 = v_F \frac{2\pi}{L} \sum_{k>0} \rho_R(k)\rho_R(-k) + v_F \frac{2\pi}{L} \sum_{k<0} \rho_L(k)\rho_L(-k)$$

For a density-density type of interaction, we also have

$$H_{int} = \frac{1}{2L} \sum_k V(k) \left(\rho_R(k)\rho_R(-k) + \rho_L(k)\rho_L(-k) + 2\rho_R(k)\rho_L(-k)\right)$$

In this system, the elementary excitations are bosons instead of fermions, and they can be found diagonalizing the hamiltonian by means of a Bogoliubov transformation:

$$\begin{pmatrix} \rho_L \\ \rho_R \end{pmatrix} = \begin{pmatrix} \cosh\phi & \sinh\phi \\ \sinh\phi & \cosh\phi \end{pmatrix} \begin{pmatrix} \tilde{\rho}_L \\ \tilde{\rho}_R \end{pmatrix}$$

If we recast the change of variables

$$\rho_L + \rho_R = \sqrt{K}(\tilde{\rho}_L + \tilde{\rho}_R) \quad , \quad \rho_L - \rho_R = \frac{1}{\sqrt{K}}(\tilde{\rho}_L - \tilde{\rho}_R)$$

we get for the total hamiltonian

$$H_0 + H_{int} = \tilde{v}_F \frac{2\pi}{L} \sum_{k>0} \tilde{\rho}_R(k)\tilde{\rho}_R(-k) + \tilde{v}_F \frac{2\pi}{L} \sum_{k<0} \tilde{\rho}_L(k)\tilde{\rho}_L(-k)$$

with

$$K = \frac{1}{\sqrt{1 + V/\pi v_F}} \quad \text{and} \quad \tilde{v}_F = \frac{v_F}{K}$$

The K parameter governs the different correlations of charge $\rho(x) = \rho_L(x) + \rho_R(x)$ and current $\Pi(x) = \rho_L(x) - \rho_R(x)$

$$\begin{aligned} \langle \rho(x)\rho(0) \rangle &\approx \frac{K}{\pi^2} \frac{1}{x^2} + \dots \\ \langle \Pi(x)\Pi(0) \rangle &\approx \frac{1}{\pi^2 K} \frac{1}{x^2} + \dots \end{aligned}$$

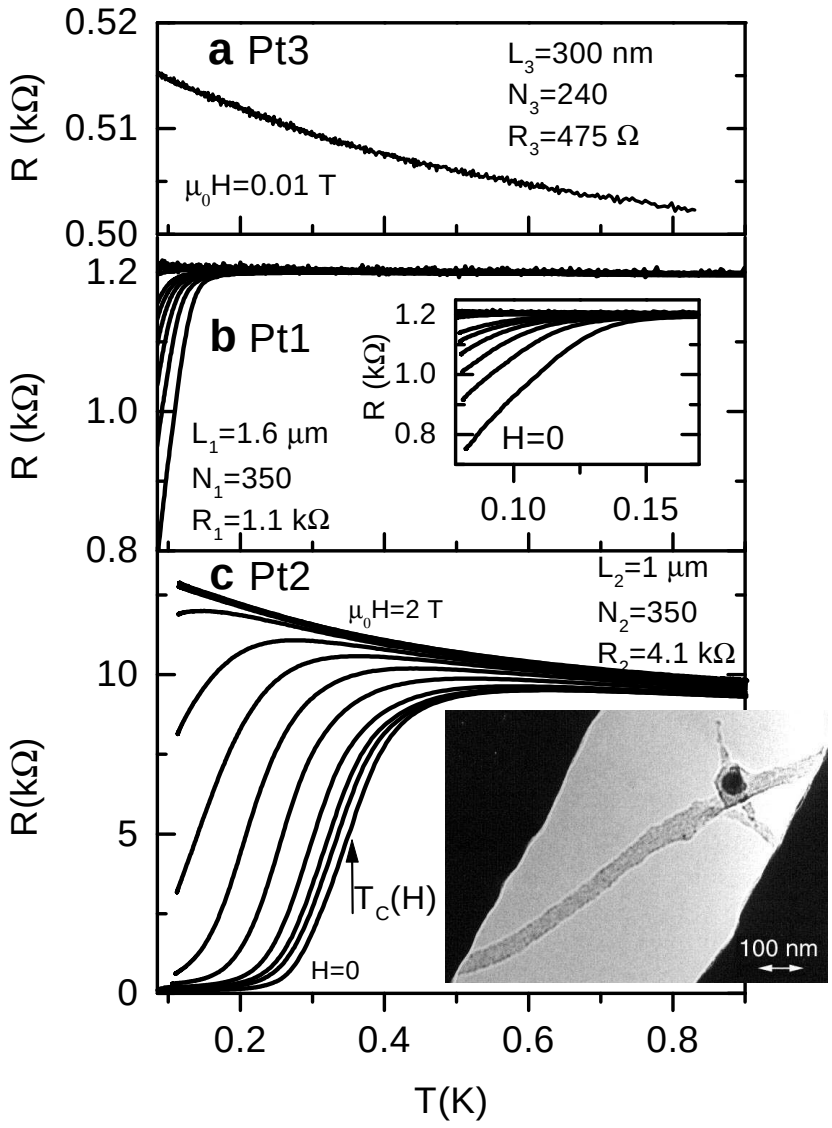
the electron propagator

$$G_R(x,t) \sim \frac{1}{(x - \tilde{v}_F t)^{(K+1/K+2)/8}} \frac{1}{(x + \tilde{v}_F t)^{(K+1/K-2)/8}} \frac{1}{(x - v_F t)^{1/2}}$$

and the density of states near the Fermi level

$$n(\omega) \sim |\omega|^{(K+1/K-2)/4}$$

This behavior characterizes the so-called Luttinger liquid. The power-law dependences provide distinctive signatures to be found when measuring the tunneling of electrons into the liquid.



(from M. Kociak *et al.*, Phys. Rev. Lett. **86**, 2416 (2001))

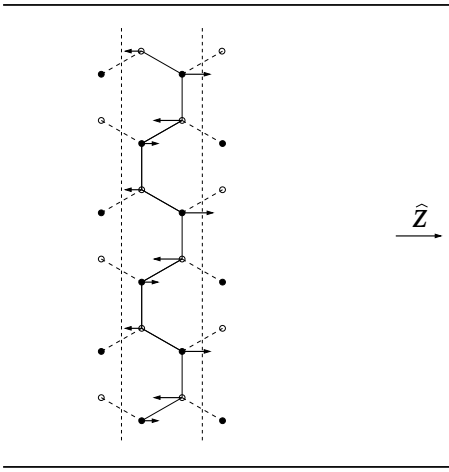
We analyze first the role of **phonons in carbon nanotubes**. The electron-phonon interactions provide an effective attractive interaction

$$V(q,\omega) = -g_{p,p'}(k,k')g_{q,q'}(k,k')\frac{\omega_{k-k'}}{-\omega^2+\omega_{k-k'}^2}$$

below the phonon energy ω_k .

The electron-phonon coupling is

$$g_{p,p'}(k,k') = \frac{1}{(\mu\,\omega_{k-k'})^{1/2}}\sum_{\langle s,s'\rangle} u_s^{(p)*}(k)u_{s'}^{(p')}(k') \\ (\boldsymbol{\epsilon}_s(k-k') - \boldsymbol{\epsilon}_{s'}(k-k'))\cdot\boldsymbol{\nabla} J(s,s')$$



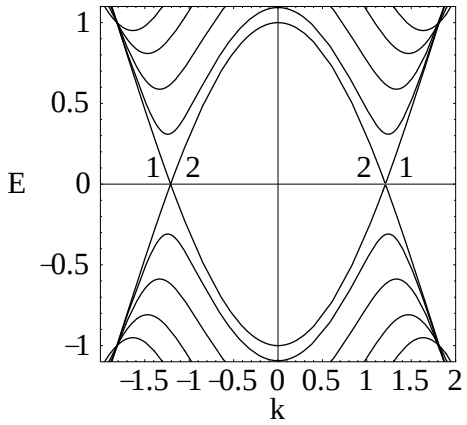
Acoustic phonons: $\omega_{k-k'} \approx v_s|k-k'|$ at low momentum transfer. In that case, the effect or retardation is important

$\Rightarrow$ the influence on the electronic properties is very weak (except for $|k-k'| \sim 2k_F$).

Optical phonons: $\omega_k \sim \omega_D \sim 0.2$ eV . The order of magnitude of the coupling for the effective interaction is

$$\sim \frac{|g_{p,p'}|^2}{\omega_D} \sim \frac{a^2|\boldsymbol{\nabla} J|^2}{\mu v_s^2} \sim 0.2\ v_F$$

The coupling to longitudinal and transverse phonons gives rise to different selection rules, since the modes in 1 and 2 have different symmetry in the honeycomb lattice

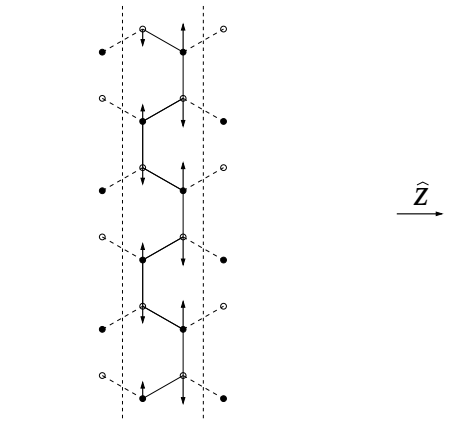


Computing the expression

$$g_{p,p'}(k,k') = \frac{1}{(\mu\,\omega_{k-k'})^{1/2}} \sum_{\langle s,s'\rangle} u_s^{(p)*}(k) u_{s'}^{(p')}(k') \\ (\boldsymbol{\epsilon}_s(k-k') - \boldsymbol{\epsilon}_{s'}(k-k'))\cdot\boldsymbol{\nabla} J(s,s')$$

it can be checked that, in the case of the transverse optical phonons,

$$g_{1,1}(k,k') = -g_{2,2}(k,k')$$
$$g_{1,2}(k,k') = g_{2,1}(k,k') = 0$$



but for longitudinal optical phonons

$$g_{1,1}(k,k') = g_{2,2}(k,k') = 0$$
$$g_{1,2}(k,k') = -g_{2,1}(k,k')$$

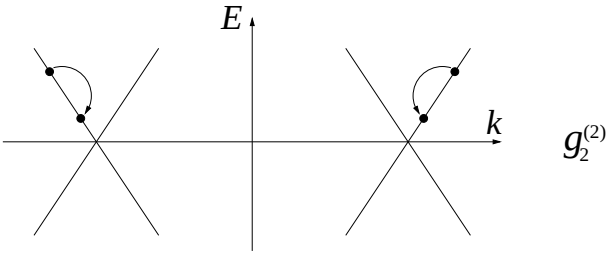
Below the Debye frequency ω_D, there is a competition between the

Coulomb interaction

$$V_C(k) = \frac{e^2}{2\pi} \log |1 + \frac{k_c}{k}|$$

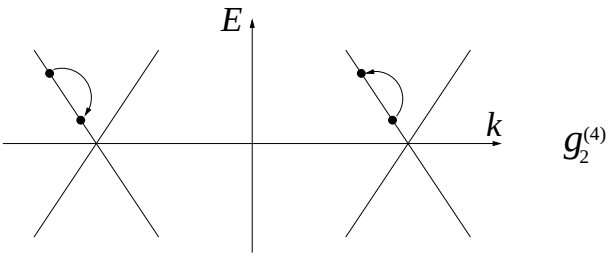
and the effective attractive interaction:

Interbranch and intrabranch processes



$g_2^{(2)}$

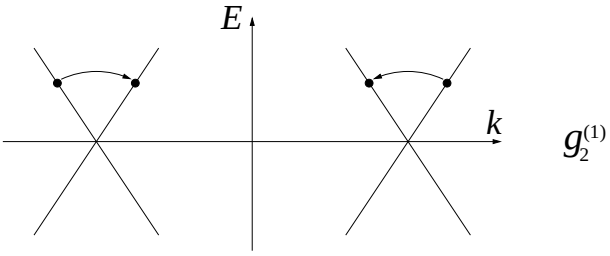
— strong contribution from V_C , $g^{(2)}_{\text{eff},2} \sim -|g_{1,1}|^2/\omega_D < 0$



$g_2^{(4)}$

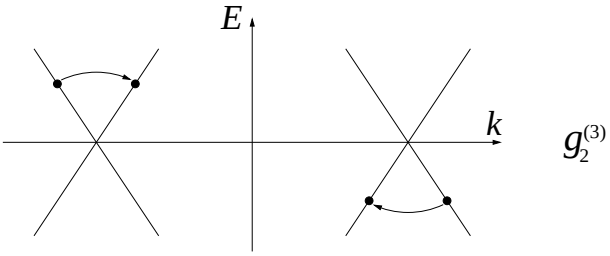
— strong contribution from V_C , $g^{(4)}_{\text{eff},2} \sim -g_{1,1}g_{2,2}/\omega_D > 0$

Backscattering and Umklapp processes



$g_2^{(1)}$

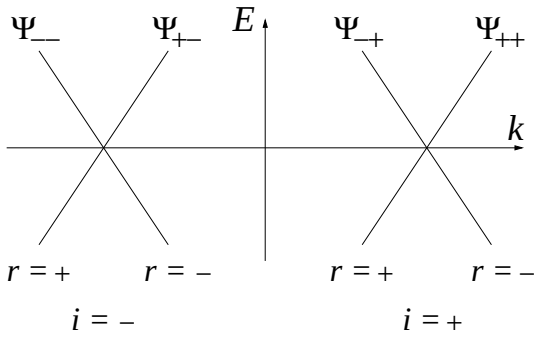
— weak contribution from V_C , $g^{(1)}_{\text{eff},2} \sim -|g_{1,2}|^2/\omega_D < 0$



$g_2^{(3)}$

— weak contribution from V_C , $g^{(3)}_{\text{eff},2} \sim -g_{1,2}g_{2,1}/\omega_D > 0$

We develop a model to deal with the competition between the Coulomb and the phonon-exchange interaction:



$$
\begin{aligned}
H_0 &= \frac{1}{2} v_F \int_{-k_c}^{k_c} dk \sum_{ari\sigma} : \rho^{(a)}_{ri\sigma}(k) \rho^{(a)}_{ri\sigma}(-k) : \\
&+ \frac{1}{2} \int_{-k_c}^{k_c} \frac{dk}{2\pi} \sum_{ari\sigma} \rho^{(a)}_{ri\sigma}(k) \sum_{bsj\sigma'} V^{(ab)}_{ri,sj}(k) \, \rho^{(b)}_{sj\sigma'}(-k)
\end{aligned}
$$

The Hamiltonian can be diagonalized by changing variables to

$$
\begin{aligned}
\tilde{\rho}^{(a)}_{1\rho}(x) &= \rho^{(a)}_{++\rho}(x) + \rho^{(a)}_{--\rho}(x) \\
\tilde{\rho}^{(a)}_{2\rho}(x) &= \rho^{(a)}_{+-\rho}(x) + \rho^{(a)}_{-+\rho}(x) \quad ,
\end{aligned}
$$

$$
\begin{aligned}
\tilde{\rho}^{(a)}_{+\rho}(x) &= \frac{1}{\sqrt{2}} \left(\tilde{\rho}^{(a)}_{1\rho}(x) + \tilde{\rho}^{(a)}_{2\rho}(x) \right) \\
\tilde{\rho}^{(a)}_{-\rho}(x) &= \frac{1}{\sqrt{2}} \left(\tilde{\rho}^{(a)}_{1\rho}(x) - \tilde{\rho}^{(a)}_{2\rho}(x) \right)
\end{aligned}
$$

The Coulomb interaction and the effective interaction from phonon exchange decouple:

$$
\begin{aligned}
H_0 &= \frac{1}{2} v_F \int_{-k_c}^{k_c} dk \sum_{ari\sigma} : \rho^{(a)}_{ri\sigma}(k) \rho^{(a)}_{ri\sigma}(-k) : \\
&+ \frac{1}{2} \int_{-k_c}^{k_c} \frac{dk}{2\pi} \left(\sum_a \tilde{\rho}^{(a)}_{+\rho}(k) \sum_b V_C(k) \, \tilde{\rho}^{(b)}_{+\rho}(-k) + g \sum_a \tilde{\rho}^{(a)}_{-\rho}(k) \, \tilde{\rho}^{(a)}_{-\rho}(-k) \right)
\end{aligned}
$$

The effective attractive interaction is an intratube effect that operates in n different channels ($n = \#$ of metallic nanotubes) while the Coulomb interaction operates in the channel of the total charge $\Rightarrow$ it is strongly suppressed at large n

This has a reflection in the behavior of the different correlations within each nanotube. At large n, the superconducting correlations are dominant, since the propagator

$$D^{(0)}_{\rm sc}(x,t) \equiv \langle \Psi^{(a)+}_{++\uparrow}(x,t)\Psi^{(a)+}_{--\downarrow}(x,t)\Psi^{(a)}_{--\downarrow}(0,0)\Psi^{(a)}_{++\uparrow}(0,0)\rangle$$

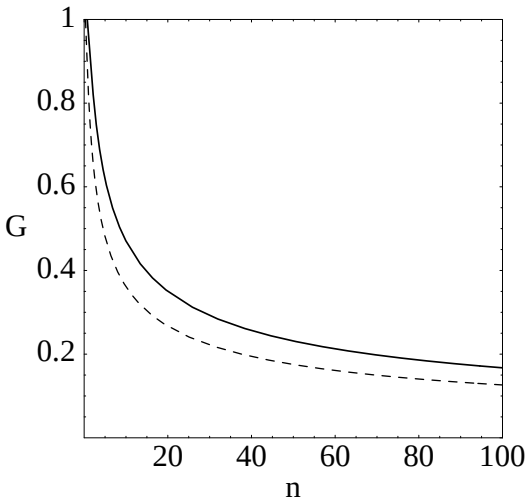
has a decay

$$D^{(0)}_{\rm sc}(x,0) \sim \frac{1}{x^{2+\gamma}}$$

with

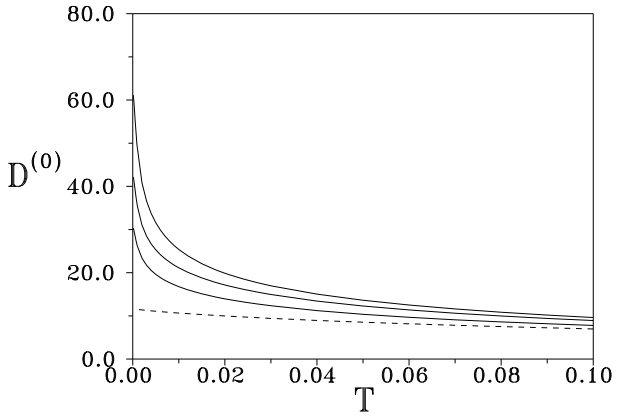
$$\gamma = \frac{1}{2n}\sqrt{1+4nV/\pi v_F} - \frac{1}{2n} + \frac{1}{2}\sqrt{1-4|g|/\pi v_F} - \frac{1}{2} - \frac{1}{\pi v_F}2|g|$$

Negative values of γ imply the divergence of the correlator at $\omega = k = 0$, and correspond to a phase with a potential superconducting instability.



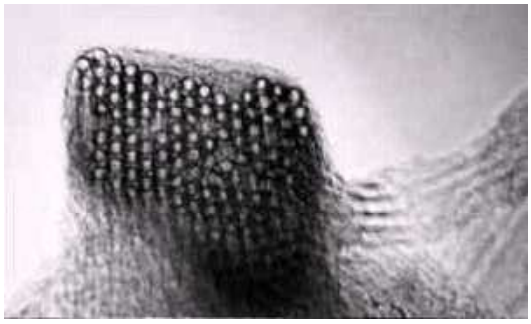
(J. González, Phys. Rev. Lett. **88**, 76403 (2002);
Eur. Phys. J. B **36** 317 (2003))

However, at temperature $T \neq 0$, the divergences are cut off



and the development of a true superconducting instability requires the coupling by tunneling between the metallic nanotubes.

In a compositionally disordered rope



(from A. Thess *et al.*, Science **273**, 483 (1996))

the hopping amplitude between nanotubes is quite small,

$$t_{SP} \sim 0.005 \times t_T \sim 0.5 \times 10^{-4} \text{ eV}$$

with a relative weight $w_{SP} \sim t_{SP} R/v_F \sim 0.5 \times 10^{-3}$.
In comparison, the tunneling of the Cooper pairs is not affected by the compositional disorder and has a larger rate $w_{CP} \sim (t_T R/v_F)^2 \sim 0.01$.

In disordered ropes, the effect of pair hopping is therefore more important than single-particle hopping between neighboring nanotubes.

(J. González, Phys. Rev. Lett. **88**, 76403 (2002))

The above description has to be corrected by the addition of a term accounting for the pair hopping between neighboring nanotubes $\langle a, b\rangle$

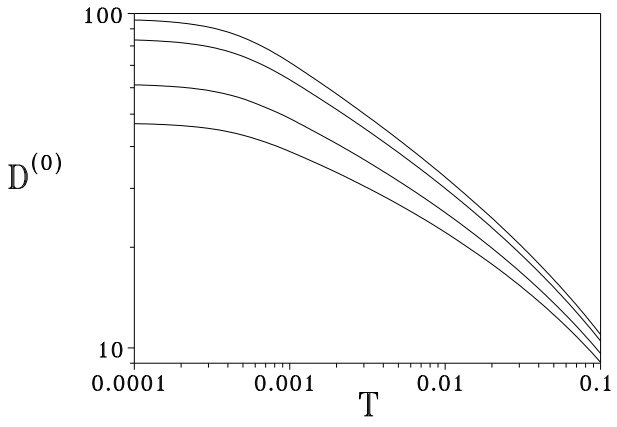
$$H_2 = \sum_{\langle a,b\rangle} (\lambda_2)_{ab} \int_{-k_c}^{k_c} dk \int_{-k_c}^{k_c} dp \int_{-k_c}^{k_c} dp'$$
$$\Psi^{(a)\dagger}_{ri\uparrow}(k+p)\Psi^{(a)\dagger}_{-r-i\downarrow}(-p)\Psi^{(b)}_{-s-j\downarrow}(-p')\Psi^{(b)}_{sj\uparrow}(k+p')$$

which is essential to explain the intertube coherence.

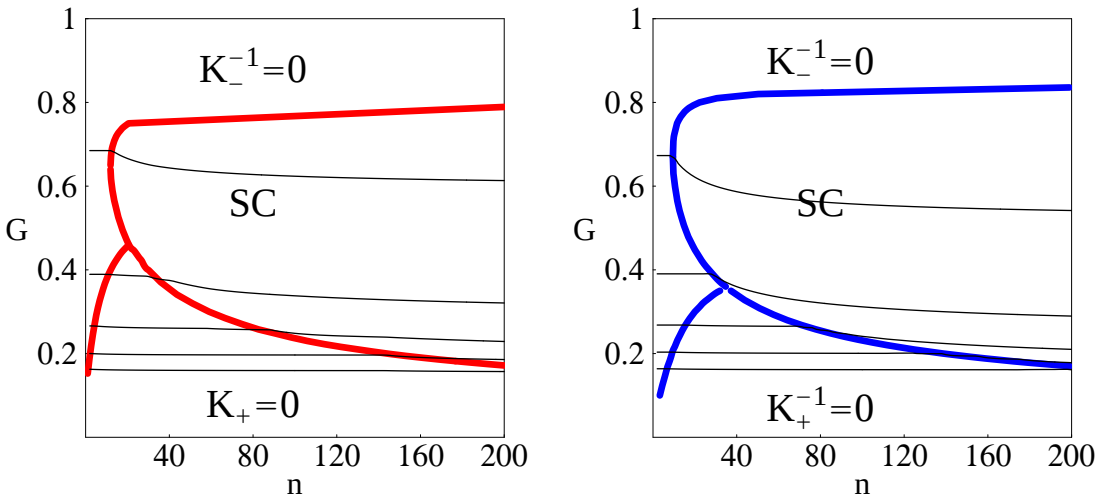
The Cooper pair propagator in the rope depends on the points z_a, z_b in the transverse section, $D(x,t;z_a,z_b)$, and it may have a singularity at finite temperature. Actually, the Fourier transform $\widetilde{D}(k,\omega_k;q)$ is given at zero frequency and momentum by

$$\widetilde{D}(0,0;0) = \frac{\widetilde{D}^{(0)}_{\rm sc}(0,0)}{1-\lambda_2(0)\widetilde{D}^{(0)}_{\rm sc}(0,0)}$$

(J. González, Phys. Rev. Lett. **88**, 76403 (2002))
The pole in $\widetilde{D}(0,0;0)$ is the signature of a superconducting transition. In practice, a factor of suppression is introduced by the finite length L of the ropes. The correlations are cut off at T about one order of magnitude below v_F/L . Taking for instance $L \sim 1\ \mu$m , we have

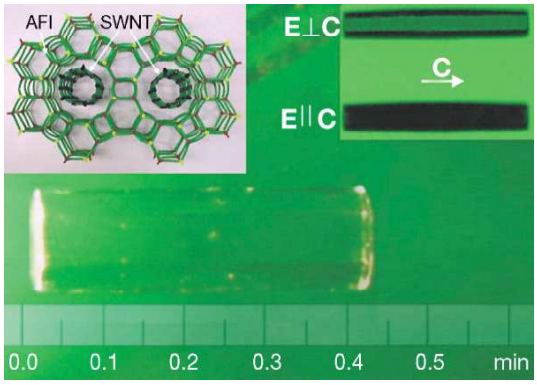


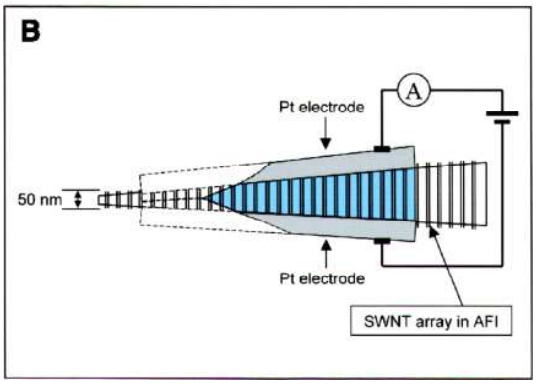
The superconducting phase of the ropes has to be mapped by looking for the development of intertube coherence and the consequent superconducting transition. When this is not achieved, exotic strong-coupling phases arise, due to either the decoupling of the metallic nanotubes in the rope or the onset of phase separation under very strong attraction.



(J. V. Alvarez and J. González, Phys. Rev. Lett. **91**, 076401 (2003))

Strong-coupling phases have been measured in 4 Angstrom nanotubes by Z. K. Tang *et al.*, Science **292**, 2462 (2001) :





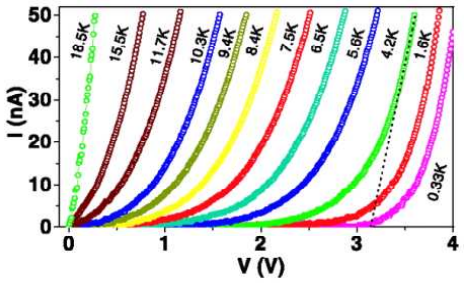
This is however a different kind of experiment in which the carbon nanotubes are forming a 3D array within the channels of a zeolite matrix. This implies that

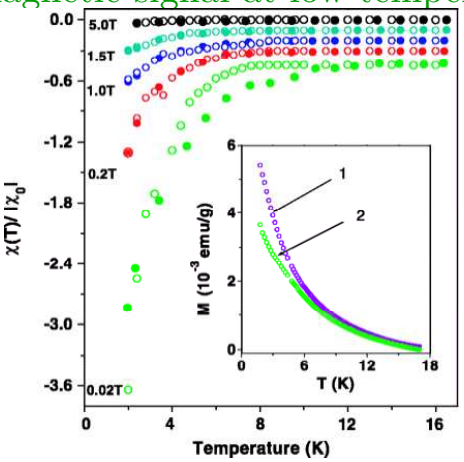
— there is no tunneling between different carbon nanotubes

— there is a more conventional screening of the Coulomb interaction, such as $V(k) \to \text{const}$ as $k \to 0$

— the electron-phonon coupling is much enhanced due to the large curvature of the tubes

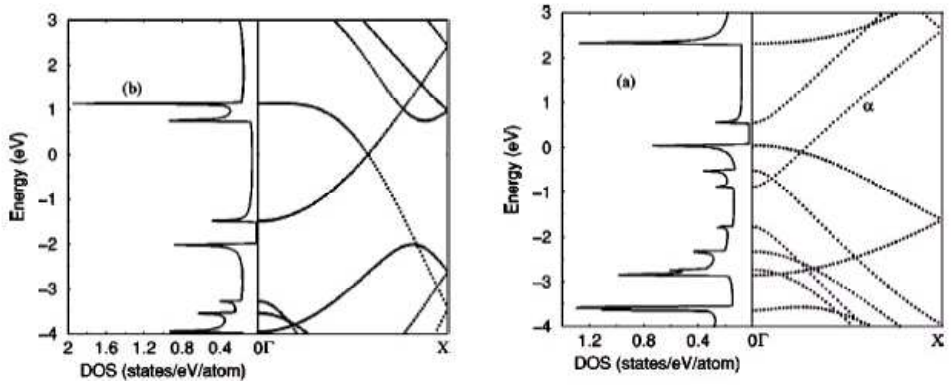
The signatures of strong coupling are the development of a gap in the differential conductance and a large diamagnetic signal at low temperatures





(from Z. K. Tang *et al.*, Science **292**, 2462 (2001))

The development of the gap is the signature of the breakdown of the metallic Luttinger liquid picture. However, the physics is very different depending on whether the nanotubes have a (3,3) or a (5,0) geometry :

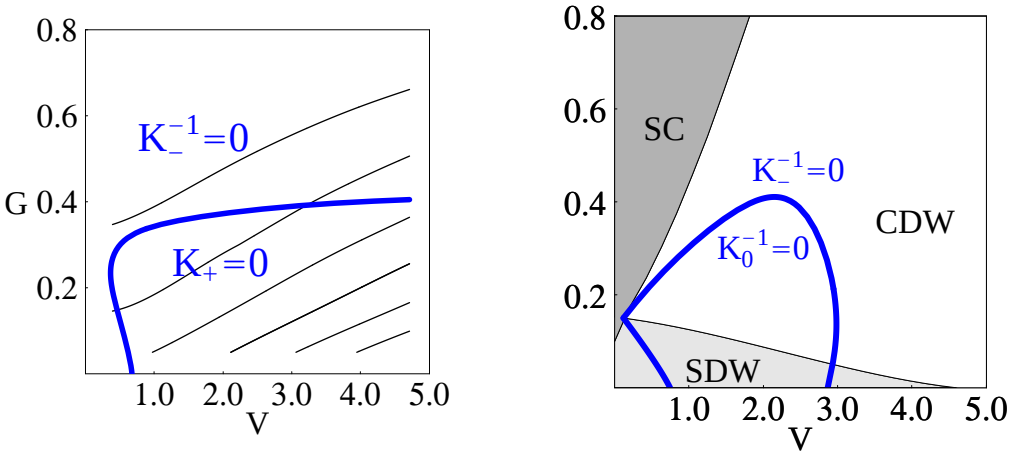


(from H.J. Liu and C.T. Chan, Phys. Rev. B **66**, 115416 (2002))

Again, it is a question of studying the behavior of the renormalized velocities and K parameters in the symmetric and antisymmetric subbands (and zero angular-momentum subband in (5,0) nanotubes)

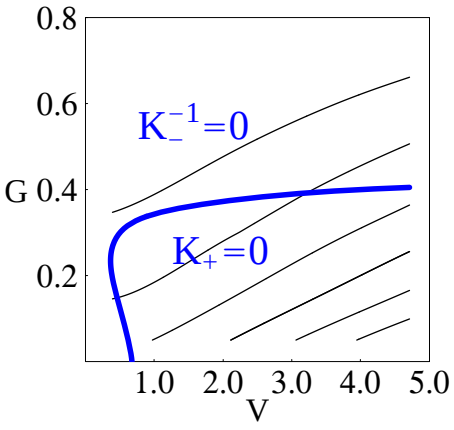
$$H_{LL} = \frac{1}{2}\int dx \sum_{s=\pm,0} \left(v_{Js}(\Pi_s(x))^2 + v_{Ns}(\partial_x \Phi_s(x))^2 \right)$$

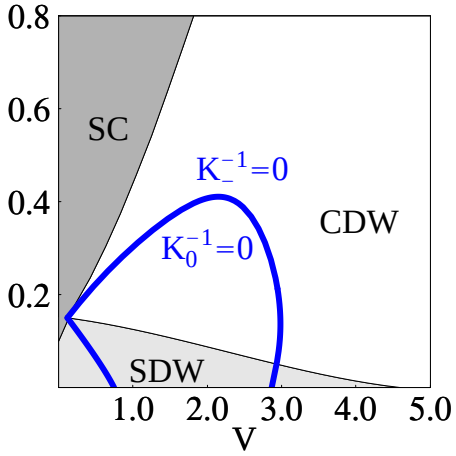
$$K_s = \sqrt{v_{Js}/v_{Ns}} \quad , \quad \tilde{v}_s = \sqrt{v_{Ns} v_{Js}}$$



(J. González, report cond-mat/0409347)

The estimates for the Coulomb potential in the 3D array of nanotubes in the zeolite matrix give $V \approx 0.5 - 0.9\, e^2$, where $e^2 \approx 2.7\, v_F$.



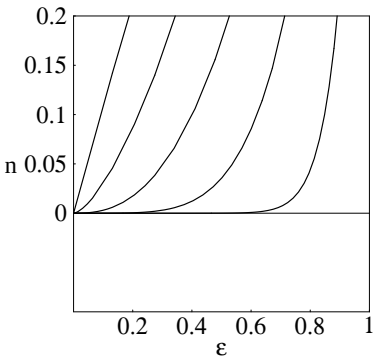


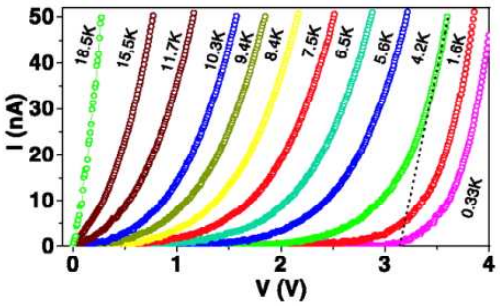
Thus, the existence of superconducting correlations is unlikely in the small-diameter nanotubes.

The singularity in the K parameters is consistent anyhow with the appearance of a pseudogap at low temperatures, since the density of states is given by

$$n(\varepsilon) \sim \varepsilon^{(K_+ + 1/K_+ + K_- + 1/K_- - 4)/8}$$

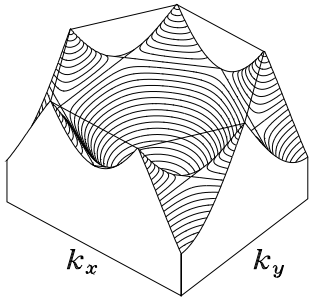
For the $(3,3)$ nanotubes, we obtain for instance a favorable comparison with the experiments in the phase with $K_+ \to 0$





Can we account for the strong diamagnetic experimental signal within the strong-coupling phase of the nanotubes?

We recall the coupling of the vector potential $\mathbf{A}$ in the 2D model for a graphite layer



$$\varepsilon(\mathbf{k}) \approx \pm v_F |\mathbf{k}|$$

$$H_G = -iv_F \int d^2r \; \Psi^\dagger(\mathbf{r}) \boldsymbol{\sigma} \cdot (\boldsymbol{\nabla} - i(e/c)\mathbf{A}) \Psi(\mathbf{r})$$

The 1D projection onto the low-energy subbands of the carbon nanotube gives

$$H_{1D} = v_F \int dk d\varphi \; (k - (e/c)A_{\parallel}(\varphi))(\Psi_R^\dagger(k)\Psi_R(k) - \Psi_L^\dagger(k)\Psi_L(k))$$

$\Rightarrow$ the component $A_{\parallel}$ couples to the charge asymmetry
$\Pi_+ = \rho_{R1} - \rho_{L1} + \rho_{R2} - \rho_{L2}$.

The response function for the current Π_+ is

$$\langle \Pi_+(\omega, k) \Pi_+(-\omega, -k) \rangle = \frac{1}{K_+} \frac{u_+ k^2}{\omega^2 - u_+^2 k^2}$$

so that we find a divergent susceptibility in the phase $K_+ = 0$.

The $K_+ = 0$ phase of the (3,3) nanotubes seems to be therefore consistent with the main properties (diamagnetism, pseudogap) measured in the experiment.

(J. González, report cond-mat/0409347)

To conclude, we have seen that the intertube coherence is an essential factor for the development of superconductivity in carbon nanotubes.

— Critical temperatures of the order of ~ 1 K seem to be typical of ropes with ~ 100 metallic nanotubes. A slight increase of T_c may be expected by enlarging the content of metallic nanotubes in the ropes.

— The influence of statistical effects should be studied on more quantitative grounds, in particular the mechanism of percolation of the Cooper pairs in the rope.

— Superconductivity seems to be unlikely in the small-diameter carbon nanotubes, since the strong-coupling regime is dominated by other instabilities (phase separation, charge-density-wave).