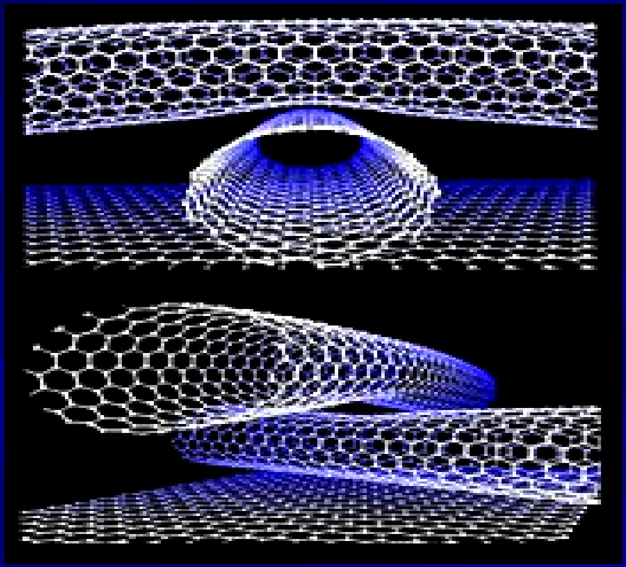
SUPERCONDUCTIVITY OF CARBON NANOTUBES



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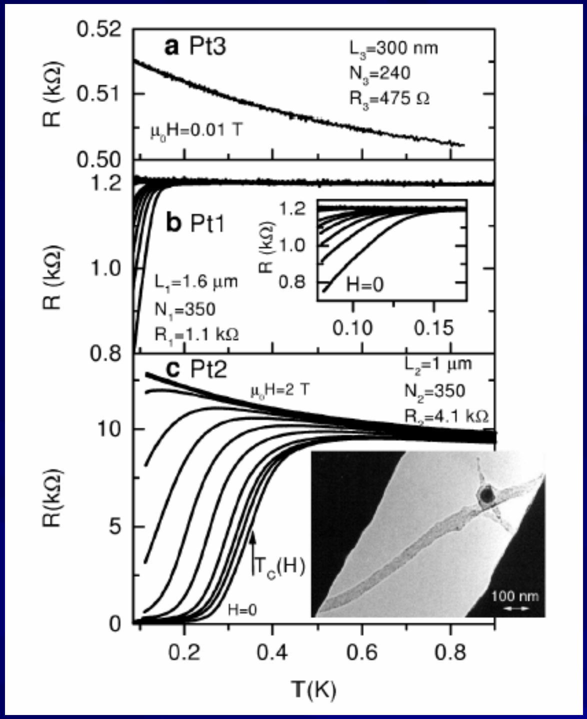
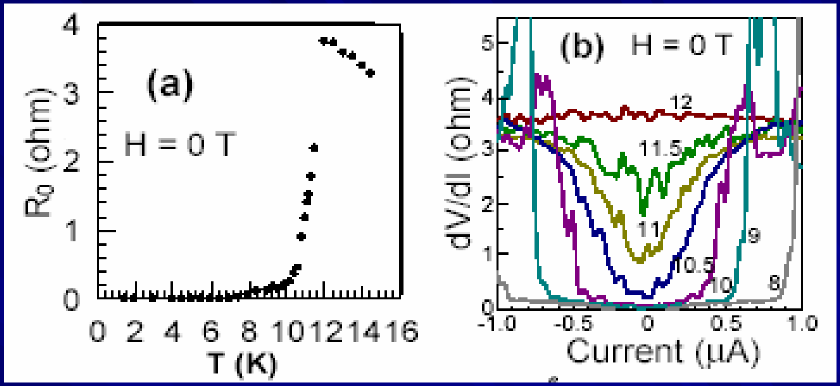




I. Takesue *et al.*, Phys. Rev. Lett. **96**, 057001 (2006)

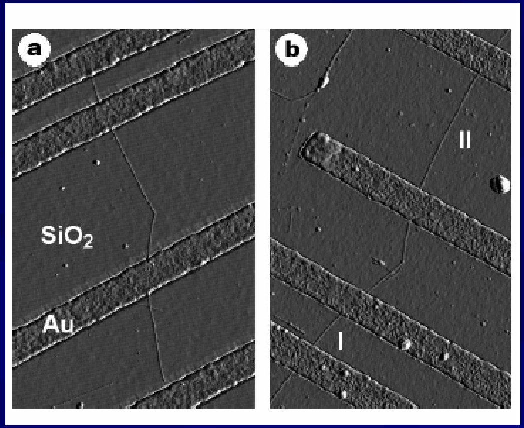
M. Kociak *et al.*, Phys. Rev. Lett. **86**, 2416 (2001)

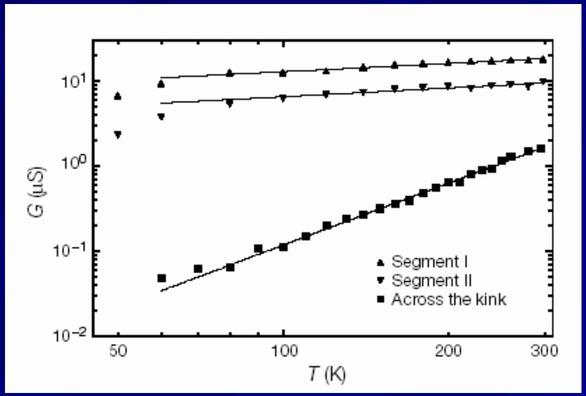
The superconductivity of the carbon nanotubes poses two relevant questions:

- when is the dominant interaction repulsive or attractive in the nanotubes?
- how large are the transition temperatures that can be reached?

TRANSPORT PROPERTIES OF CARBON NANOTUBES

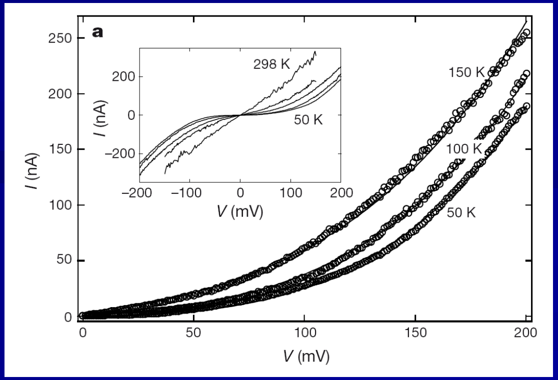
When the thermal energy *kT* is larger than the electronic level spacing ΔE, transport measurements reflect the many-body properties of carbon nanotubes





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

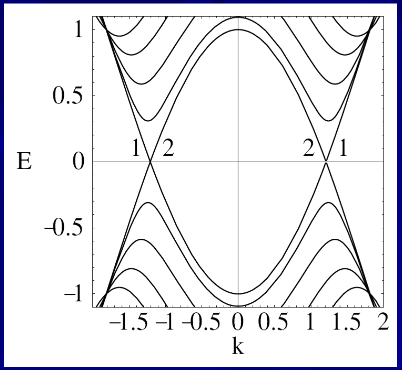
The conductance suffers a remarkable attenuation as the temperature or bias voltage is lowered, which is the signature of a novel electron liquid where the quasiparticles are suppressed at the Fermi level



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

TRANSPORT PROPERTIES OF CARBON NANOTUBES

The absence of electron quasiparticles comes from the strong correlation of the 1D electron system, where the slightest interaction destroys the Fermi liquid



The hamiltonian for a density-density interaction

$$H = \frac{1}{2} v_F \int dk \; \rho_L(k)\rho_L(-k) \;+\; \frac{1}{2} v_F \int dk \; \rho_R(k)\rho_R(-k)$$

$$+ \; \frac{1}{2}\int dk \;\; V(k) \; (\rho_L(k)\rho_L(-k) \; + \rho_R(k)\rho_R(-k) \; + 2\rho_L(k)\rho_R(-k))$$

can be diagonalized by a canonical transformation

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

We end up with the noninteracting hamiltonian

$$H = \frac{1}{2}\int dk \; \tilde{v}_F \; \tilde{\rho}_L(k)\tilde{\rho}_L(-k) \;+\; \frac{1}{2}\int dk \; \tilde{v}_F \; \tilde{\rho}_R(k)\tilde{\rho}_R(-k)$$

with $$K = \frac{1}{\sqrt{1 + 2V(k)/v_F}} \quad , \quad \tilde{v}_F = \frac{v_F}{K}$$

TRANSPORT PROPERTIES OF CARBON NANOTUBES

Under very general conditions, the excitations of the 1D electron liquid are given by charge density fluctuations represented by $\tilde{\rho}_{\mathrm{L}}$ and $\tilde{\rho}_{\mathrm{R}}$ (and spin density fluctuations with corresponding operators $\tilde{\sigma}_{\mathrm{L}}$, $\tilde{\sigma}_{\mathrm{R}}$).

The properties of the liquid are characterized basically by K and $\tilde{v}_F$,

$$\left\langle \left(\rho_L(x,t)+\rho_R(x,t)\right)\left(\rho_L(0,0)+\rho_R(0,0)\right)\right\rangle \sim K/(x^2-\tilde{v}_F^2 t^2)$$

The electron propagator does not show well-defined quasiparticles:

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

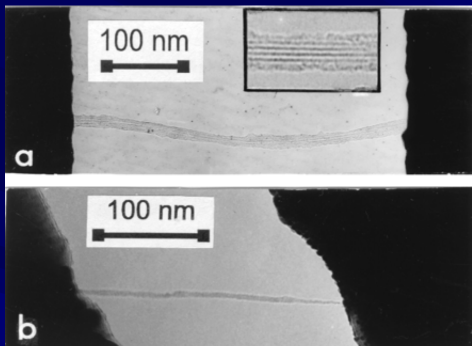
and the density of states near the Fermi level becomes

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

This behavior characterizes the so-called Tomonaga-Luttinger liquid. The power-law dependences provide distinctive signatures that can be tested experimentally.

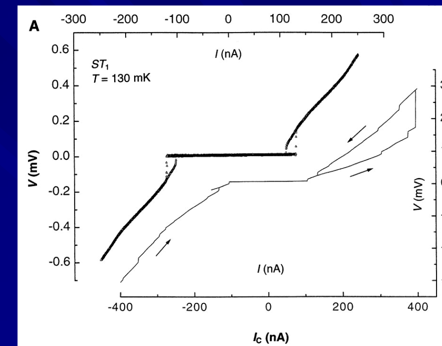
SUPERCONDUCTIVITY IN NANOTUBE ROPES

There is however something more than repulsion in the nanotubes. By using superconducting contacts, supercurrents have been observed in nanotube ropes

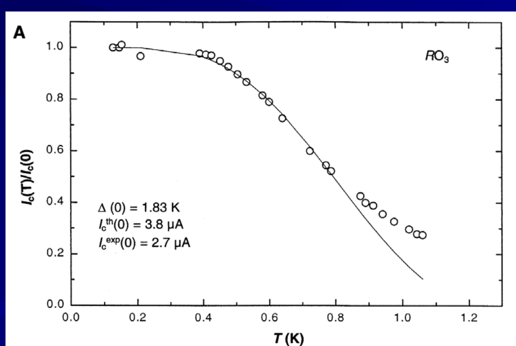


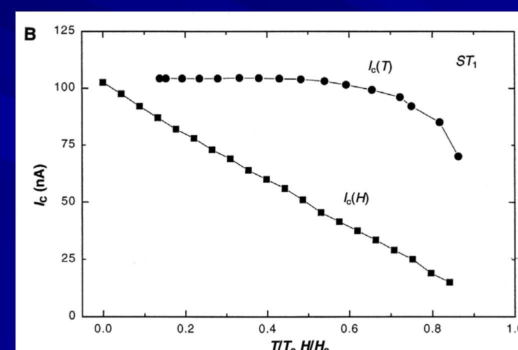
A. Kasumov *et al.*,

Science **284**, 1508 (1999)



The temperature dependence of the supercurrents is quite unusual,

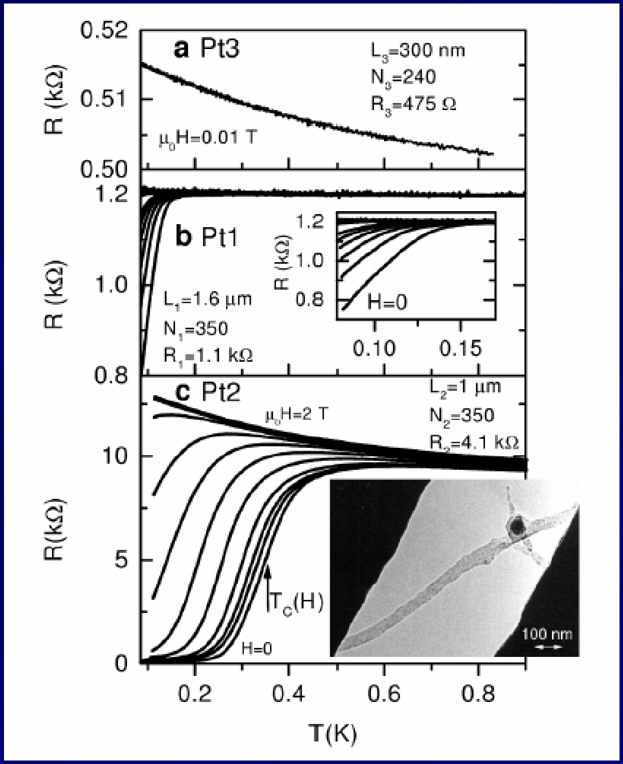




but it can be explained as a result of the propagation of the Cooper pairs along the nanotube (J. G., Phys. Rev. Lett. **87**, 136401 (2001)).

SUPERCONDUCTIVITY IN NANOTUBE ROPES

It has been even more remarkable the observation of superconducting transitions in nanotube ropes.



The transition is not observed in all the ropes, and apparently it requires several conditions:

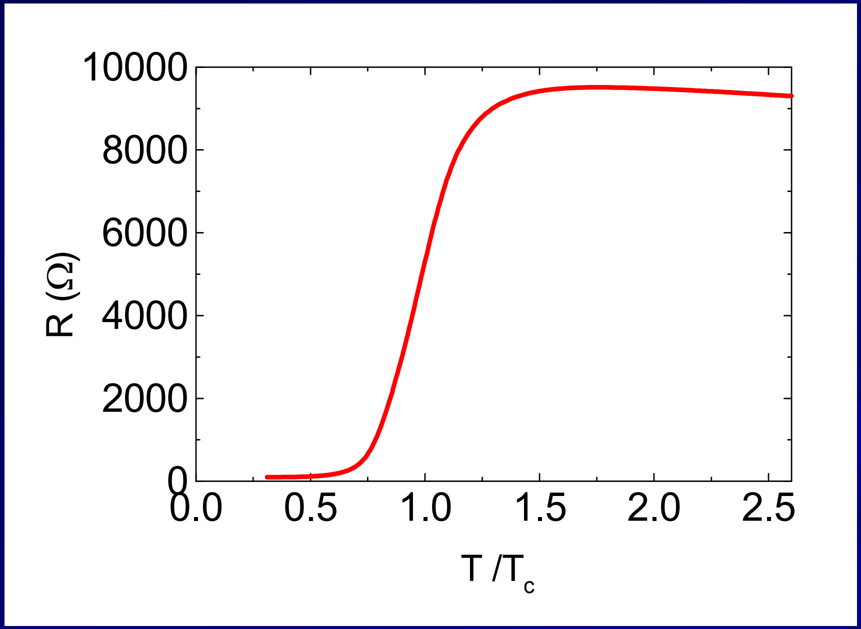
- the nanotube length must be sufficiently large (larger than the coherence length) to make room for the Cooper pairs
- the number of nanotubes in the rope must be above a certain value, otherwise the transition may not be completed

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

Transitions supraconductrices

Corde de 350 tubes

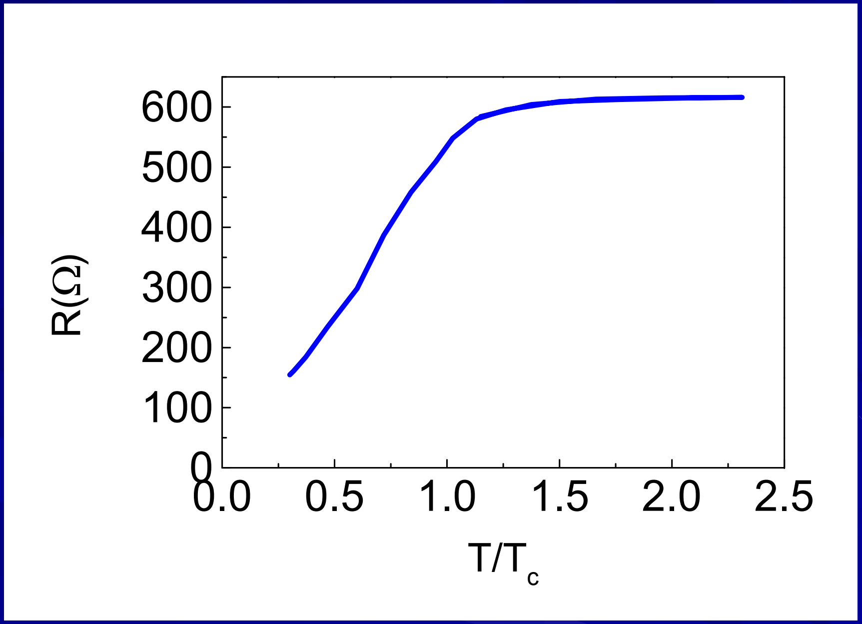
M. Kociak



T_c = 350 mK

H_c = 2 T

Corde de 40 tubes



T_c = 80 mK

H_c = 0.2 T

(courtesy of A. Kasumov)

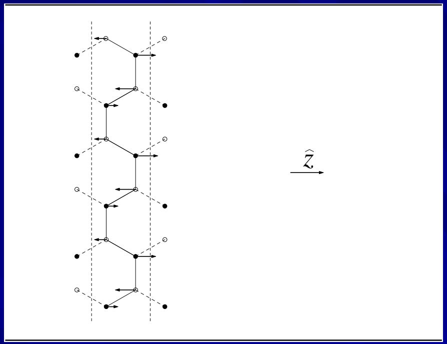
SUPERCONDUCTIVITY IN NANOTUBE ROPES

The source of the attractive interaction comes from the coupling to phonons

$$V_{eff}(q,\omega) = g(k,k-q)\, g(k',k'+q)\, \frac{\omega_q}{\omega^2 - \omega_q^2}$$

The electron-phonon couplings are

$$g_{\alpha,\beta}(k,k') = \frac{1}{\sqrt{\mu\omega_{k-k'}}} \sum_{\langle i,j\rangle} u_i^{(\alpha)*}(k)\, u_j^{(\beta)}(k') \times \left(\boldsymbol{\varepsilon}_i(k-k') - \boldsymbol{\varepsilon}_j(k-k')\right)\cdot \nabla J(i,j)$$



- acoustic phonons: $\omega_{k-k'} \approx v_s |k-k'|$ at low momentum-transfer, and retardation effects are important (except for $|k-k'| \sim 2K_F$)

- optical phonons: $\omega_k \sim \omega_D \approx 0.2\ \text{eV}$, for which the order of magnitude of the phonon-mediated interaction is

$$\lambda \sim \frac{|g_{\alpha,\beta}|^2}{\omega_D} \sim \frac{|\nabla J|^2}{\mu\omega_D^2} \sim 0.1\ v_F$$

SUPERCONDUCTIVITY IN NANOTUBE ROPES

The Coulomb interacción $V_C(k) \sim e^2 \log(k_c / k)$ is dominant in individual nanotubes. In the ropes, it may couple a large number N of nanotubes

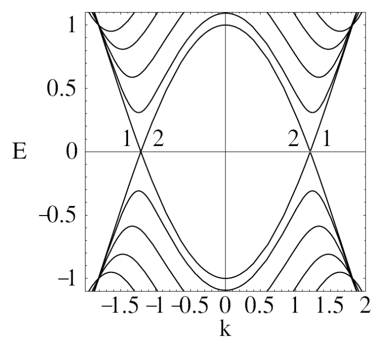
$$H = \frac{1}{2} v_F \int dk \sum_{a=1}^{N} \rho_r^{(a)}(k) \rho_r^{(a)}(-k) + \frac{1}{2} \int \frac{dk}{2\pi} \left(\sum_{a=1}^{N} \rho_r^{(a)}(k) \sum_{b=1}^{N} V^{(a,b)}(k) \, \rho_r^{(b)}(-k) \right)$$

In armchair nanotubes, for instance,

V_C and V_{eff} act in different channels:

$$\rho_+^{(a)} = \frac{1}{\sqrt{2}} \left(\rho_1^{(a)} + \rho_2^{(a)} \right)$$

$$\rho_-^{(a)} = \frac{1}{\sqrt{2}} \left(\rho_1^{(a)} - \rho_2^{(a)} \right)$$



$$H = \frac{1}{2} v_F \int dk \sum_{a=1}^{N} \rho_r^{(a)}(k) \rho_r^{(a)}(-k) + \frac{1}{2} \int \frac{dk}{2\pi} \left(4 \, V_C(k) \sum_{a=1}^{N} \rho_+^{(a)}(k) \sum_{b=1}^{N} \rho_+^{(b)}(-k) \right)$$

$$+ \frac{1}{2} \int \frac{dk}{2\pi} \left(4 \, \lambda \sum_{a=1}^{N} \rho_-^{(a)}(k) \, \rho_-^{(a)}(-k) \right)$$

SUPERCONDUCTIVITY IN NANOTUBE ROPES

- the phonon-mediated interaction is an intratube effect that operates in N different channels, where N is the number of metallic nanotubes in the rope
- the Coulomb interaction operates in a single channel, corresponding to the total charge, therefore its effects are strongly suppressed at large N

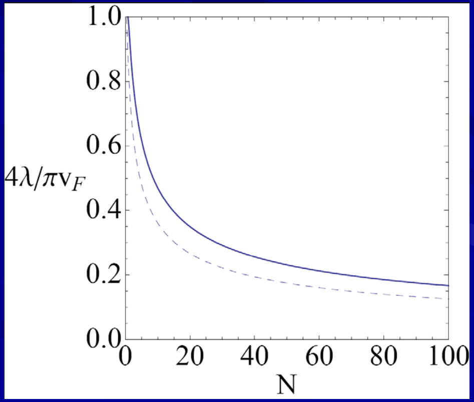
In the case of a superconducting correlation function,

$$D_{\rm SC}^{(0)}(x,0) = \left\langle \Psi_{\alpha\uparrow}^{(a)+}(x,0)\, \Psi_{-\alpha\downarrow}^{(a)+}(x,0)\;\; \Psi_{\beta\uparrow}^{(a)}(0,0)\, \Psi_{-\beta\downarrow}^{(a)}(0,0) \right\rangle$$

$$\approx \frac{1}{|x|^{1/2NK_C}} \prod_{a=1}^{N} \frac{1}{|x|^{1/2NK_\lambda}} \prod_{a=1}^{3N-1} \frac{1}{|x|^{1/2N}} \approx \frac{1}{|x|^{2-\gamma}}$$

$$\gamma = \frac{1}{2N}\sqrt{1+4NV_C/\pi v_F} - \frac{1}{2N} + \frac{1}{2}\sqrt{1-4\lambda/\pi v_F} - \frac{1}{2} - \frac{2\lambda}{\pi v_F}$$

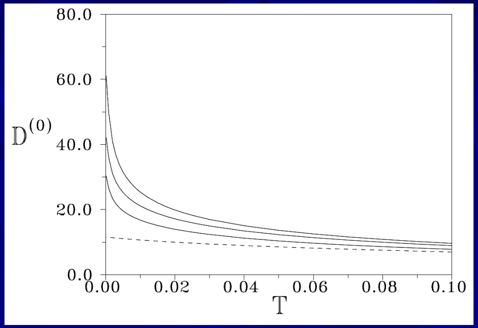
Negative values of γ imply the divergence of the correlator at $k=\omega=0$, and a phase with potential superconducting instability

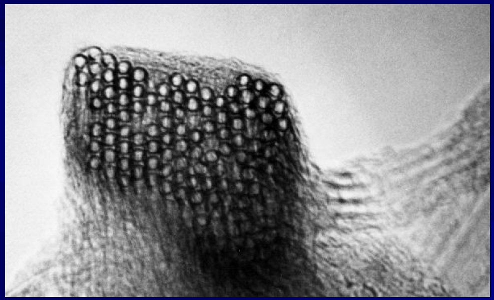


(J. G., Phys. Rev. Lett. **88**, 76403 (2002))

SUPERCONDUCTIVITY IN NANOTUBE ROPES

However, at temperature $T \neq 0$ the superconducting correlations do not show a real divergence, and the development of an instability requires the tunneling of Cooper pairs between different tubes in a rope.





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

In a disordered rope, the tunneling amplitude between nanotubes is quite small:

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

with a relative weight

$$w_{SP} \sim t_{SP} R / v_F \sim 0.5 \times 10^{-3}$$

In contrast, the tunneling of the Cooper pairs is not affected by the compositional disorder

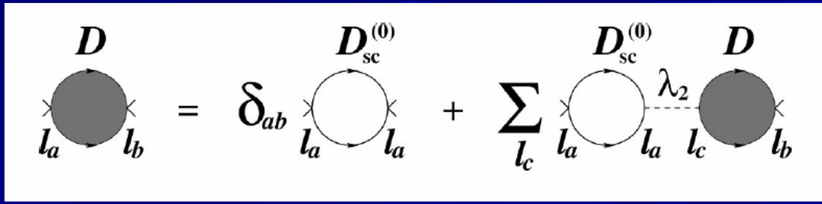
$$w_{CP} \sim (t_T R / v_F)^2 \sim 0.01$$

SUPERCONDUCTIVITY IN NANOTUBE ROPES

The description has to be completed with Cooper pair hopping between nanotubes:

$$H_2 \approx \sum_{\langle a,b \rangle} (\lambda_2)_{ab} \int dk \int dp \int dq \; \Psi^{(a)+}_{\alpha\uparrow}(k+p)\, \Psi^{(a)+}_{\alpha\downarrow}(-p)\, \Psi^{(b)}_{\beta\uparrow}(k+q)\, \Psi^{(b)}_{\beta\downarrow}(-q)$$

The full Cooper pair propagator in the rope $D(k,\omega_k;l_a,l_b)$ depends on the position of the nanotubes l_a and l_b in the transverse section

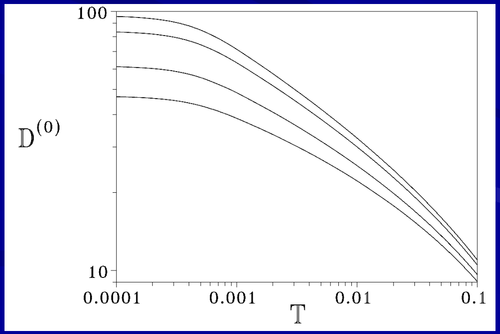


For the Fourier transform $\tilde{D}(k,\omega_k;s)$ we have

$$\tilde{D}(0,0;0) = \frac{D^{(0)}(0,0)}{1-\lambda_2(0)D^{(0)}(0,0)}$$

$L \approx 1\ \mu\mathrm{m}$

The pole in $\tilde{D}(0,0;0)$ is the signature of a superconducting transition. The critical temperature can be computed taking into account that the correlations are cut off at kT about one order of magnitude below v_F / L



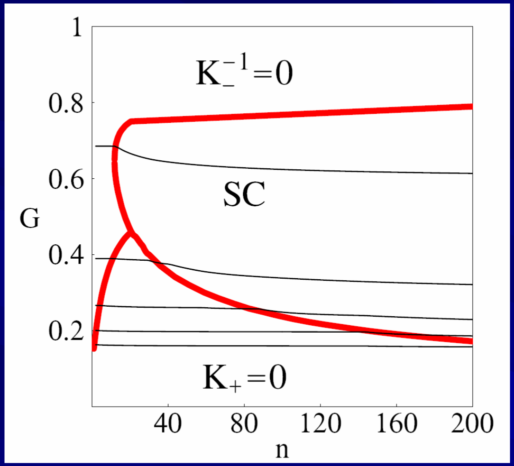
$(\times 0.1\,\mathrm{eV})$

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

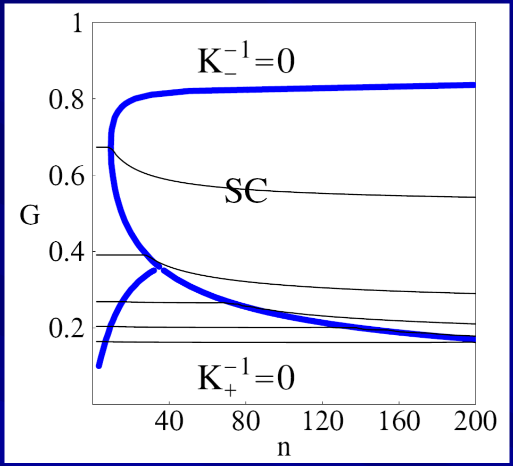
SUPERCONDUCTIVITY IN NANOTUBE ROPES

When intertube coherence is not achieved, exotic phases may arise from the strong correlation, due to either the decoupling of the metallic nanotubes in the rope or the onset of phase separation under very strong attraction

$(G \equiv 4\lambda / \pi v_F)$



undoped armchair

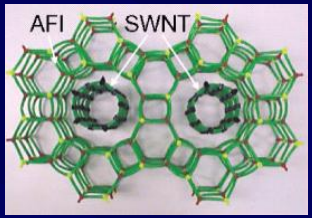


undoped zig-zag

(J. V. Alvarez and J. G., PRL **91**, 076401 (2003))

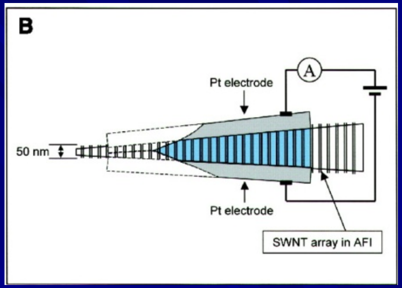
SMALL-DIAMETER NANOTUBES

There have been hopes that in nanotubes of minimum radius $R \approx 0.2$ nm the superconducting correlations could be enhanced

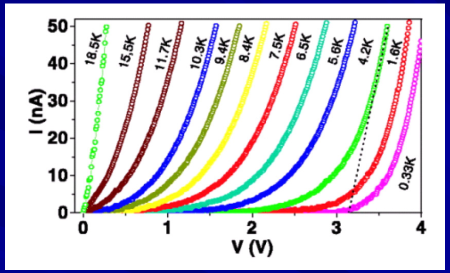


Z. K. Tang *et al.*,

Science **292**, 2462 (2001)

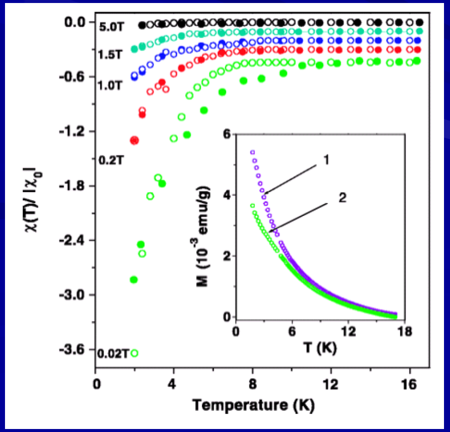


Small-diameter nanotubes have been synthesized in the channels of a zeolite matrix, and evidence of superconductivity has been claimed (pseudogap, diamagnetic susceptibility). However,



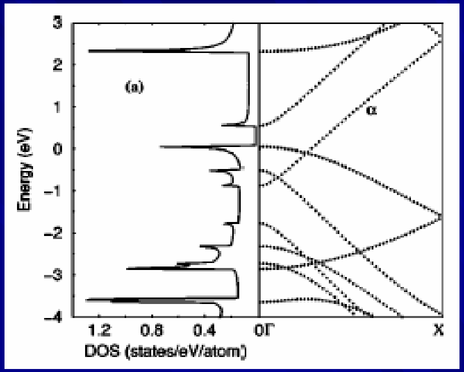
although the electron-phonon couplings must be enhanced due to the large curvature of the tubes,

- in the array of nanotubes, there can be only a moderate screening of the Coulomb interaction
- the intertube tunneling must be negligible, what prevents the development of a true condensate



SMALL-DIAMETER NANOTUBES

There are two geometries consistent with a radius $R \approx 0.2$ nm, namely the armchair (3,3) and the zig-zag (5,0) nanotubes. The latter have a large density of states at the Fermi level,

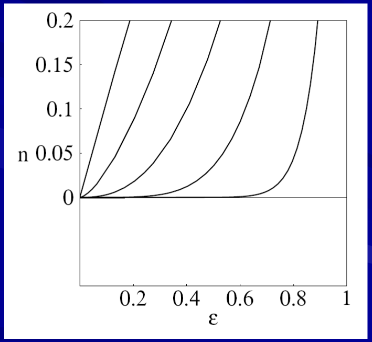


but different computational methods have shown that they do not support large superconducting correlations

- D. Connétable *et al.*, PRL **94**, 015503 (2005)
- J. G. and E. Perfetto, PRB **72**, 205406 (2005)

The pseudogap may well be the consequence of the breakdown of the Luttinger liquid behavior when any of the *K*'s becomes singular at small *T*,

$$n(\varepsilon) \sim \varepsilon^{\sum_a (K_a + 1/K_a - 2)/8}$$

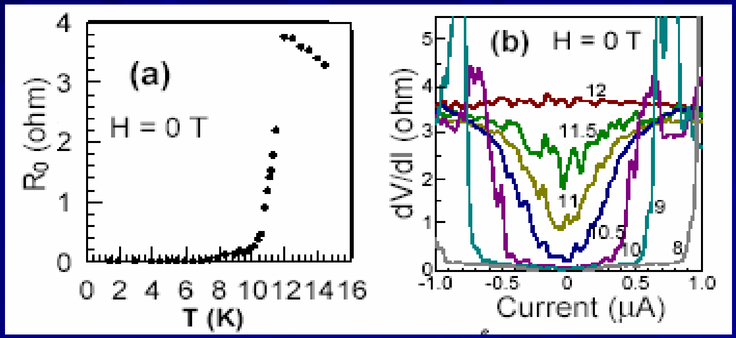


while the diamagnetism may be also the consequence of an enhanced susceptibility for orbital currents.

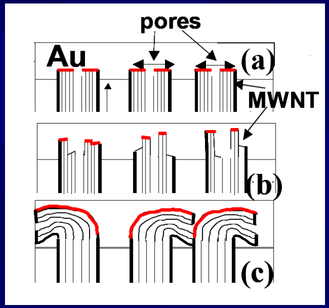
(J. G., PRB **72**, 073403 (2005))

SUPERCONDUCTIVITY IN MULTI-WALLED NANOTUBES

More recently, abrupt transitions have been observed in the resistance of multi-wall nanotubes, at temperature $T \sim 10$ K,

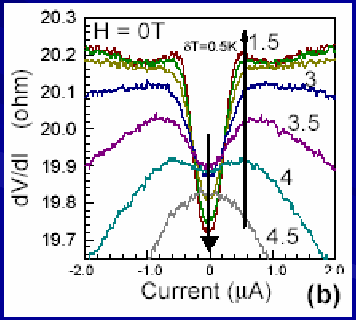


I. Takesue *et al.*, Phys. Rev. Lett. **96**, 057001 (2006)



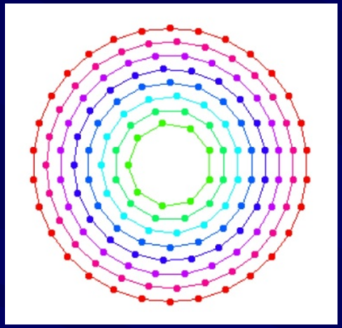
These MWNT have been synthesized in the channels of an alumina template, and the observation of the transition seems to require the contact to most part of the shells in the nanotube (entire "end-bonding").

Otherwise, when there is only partial end-bonding, the transition does not take place, and there is only evidence of a dip superposed to the broad peak in the plot of *dV/dI* .

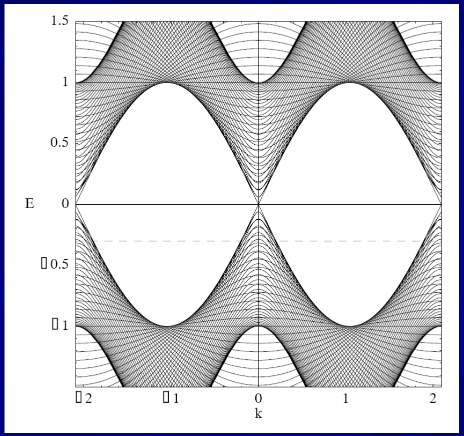


All this is in contrast to the case of conventional bulk-junctions, where the behavior of *dV/dI* is monotonous with temperature.

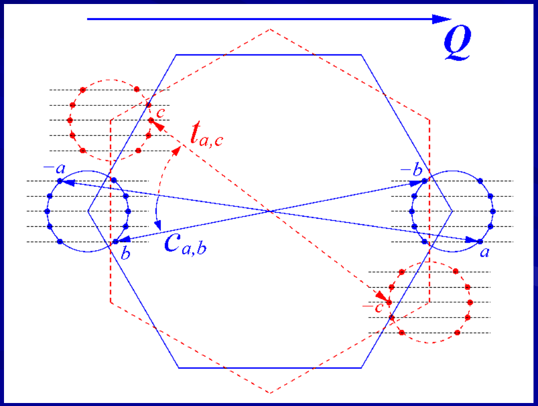
SUPERCONDUCTIVITY IN MULTI-WALLED NANOTUBES



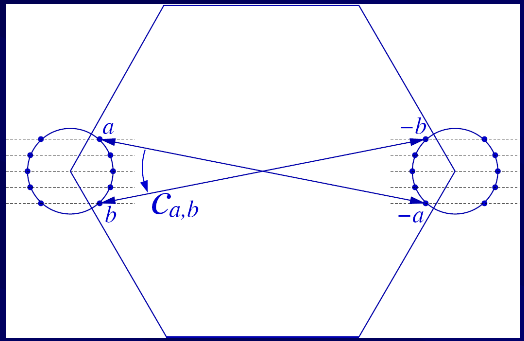
The MWNT are good candidates to support superconducting behavior since upon doping they may have many subbands crossing the Fermi level (large screening of the Coulomb interaction).



The carbon lattices of nearest shells are not commensurate in general, which places a severe constraint in single-electron tunneling. The tunneling of Cooper pairs (zero total momentum) remains however unaffected, and may open the 3D coherence in the MWNT.



SUPERCONDUCTIVITY IN MULTI-WALLED NANOTUBES

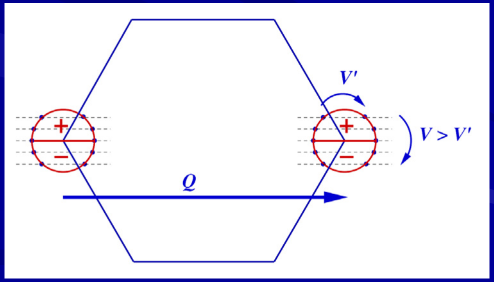


In the shells of the MWNT, the electron-phonon interaction is much weaker than in single-walled nanotubes, leading to a coupling of the phonon-mediated interaction $\lambda \sim 1/R$. In the manifold of Fermi points, however, the Coulomb interaction is screened anisotropically, which may open a channel of attraction.

The Cooper-pair vertex can be expanded in a basis of the irreducible representations of the symmetry group of the manifold of Fermi points:

$$V(\theta_a,\theta_b) \approx V_0 + V_1 \cos(\theta_a)\cos(\theta_b) + V_2 \sin(\theta_a)\sin(\theta_b) + V_3 \cos(2\theta_a)\cos(2\theta_b) + V_4 \sin(2\theta_a)\sin(2\theta_b) + \ldots$$

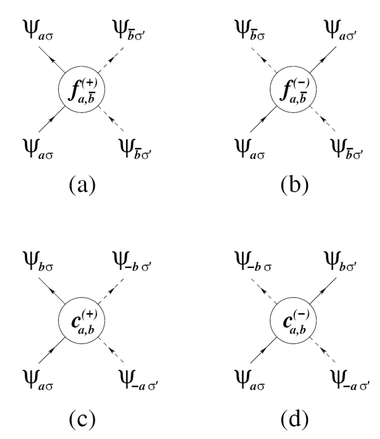
It can be checked that, as long as the *e-e* interaction gets less screened as the momentum-transfer in the transverse direction becomes larger, the Cooper-pair scattering develops an attractive interaction in the $\sin(\theta)$ channel $(V_2 < 0)$.



(E. Perfetto and J. G., PRB **74,** 201403(R) (2006))

SUPERCONDUCTIVITY IN MULTI-WALLED NANOTUBES

$$
\begin{aligned}
H_{\rm int} \;=\; \int dp dp' dq \Big[& \psi^+_a(p+q)\psi_a(p)\; f^{(+)}_{a,-b}\; \psi^+_{-b}(p'-q)\psi_{-b}(p') \\
& +\psi^+_{-b}(p+q)\psi_a(p)\; f^{(-)}_{a,-b}\; \psi^+_a(p'-q)\psi_{-b}(p') \\
& +\psi^+_b(p+q)\psi_a(p)\; c^{(+)}_{a,b}\; \psi^+_{-b}(p'-q)\psi_{-a}(p') \\
& +\psi^+_{-b}(p+q)\psi_a(p)\; c^{(-)}_{a,b}\; \psi^+_b(p'-q)\psi_{-a}(p') \Big]
\end{aligned}
$$



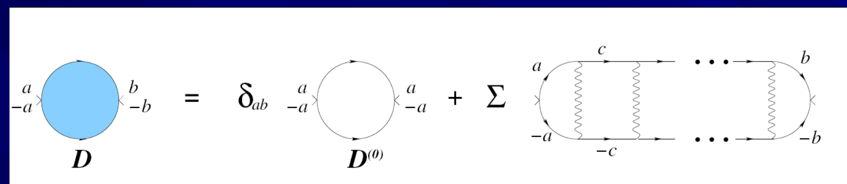
$$
\begin{aligned}
\frac{\partial f^{(+)}_{a,b}}{\partial l} &= -\frac{1}{2\pi v_{ab}}((f^{(-)}_{a,b})^2 - (c^{(+)}_{a,-b})^2) \\
\frac{\partial f^{(-)}_{a,b}}{\partial l} &= -\frac{1}{\pi v_{ab}}((f^{(-)}_{a,b})^2 + (c^{(-)}_{a,-b})^2 - c^{(-)}_{a,-b}c^{(+)}_{a,-b}) \\
\frac{\partial c^{(+)}_{a,b}}{\partial l} &= -\sum_{c,s}\frac{1}{2\pi v_c}(c^{(s)}_{a,c}c^{(s)}_{c,b} + t^{(s)}_{a,c}t^{(s)}_{c,b}) \\
&\quad +\frac{1}{2\pi v_{ab}}c^{(+)}_{a,b}h^{(+)}_{a,-b} \\
\frac{\partial c^{(-)}_{a,b}}{\partial l} &= -\sum_{c,s}\frac{1}{2\pi v_c}(c^{(s)}_{a,c}c^{(-s)}_{c,b} + t^{(s)}_{a,c}t^{(-s)}_{c,b}) \\
&\quad -\frac{1}{\pi v_{ab}}c^{(-)}_{a,b}h^{(-)}_{a,-b} - \frac{1}{2\pi v_{ab}}\sum_s c^{(s)}_{a,b}h^{(-s)}_{a,-b} \\
\frac{\partial t^{(\pm)}_{a,b}}{\partial l} &= -\sum_{c,s}\frac{1}{2\pi v_c}(c^{(s)}_{a,c}t^{(\pm s)}_{c,b} + t^{(s)}_{a,c}c^{(\pm s)}_{c,b})
\end{aligned}
$$

with $h^{(s)}_{a,-b} \equiv 2f^{(s)}_{a,-b} - \delta_{ab}c^{(s)}_{a,a}$.

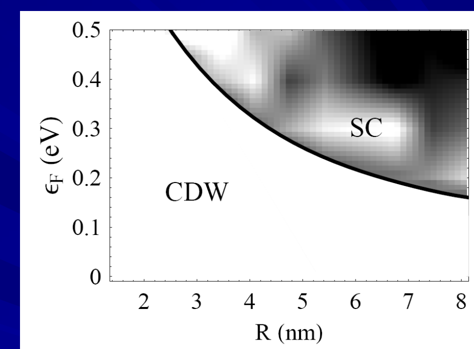
$$
\begin{aligned}
\frac{\partial \overline{R}_g(\Lambda)}{\partial \log(\Lambda)} &= \sum_{a,b,s} g^{(s)}_{a,b}\, c^{(s)}_{a,b}(\Lambda)\, \overline{R}_g(\Lambda) \\
\frac{\partial \overline{T}_g(\Lambda)}{\partial \log(\Lambda)} &= \sum_{a,b,s} g^{(s)}_{a,b}\, t^{(s)}_{a,b}(\Lambda)\, \overline{R}_g(\Lambda)
\end{aligned}
$$

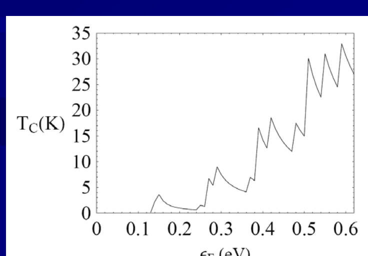
SUPERCONDUCTIVITY IN MULTI-WALLED NANOTUBES

Once we have a negative coupling in a given channel of the manifold of Fermi points, the attractive interaction is enhanced from the delocalization of the Cooper pairs in the different subbands and nanotube shells



This effect can be studied precisely analyzing the scaling of the different couplings, to conclude that the Cooper-pair susceptibility diverges at a critical scale that depends essentially on the number of Fermi points (in practice above 12 per shell)





The critical scale of superconductivity has in general abrupt jumps at the opening of new subbands, reflecting the divergences in the density of states.

(E. Perfetto and J. G., PRB **74**, 201403(R) (2006))

In conclusion,

- there are good perspectives to observe superconductivity in carbon nanotubes, but the quality of the contacts seems to be essential (in ropes as well as in MWNT)
- there is also the question of how the superconductivity of MWNT is related to that of doped graphite (intercalated compounds)
- finally, there is the question of the maximum transition temperatures that can be reached, and whether they can match those of the alkaline salts of fullerenes