NT’06
NAGANO JAPAN
Tutorial Program
June 18, 2006

Electrical and thermal transport in macroscopic carbon nanotube assemblies, and polymer composites

John E. (Jack) Fischer
Department of Materials Science and Engineering
University of Pennsylvania
3231 Walnut St.
Philadelphia PA 19104-6272

OUTLINE

- **Brief review of macroscopic (3-D) electrical conductors**
- **<u>Electrical conductivity</u> of nanotube assemblies**:

  pure tubes, SWNT/polymer composites
  - How do we even begin to think about macroscopic NT assemblies (mats, fibers, films)? Certainly not a collection of perfect ballistic conductors!
  - Beyond "free electron gas" – effects of disorder, interfaces, carrier localization, variable-range hopping, tunneling thru barriers, …..
  - How do we identify the macro-scale mechanism for a particular material? <u>Experiments vs. temperature, magnetic field, doping.</u>
  - Composites – dispersion, interfaces, SWNT alignment, percolation,…
- **Brief review of macroscopic (3-D) thermal conductors:**

  heat capacity, mean free path, phonon dispersion and sound velocity
- **Fundamentals of <u>thermal transport</u> in SWNT:** effect of 1-D subbands
  - SWNT – lots of theory, sparse experiments
  - Individual MWNT – experiments
  - SWNT assemblies and composites
- **Application to peapods - a case study**

Excuse me, Prof. Tomanek, but….

The beautiful physics of ideal tubes is largely ruined (or obscured) in real materials, by

1. Diameter polydispersity broadens everything.
2. Coupling between tubes (bundles, ropes, …..)
3. Inhomogeneities
4. Residual impurities (metals, amorphous carbon) from the growth process
5. Characterization problems, e.g. luminescence is quenched by interactions in assemblies.

Macroscopic electron transport; disorder effects in CNT materials

Free electron gas: inelastic (e-ph) and elastic (defects,impurities) scattering (elemental metals and alloys, doped semiconductors,)

Strong localization: phonon-assisted variable range hopping (VRH) *a la* Mott: (impurity bands, amorphous semiconductors, highly disordered metals)

Weak localization: power law T dependence (conjugated polymers esp PANI)

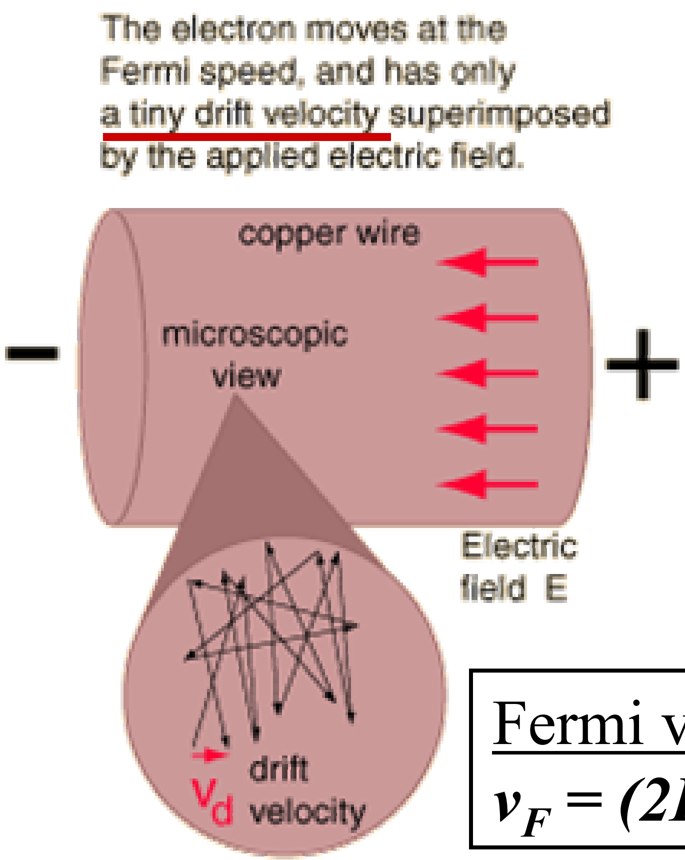
Granular metal – two-phase system, tunneling or hopping between metallic islands (doped conducting polymers)

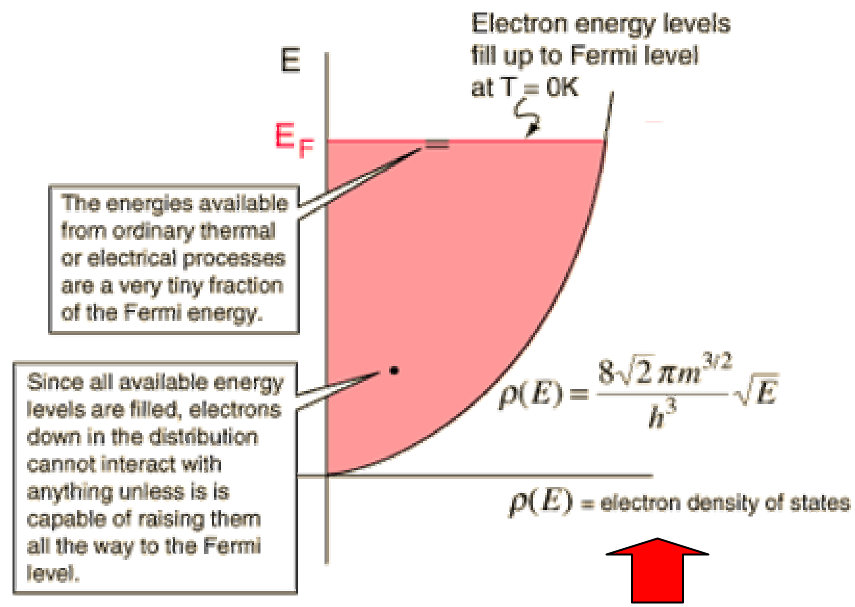
Coulomb gap – electron-electron interaction opens a gap at the Fermi energy; transport is thermally activated (same equation as VRH but the parameters have different meaning).

Combinations – to fit complex materials over wide T range (Kaiser)

Free electron gas: microscopic view of Ohm's Law
Ideal gas of electrons but with quantum statistics

Current density J = (# electrons/vol)(charge)(velocity) = $ne\vec{v}_D$





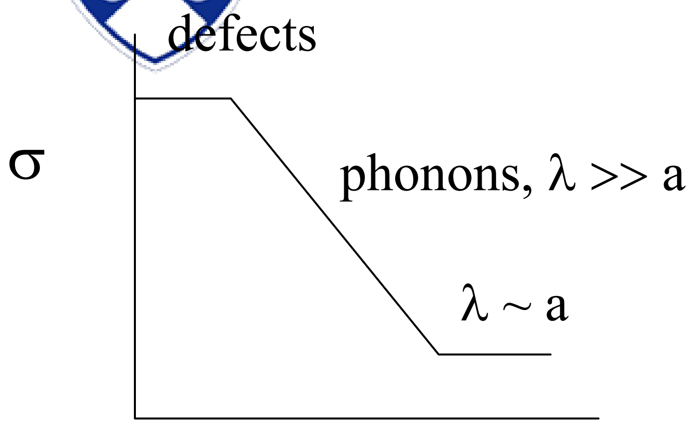
$$\boxed{\begin{array}{l}\underline{\text{Fermi velocity:}}\\ v_F = (2E_F/m)^{1/2}\end{array}}$$

Classical feg: $v = \boldsymbol{v_D} + v_{th}$

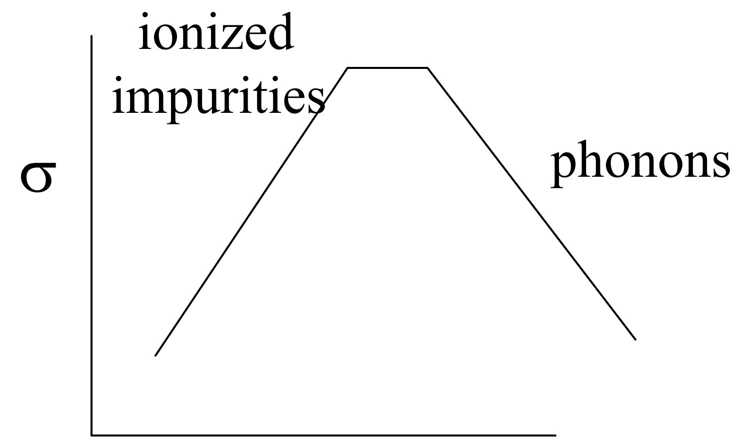
Quantum feg: $v = \boldsymbol{v_D} + v_F$

http://hyperphysics.phy-astr.gsu.edu/hbase/hframe.html

σ and κ limited by collisions

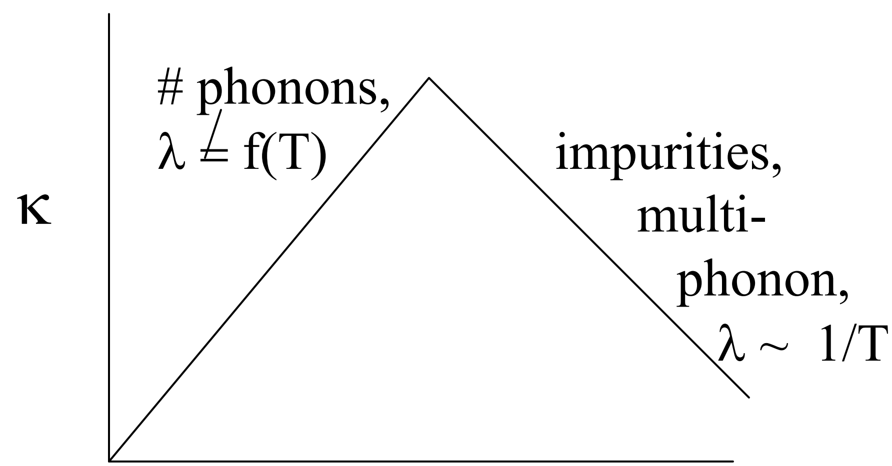


Temperature
(METAL)



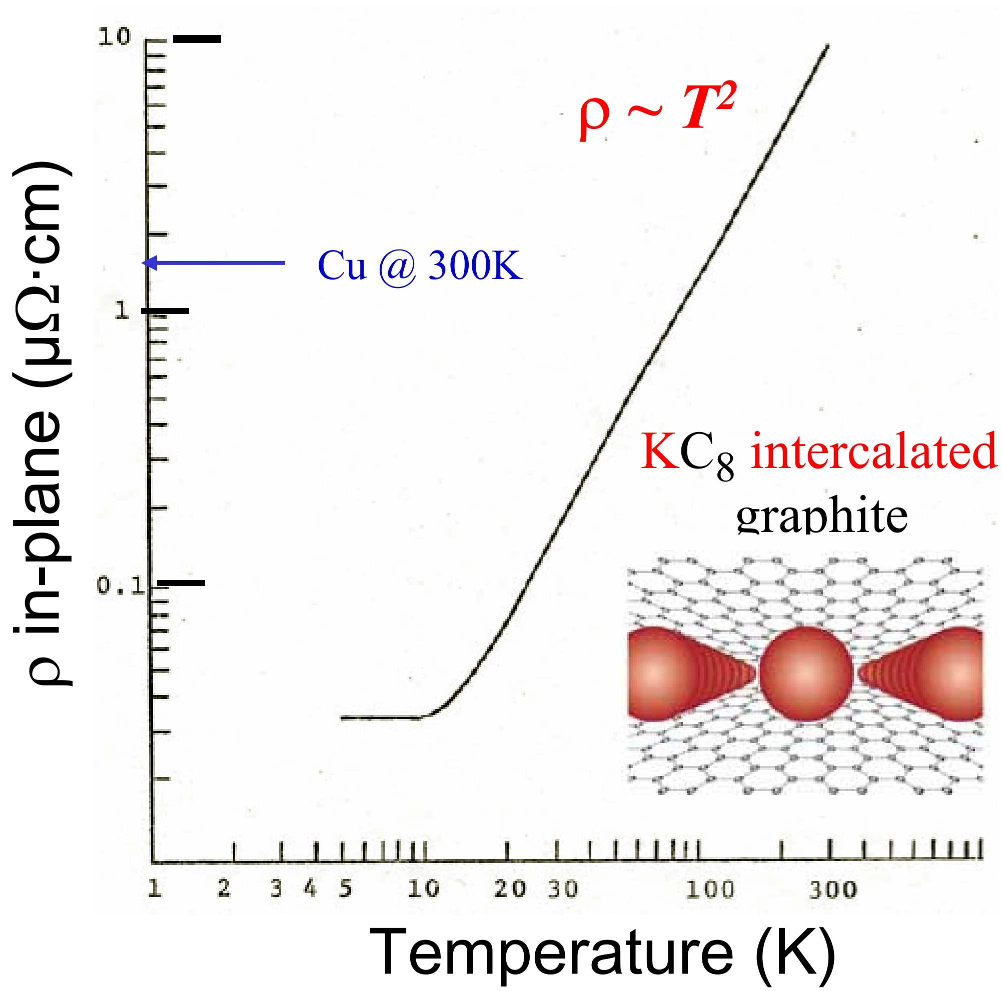
Temperature
(SEMICONDUCTOR)

Electronic conductivity only happens with delocalized electrons (or holes) but thermal conductivity can involve electrons and/or phonons.



Temperature

(anisotropic) 3-D macroscopic, ordered synthetic metal: classic behavior: electron-phonon scattering (inelastic) + residual defects (elastic): $\rho = AT^{\eta} + \rho_o$



$1/\rho = \sigma = ne\mu = ne^2\tau\ /m^*$;
n = carrier concentration;
$1/\tau$ = sum of scattering rates,
m* determined by E(k).

Crystalline material system, phonon mean free path << system size but >> atomic scale, i.e. not ballistic conduction and electron states delocalize to "fill" the system.

Very large resistance ratio: R(300K)/R(4K) = 300; very low defect/impurity concentration.

Mark Potter, Penn (1976)

For small E, v_D increases linearly with E; $v_D = eE\tau/m$
where $1/\tau$ = scattering rate, and $\tau = \lambda/v_F$ -
λ = mean free path between collisions.

What's different at the nanoscale?

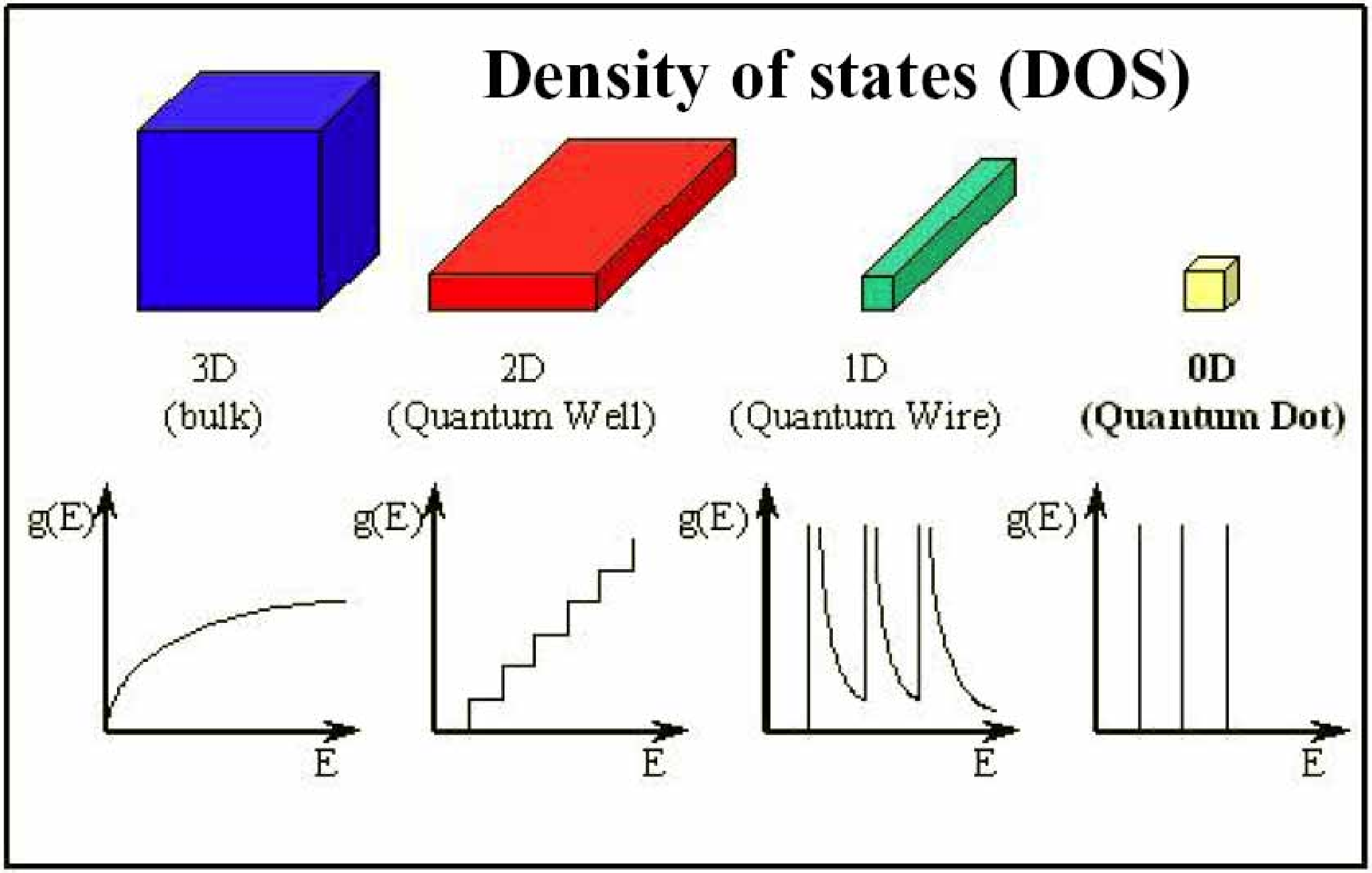
System size < λ; ballistic conduction (but what's the "system"?)
Dimensionality $\neq 3$
* Density of states no longer $\sim \sqrt{E}$; different temperature dependence of C_P, thermal conductivity κ, …..
* Only forward- or backscattering in 1-D
* Many-body effects are enhanced (e.g. Luttinger liquid)

What's different for macroscopic assemblies of nano-systems?

"disorder": electron wave function may not "fill" the system; weak and/or strong localization.
Transport mechanism different in "doped" materials.
Wide variation in transport properties from sample to sample;
Hard to establish property correlations with morphology, defects

Electronic structure

(similar for phonons)



1D:
semiconductor quantum wires
conducting polymers
nanotubes

0D:
atoms
molecules
nanocrystals
metal nanoparticles
quantum dots
short nanotubes

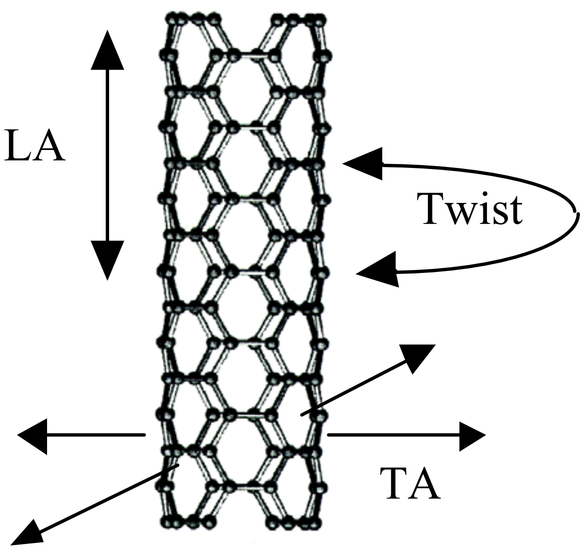
1D density of states per unit length:

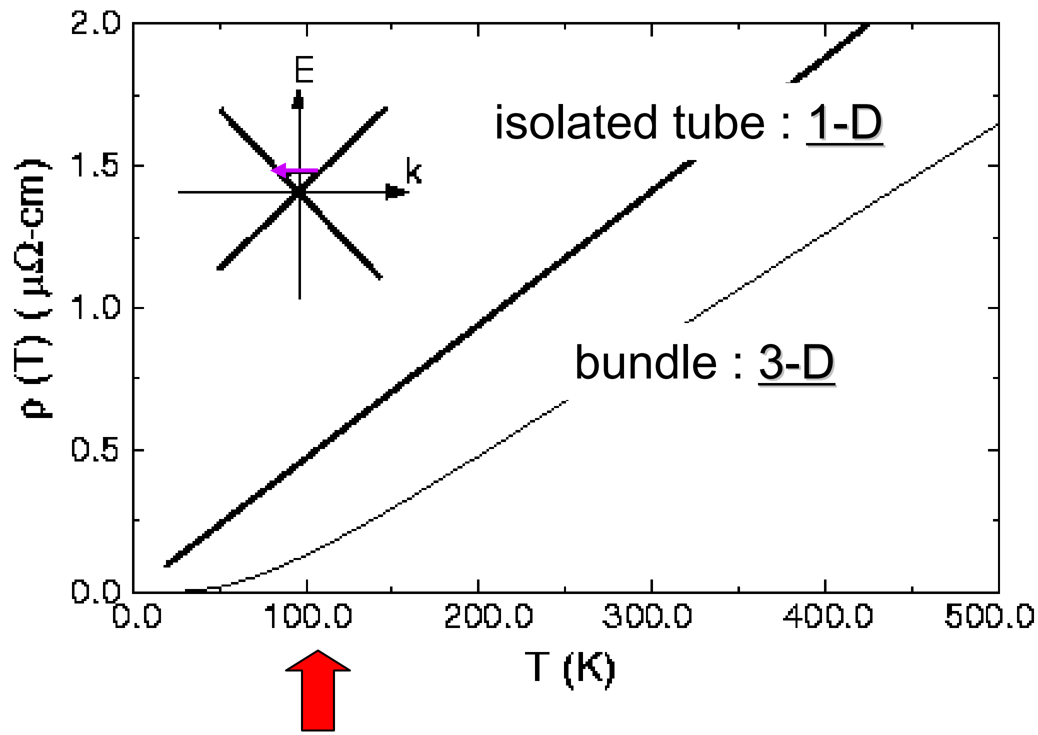
$$g_{1D}(E) = \frac{2}{h}\sqrt{\frac{2m}{E}} = \frac{2}{hv(E)} = \frac{2}{\pi}\left(\frac{dE}{dk}\right)^{-1} \qquad v_{\text{group}} = \frac{d\omega}{dk} = \frac{1}{\hbar}\frac{dE}{dk}$$

From Jesper Nygard, NT'05

“twistons” – lowest energy phonons which can scatter SWNT electrons

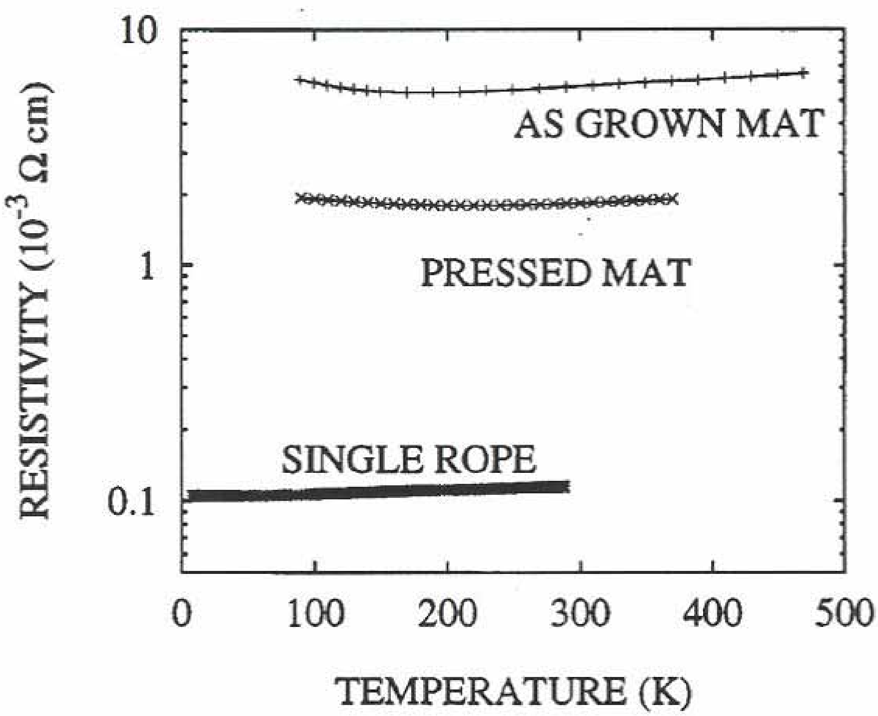
Kane & Mele, *Europhys. Letters* 41, 683-688 (1998).

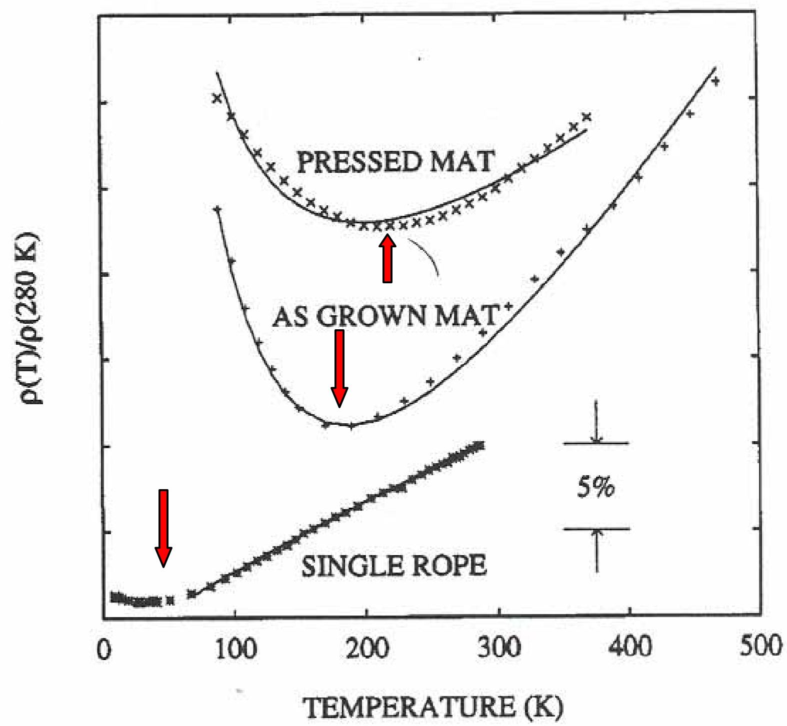




Upper curve: 1-D model, $\rho \sim T$. Lower curve: Including 3-D intertube effects (i.e bundles) in both the electron and twiston degrees of freedom, the linear $\rho(T)$ behavior in bundles occurs *only* above a relatively low crossover temperature. The inset shows the process in which an electron scatters from the right- moving to left-moving E(k) branch, emitting a low-energy (long-wavelength twiston. This model does not account for observed negative $d\rho/dT$ at low T.

Electron transport in nanotube materials





A single uniaxial rope is ~ 60 X more conductive than the disordered mat. The compressed mat is ~3X densified. For all three materials ρ(T) is quite flat.

R. S. Lee *et al*, Phys. Rev. B **55**, R4921 (1997)

On a blown-up scale, all samples show a shallow minimum in ρ(T) at a characteristic T* above which dρ/dT is positive (metallic) – a crude index of the degree of disorder.

multiple processes in the same (inhomogeneous) material

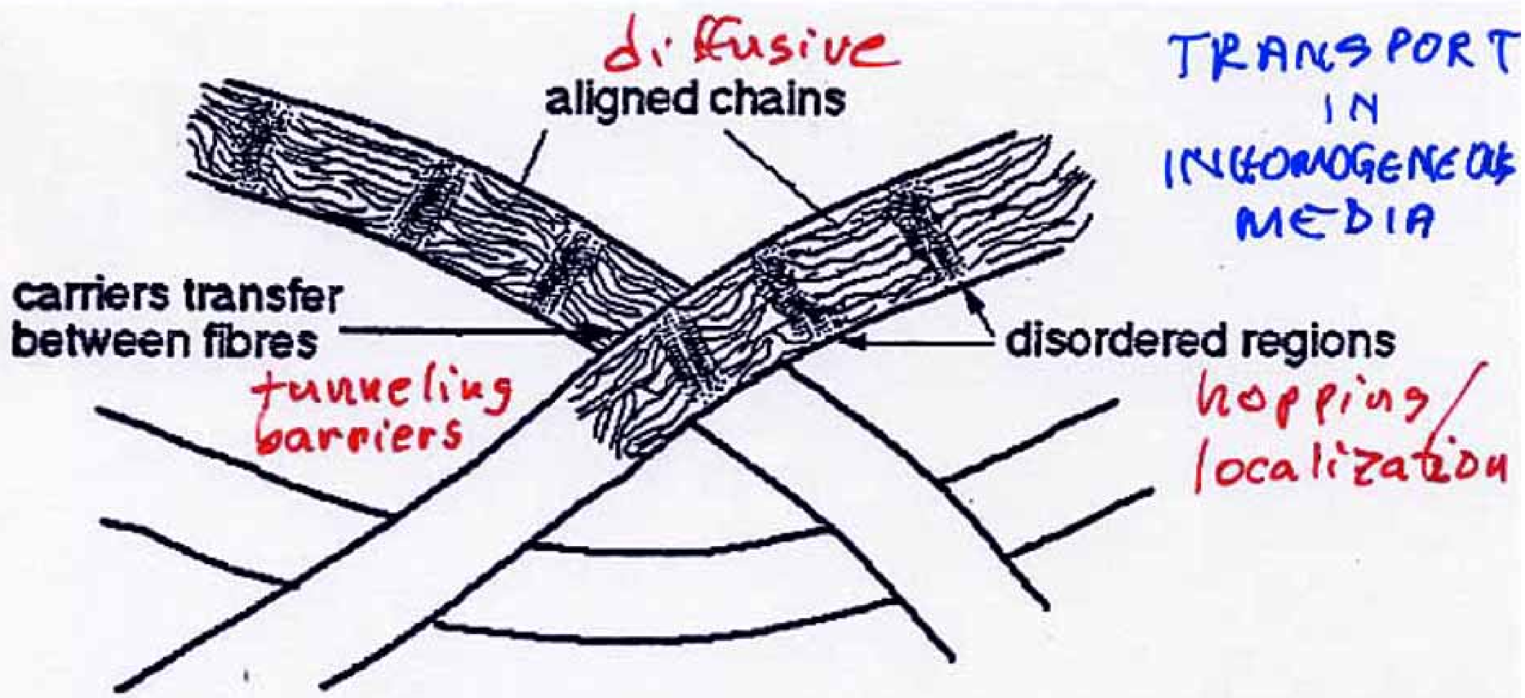
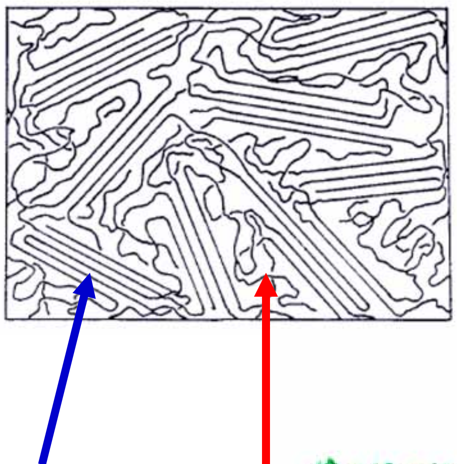
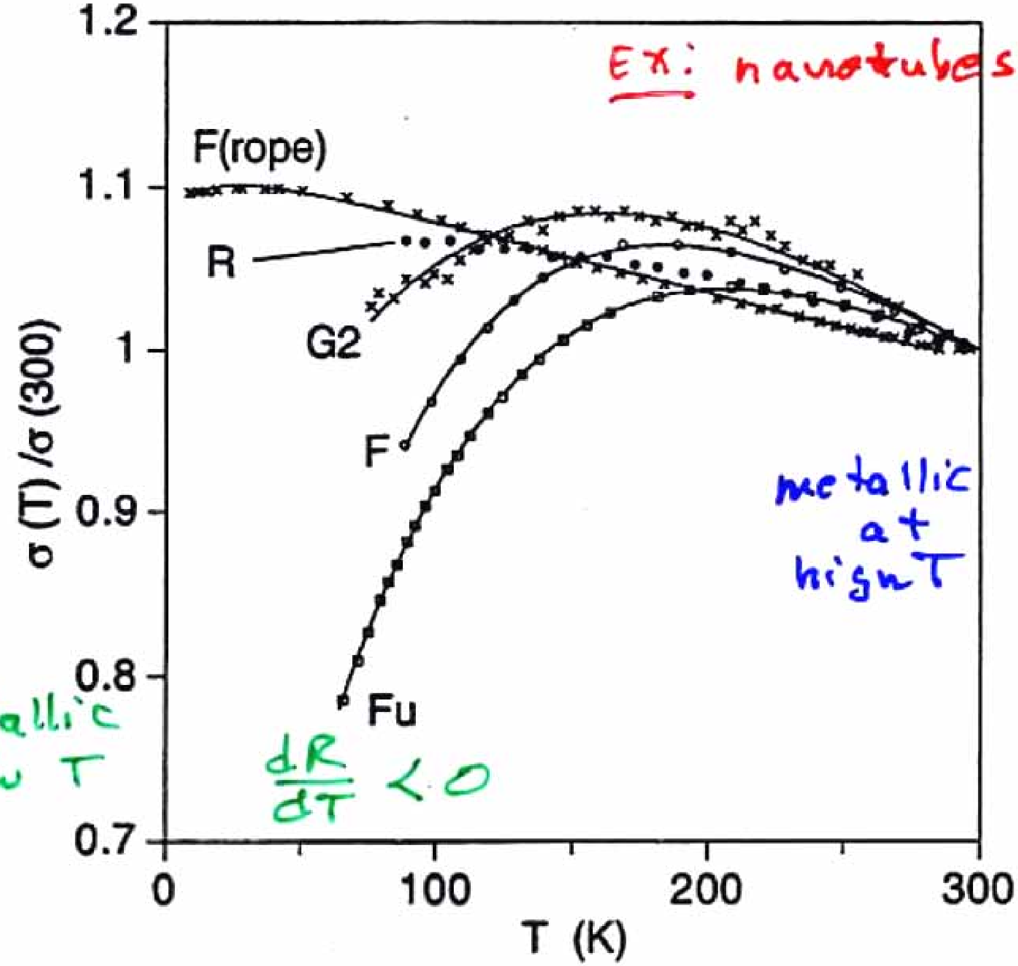


Fig. 1. Sketch of crystalline regions in fibrillar highly-conducting polyacetylene separated by disordered regions (after Ehinger and Roth [6]).





Ex: nanotubes

metallic at high T

$\frac{dR}{dT} > 0$

non-metallic at low T

$\frac{dR}{dT} < 0$

Fluctuation-induced tunneling between metallic regions; weak localization in "matrix".

α = metallic vol. fraction

kT_o = tunnel barrier height

kT_s = fluctuation energy scale

NOTE: finite ρ at $T = 0$.

A. B. Kaiser, Rev. Mod. Phys.

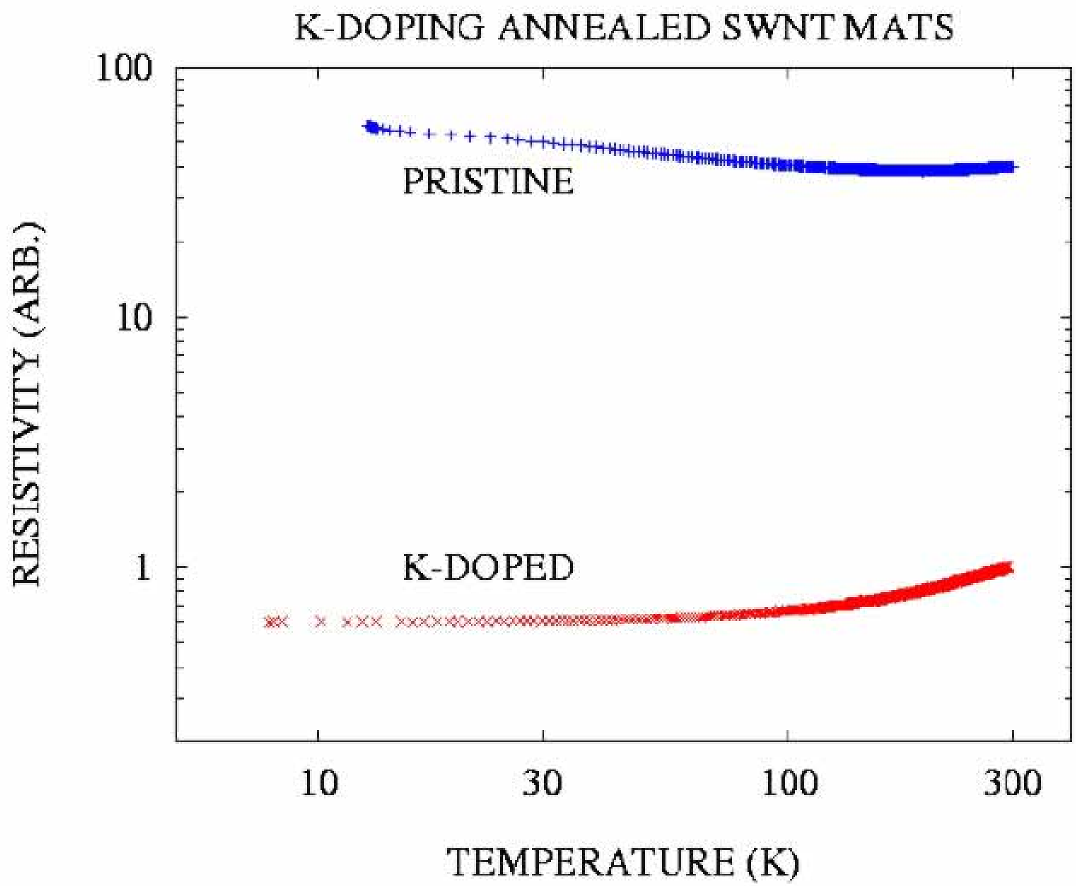
Fig. 3. Normalised conductivity of mats and a rope of single-wall carbon nanotubes measured by Fischer et al. (F) [21], Grigorian et al. (G2) [22], Rinzler et al. (R) [23] and Fuhrer et al. (Fu) [24]. The lines are fits to the heterogeneous expression

$$\sigma^{-1} = \alpha T + \beta \exp\left[\frac{T_0}{T + T_s}\right]$$

Alkali metal-doped (n-type) SWNT materials

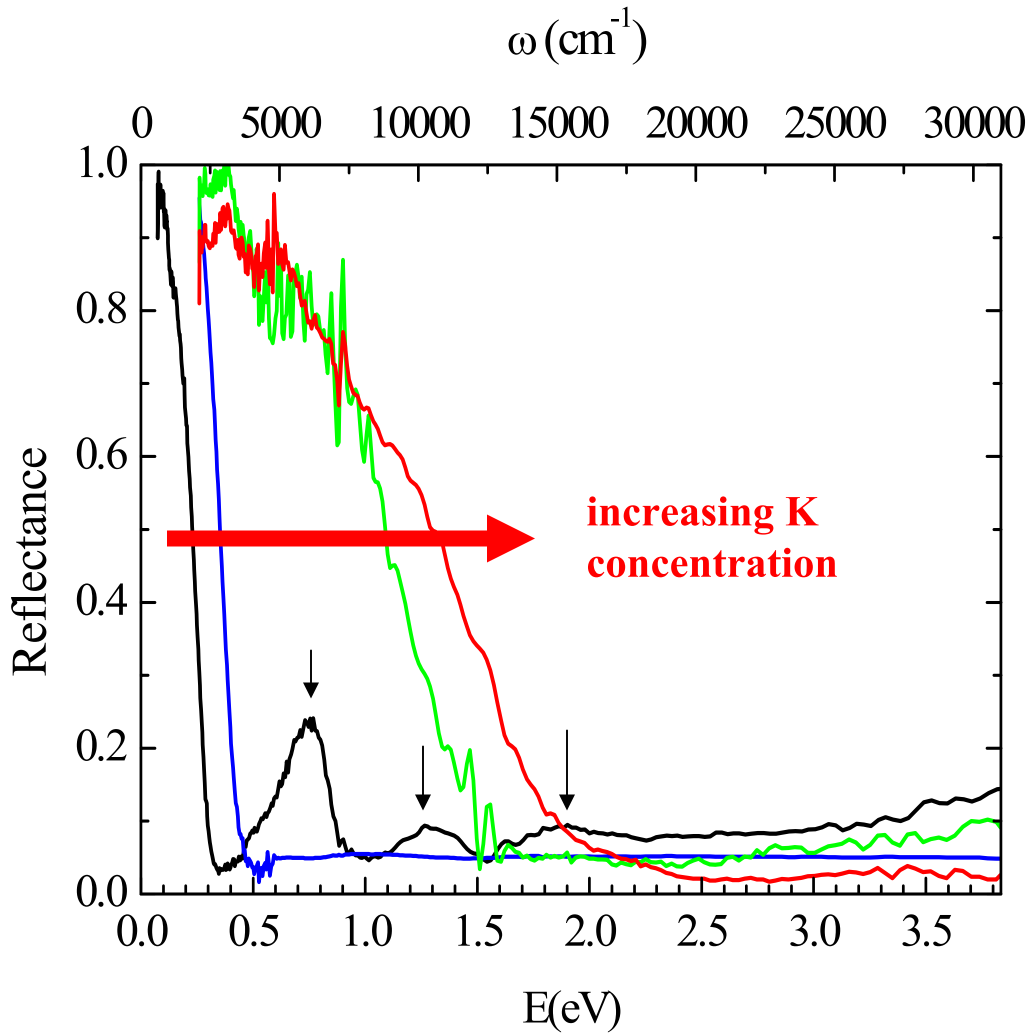
Similar to graphite, $(CH)_x$ *etc.:* alkali metal valence electron delocalized on the quasi-sp^2 carbon network. **BUT: much bigger residual resistivity than KC_8 graphite.**

$d\rho/dT > 0$ at all temperatures; "free carriers" screen out the effect of disorder; tunnel barriers no longer relevant.



R. S. Lee et al., *Nature* **388**, 255 (1997).

Reflectivity spectra:
K-doped SWNT *vs.* concentration



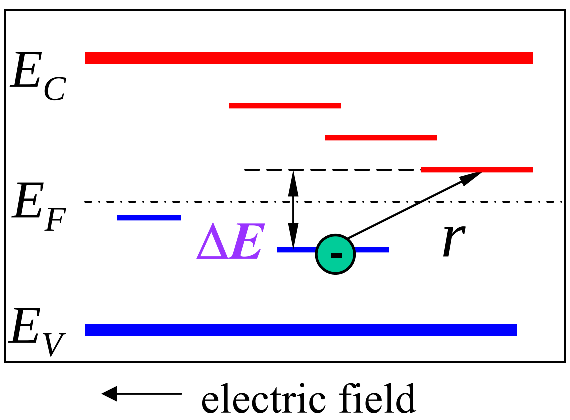
Classic Drude "plasma edge"
$(\sigma \sim \omega_P^2)$
plus 1-D interband transitions:

$\omega_P \sim \sqrt{n}$ increases with increasing K concentration, and the interband transitions are quenched as E_F shifts up into the conduction band.

W. Zhou, N. M. Nemes *et al.*, *Phys. Rev. B* **71**, 205423 (2005).

Variable range hopping

- disorder-induced localization of electronic states near the band edges of an amorphous, or heavily doped crystalline semiconductor. If the disorder is sufficiently "strong", a quasi-continuous density of localized states lies in the forbidden gap.



The **"green"** electron can carry current only by "hopping" to an **unoccupied state** nearby (say, at "*r*"), which requires a phonon of energy ΔE to promote it above E_F. The probability is $\propto \exp[-2r/a - \Delta E/k_B T]$ where

a = electron localization length.

Mott assumed that the conductivity is proportional to the probability of the most probable hop, whence the famous prediction:

$\rho \propto \exp[(T^* / T)^p]$, where

$k_B T^* = 2^{1/p} \Delta_{NN} / 2p(1-p)$;
p = 1/4, 1/3, or 1/2 in 3-D, 2-D or 1-D respectively.

VRH in amorphous semiconductors

amorphous Si films (1973):
(not shown) - crossover from 3-D (1/4 exponent to 2-D (1/3) with decreasing film thickness

GaN nanowire contacts (2005):
FIB-Pt ion beam damage creates amorphous layer (2-D)

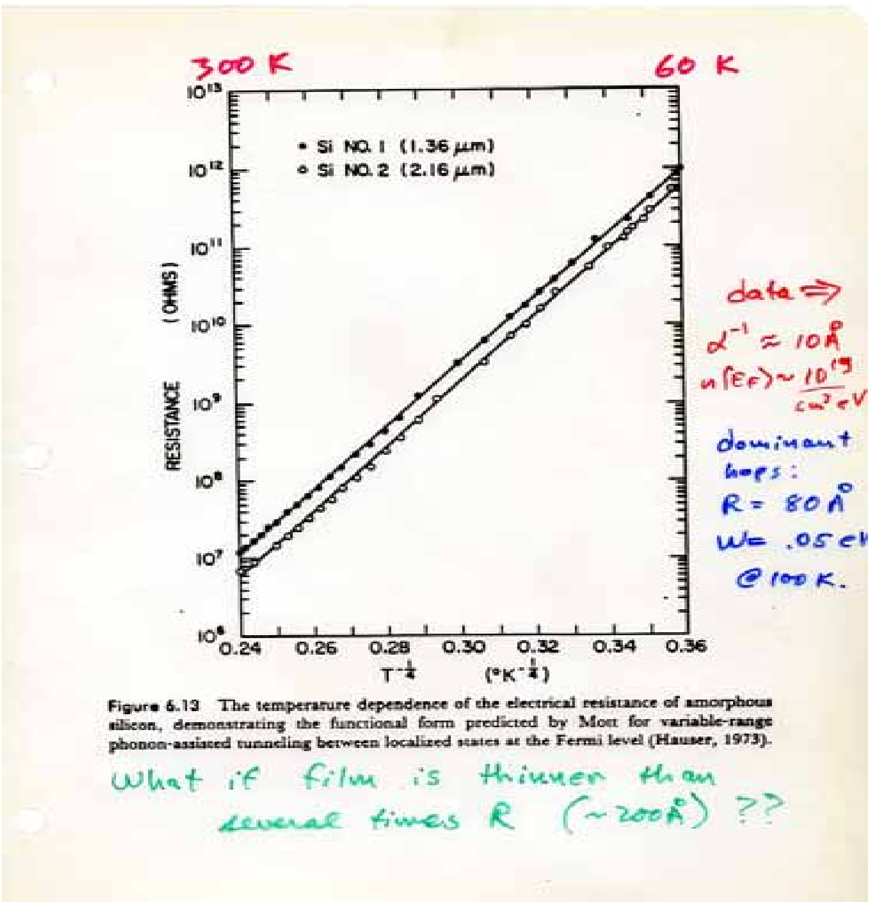
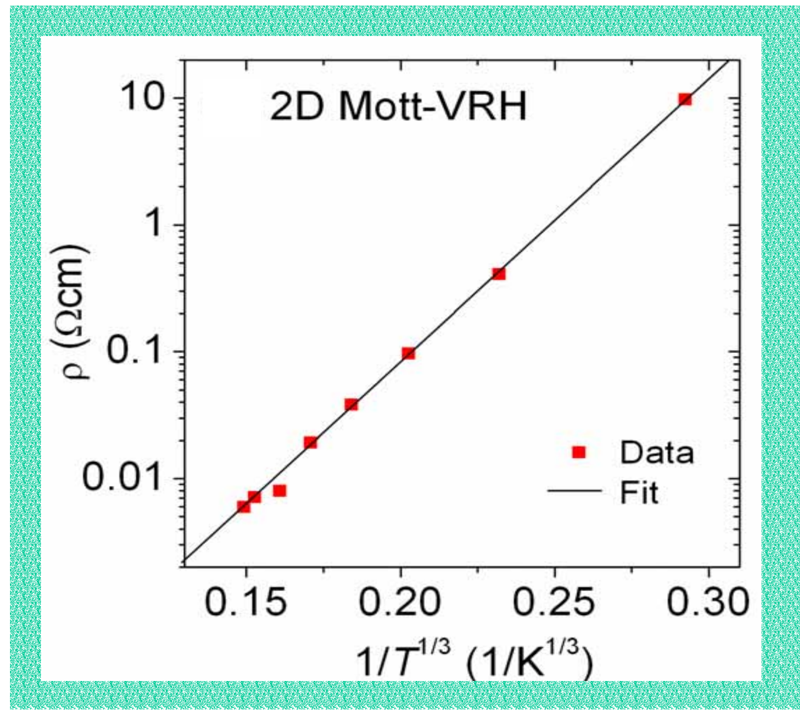
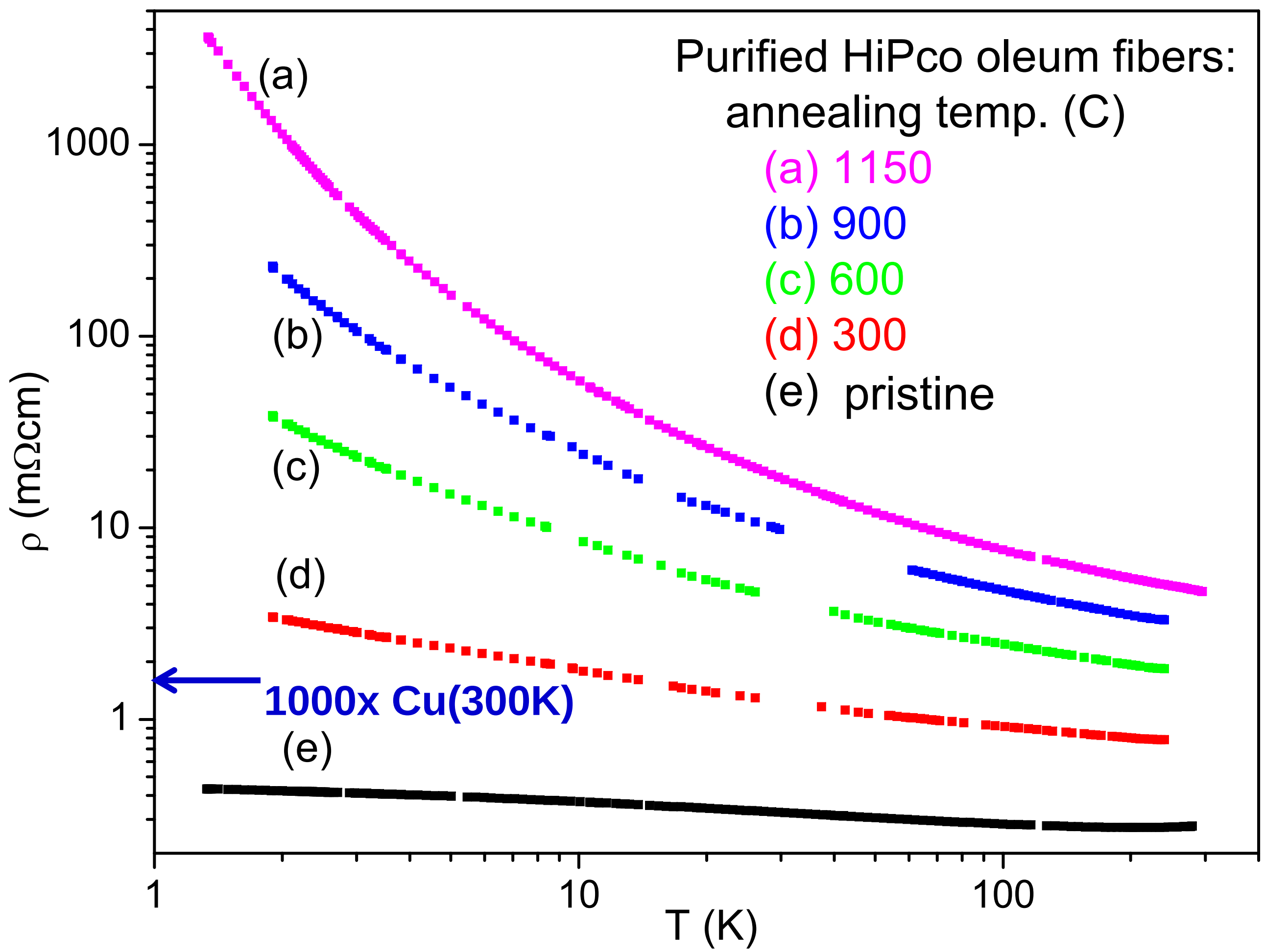


Figure 6.13 The temperature dependence of the electrical resistance of amorphous silicon, demonstrating the functional form predicted by Mott for variable-range phonon-assisted tunneling between localized states at the Fermi level (Hauser, 1973).



SWNT fibers spun from strong acid suspensions: heavily p-type in the pristine state; VRH after anneal



P-doped: (no anneal) weak localization (WL); metallic regions in "insulating" matrix (non-divergent ρ as $T \rightarrow 0$).

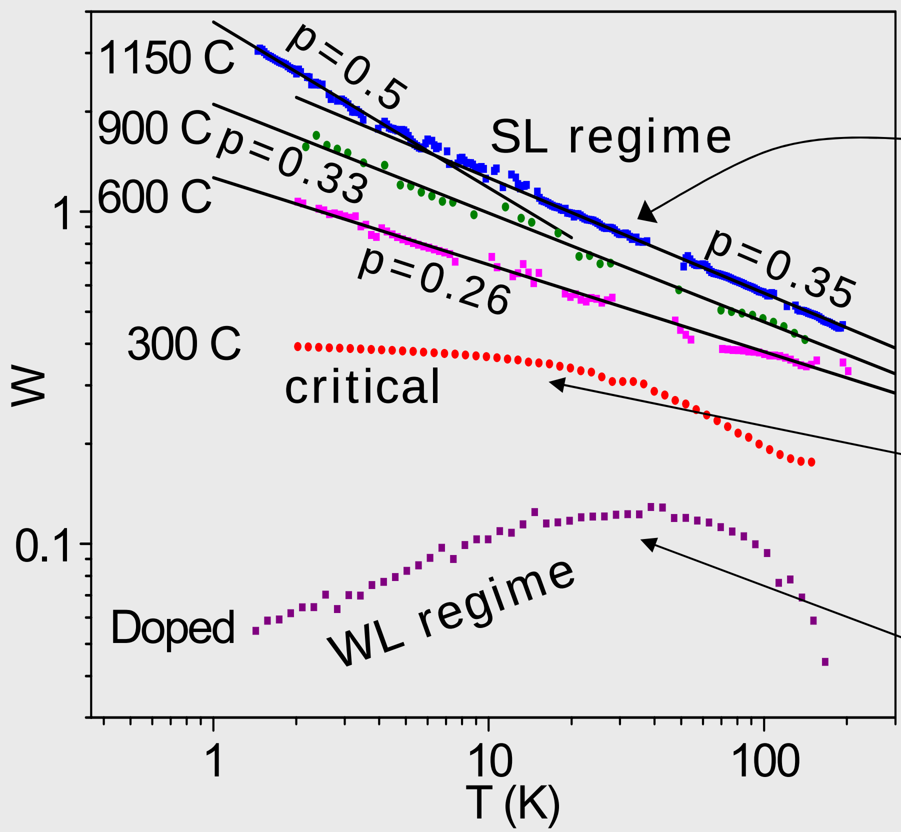
Intermediate: critical regime; metal-insulator transition.

Fully annealed: strong localization (SL) with variable range hopping.

J. Vavro et al., *Phys. Rev.* B**71,** 155410 (2005).

The concept of “reduced activation energy” to identify different regimes of behavior:

$$W \equiv \frac{d \ln \sigma}{d \ln T}$$



Variable range hopping should give a straight line on this plot.

All model exponents (1-D, 2-D, 3-D) are found in SL regime by varying annealing temperature.

$$\ln\sigma \propto -(T_0/T)^p \longrightarrow W \propto (T_0/T)^p$$

critical: $\sigma \propto T^s \longrightarrow W = s$

WL: $\sigma = \sigma_0 + aT^\gamma \longrightarrow W \propto T^\gamma$

Annealing out the dopants induces a metal-insulator transition (WL ➞ SL)

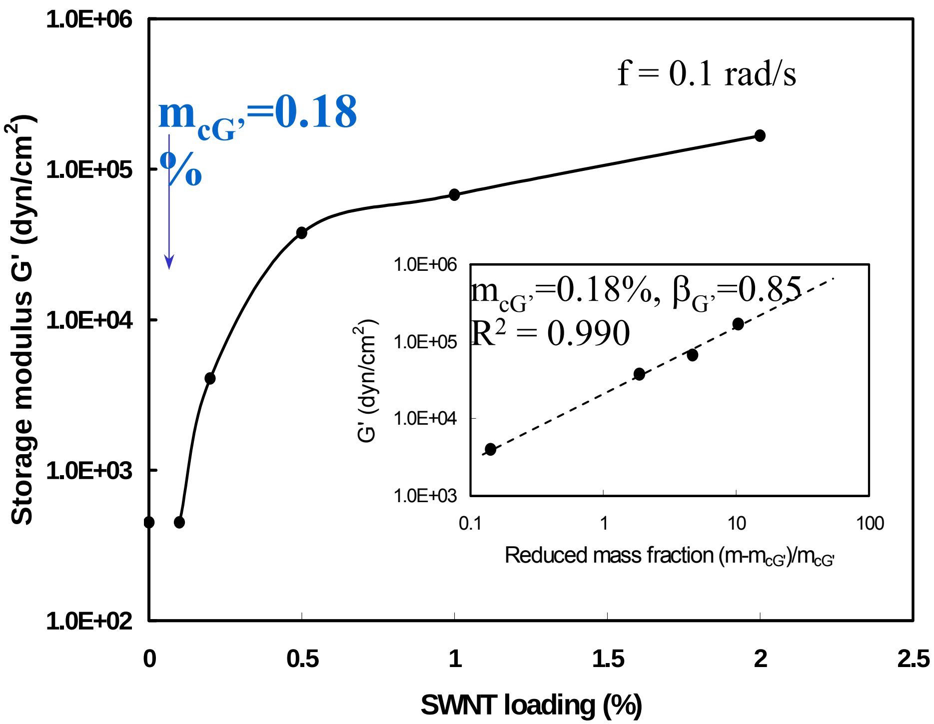
SWNT/PMMA composites: critical behavior in rheology and electrical transport

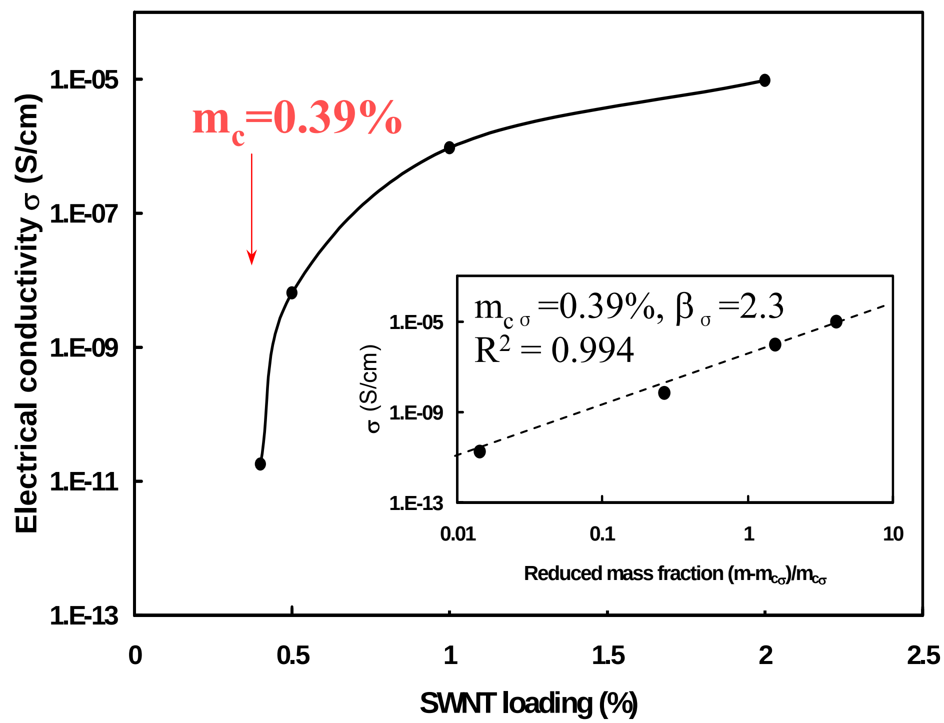
Above threshold, a hydrodynamic nanotube network impedes the motion of polymer coils

$G' \sim (m - m_{cG'})^{\beta_{G'}}$

Above threshold, a percolated network allows current to flow.

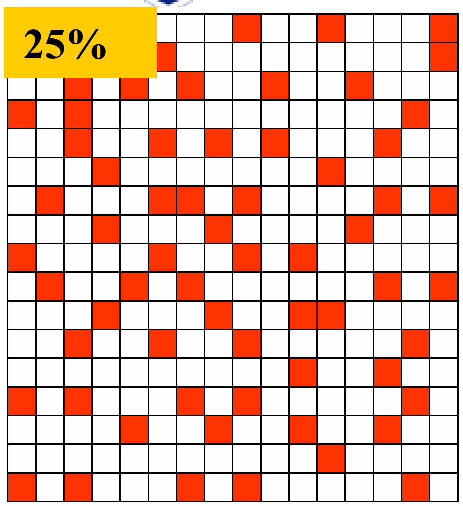
$\sigma \sim (m - m_{c\sigma})^{\beta_{\sigma}}$

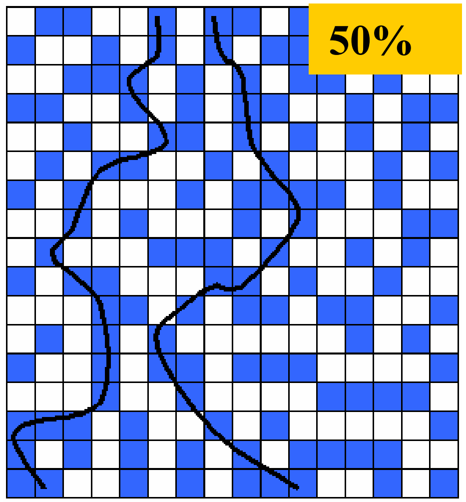




F. Du *et al.*, *Macromolecules* **2004,** *37*, 9048-9055

Percolation on a network of partly-oriented sticks

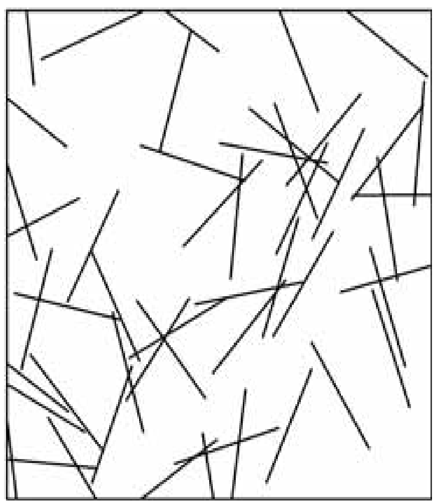




isotropic filler: high threshold,
"orientation" has no meaning

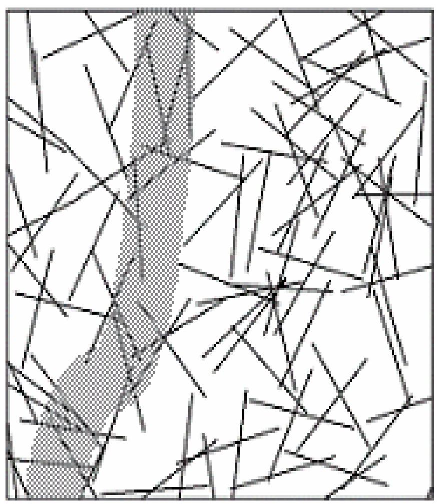
rod-like filler: onset of percolated path determined by concentration and ***mis***-alignment!

50 sticks, unaligned



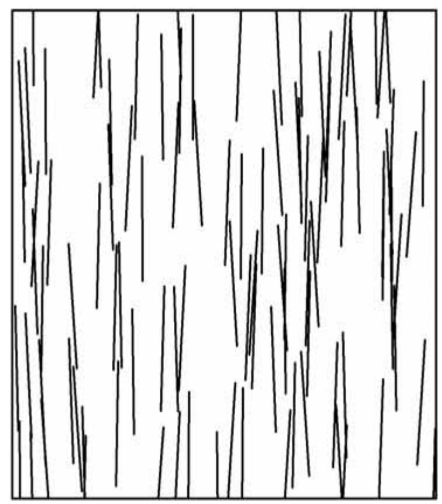
no percolation

100 sticks, unaligned



percolated

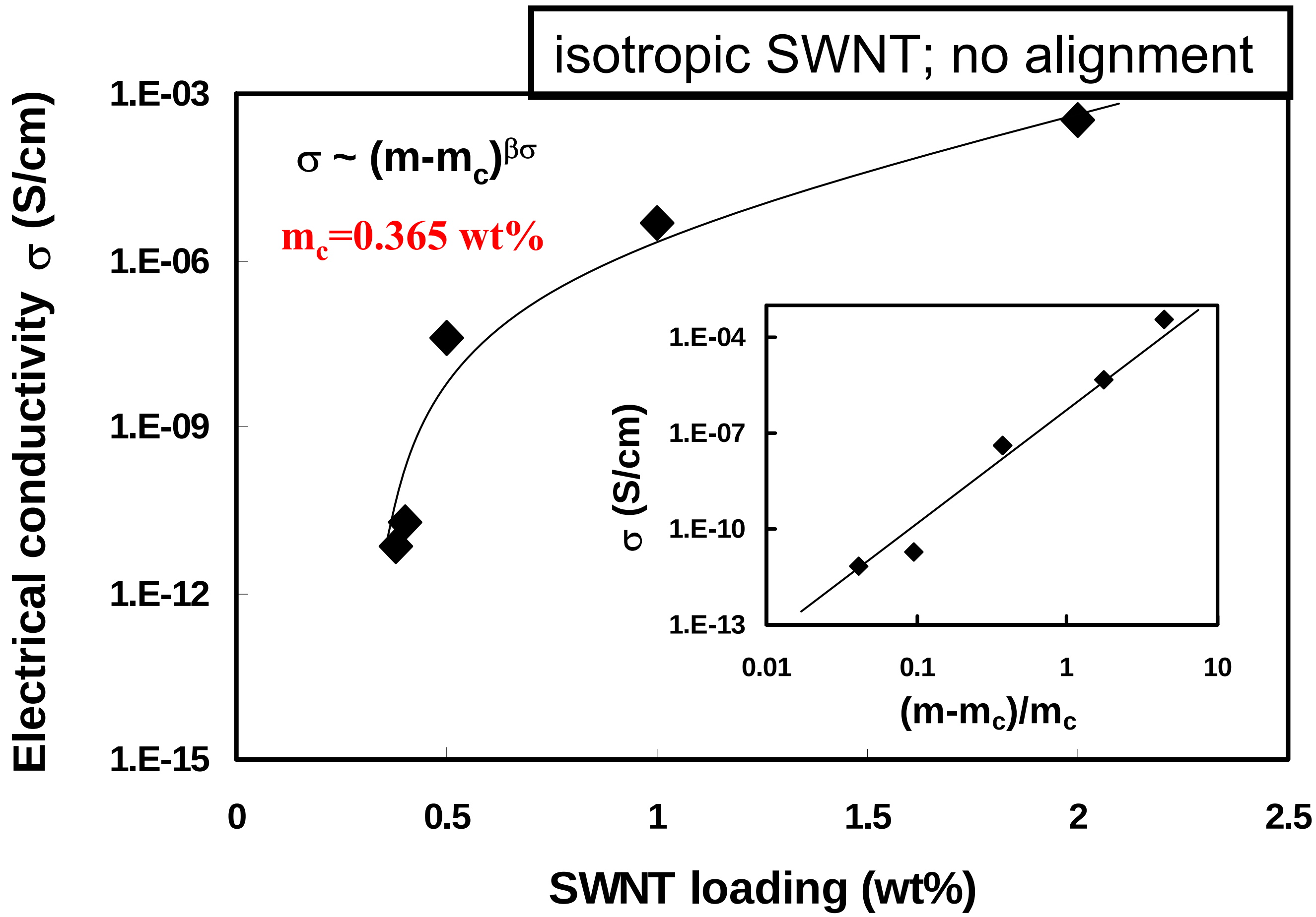
100 sticks, aligned

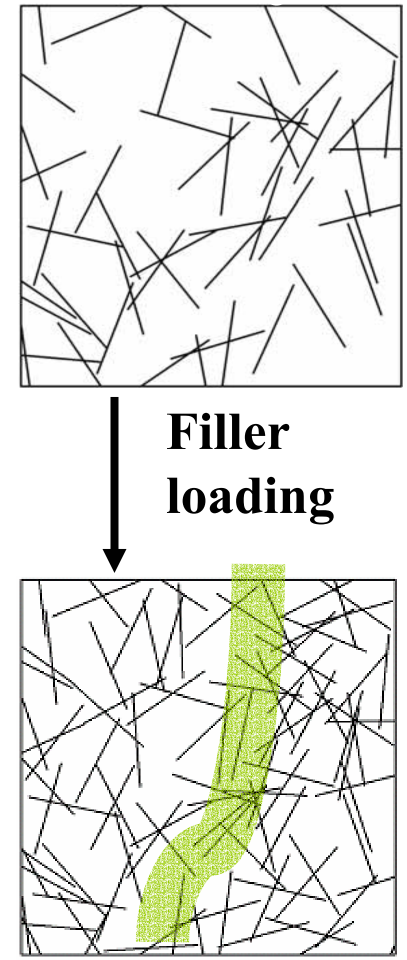


no percolation

F. Du *et al.*,
Phys. Rev.B **72**,
121404R (2005

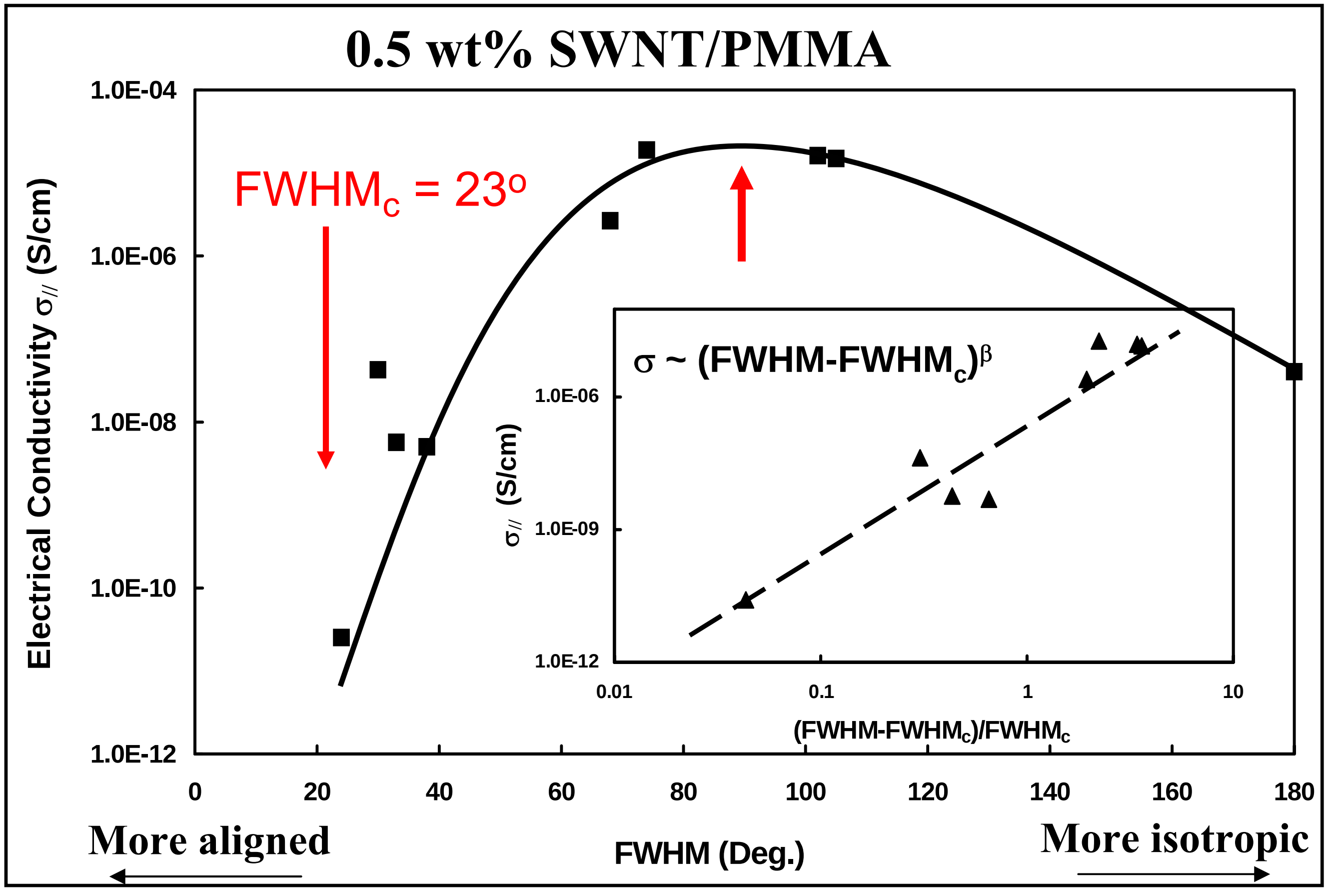
Percolation behavior vs. loading: concentration percolation



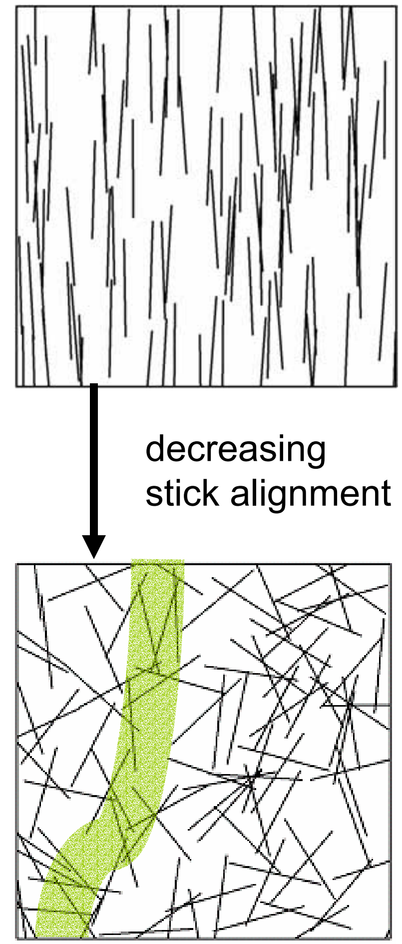


Different samples, different threshold…

Percolation behavior vs. alignment: orientation percolation



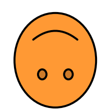
100 aligned sticks: insulating



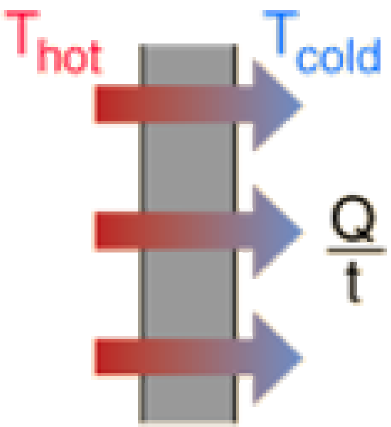
partly aligned, percolated

σ *vs*. orientation shows percolative behavior, **and max. σ occurs for partly aligned, not randomly-oriented tubes.**

Thermal transport in nanotubes

- **Brief review of macroscopic (3-D) thermal conductors**
  heat capacity, mean free path, phonon dispersion and sound velocity
- **Fundamentals of thermal transport in SWNT:**
  - effect of 1-D subbands
  – Individual SWNT – lots of theory, sparse experiments
  – Individual MWNT – several experiments
  – What's special about mean free path in nanotubes?
  – SWNT assemblies and composites - 
  – **Application to peapods - a case study**

Thermal conductivity of solids



$$Q/t = \kappa A(T_{hot} - T_{cold})/d$$

Q = heat transferred in time t
κ = thermal conductivity of the barrier
A = area normal to the heat flux
d = thickness of the barrier

Power per unit area transported

Temperature gradient

$$\frac{\Delta Q}{\Delta t\, A} = -\kappa \frac{\Delta T}{\Delta x}$$

Thermal conductivity

Particles per unit volume

Mean particle speed

Mean free path

Molar heat capacity

$$\kappa = \frac{n \langle v \rangle \lambda c_V}{3N_A}$$

Thermal conductivity

Avogadro's number

For <u>all carbons</u>, κ is dominated by the phonons, not free electrons!

Good electrical conductors are usually good thermal conductors as well ……

Conductivité thermique électronique

Conductivité électrique

$$\kappa_E = L_o \, T \, \sigma$$

Température absolue

L_o est le *nombre de Lorenz*, qui pour un $\boxed{\text{système d'électrons libres}}$ est égal à $(\pi^2/3)\,(k_B/q)^2$, soit 2,45 10^{-8} $V^2\,K^{-2}$.

But if few (or no) free electrons, heat can also be transported by phonons.

Jean-Paul Issi, Aussois 2004

strong covalent bonds, stiff lattice, large **phonon velocity** (speed of sound)

lots of free electrons, high diffusivity

Strong intramolecular bonds but weak interchain bonds – “soft” phonons, low speed of sound

Mostly empty volume – a big issue in bulk CNT materials as well!!

Material	Thermal conductivity (cal/sec)/(cm^2 C/cm)	Thermal conductivity (W/m K)
Diamond	...	**1000**
Graphite in-plane		3000
Silver	1.01	406.0
Copper	0.99	385.0
Gold	...	314
Aluminum	0.50	205.0
Iron	0.163	79.5
Lead	0.083	34.7
Ice	0.005	1.6
Glass,ordinary	0.0025	0.8
Water at 20° C	0.0014	0.6
Polystyrene (styrofoam)	...	0.033
Polyurethane	...	0.02
Air at 0° C	0.000057	0.024
Silica aerogel	...	0.003

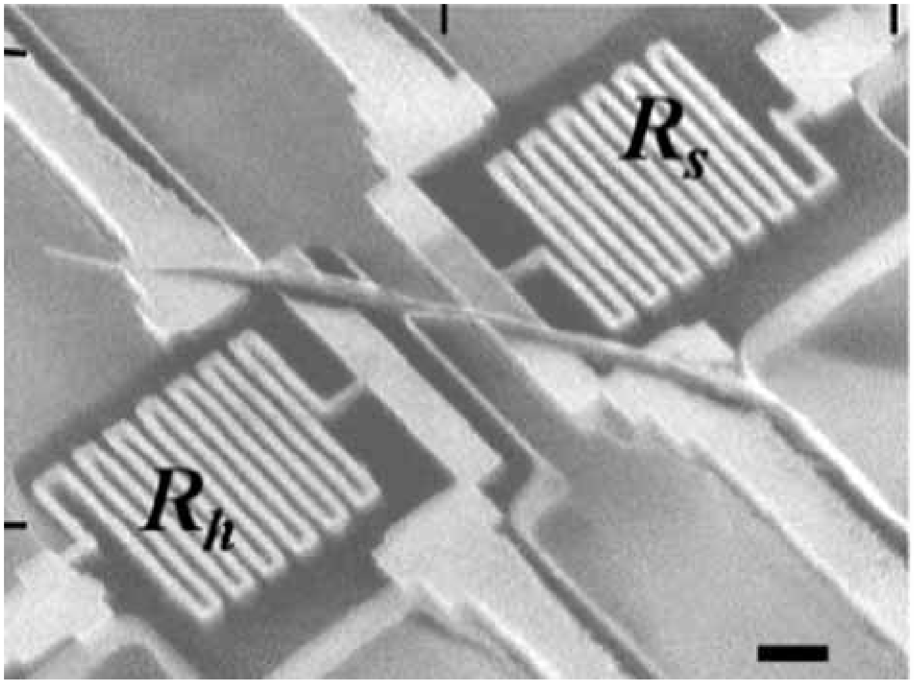
CNT: $\kappa \sim$ (speed of sound)(ht. cap.)(m.f.p.) = $v_S C_P \lambda$

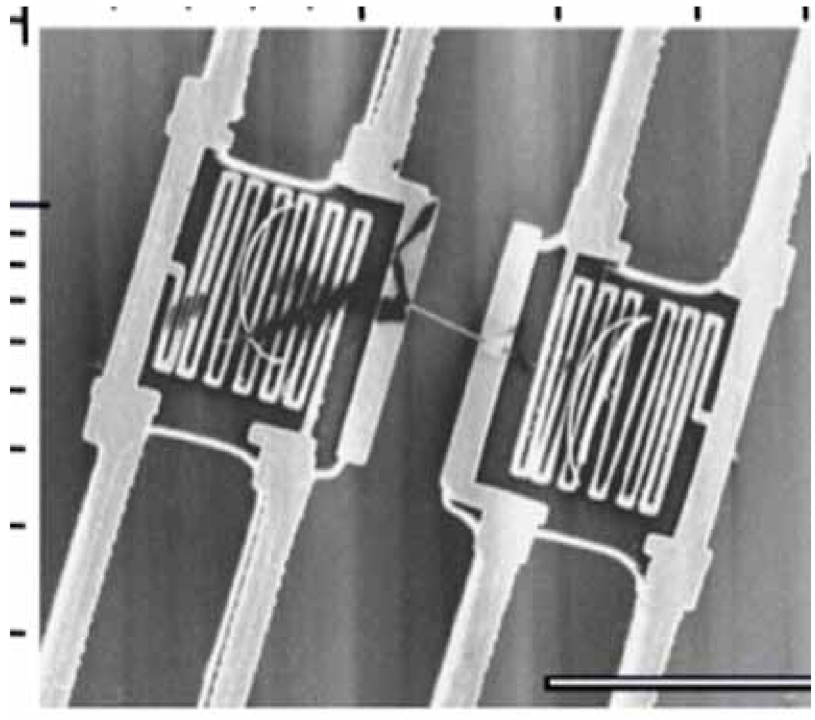
Experiments: σ is easy – κ is hard!!
General problem:
How to isolate conduction thru the sample?

- Evacuated chamber – no convection.
- Sample thermally connected "<u>ONLY</u>" to heater and heat sink – long, very fine constantin wires for thermometry.
- Radiation losses – big problem, esp. for "black" materials.
- For transient methods, sample volume and C_P determine the thermal time constant

Also: sample dimensions, density correction, alignment,…..

How to measure kappa(T) on individual tubes?





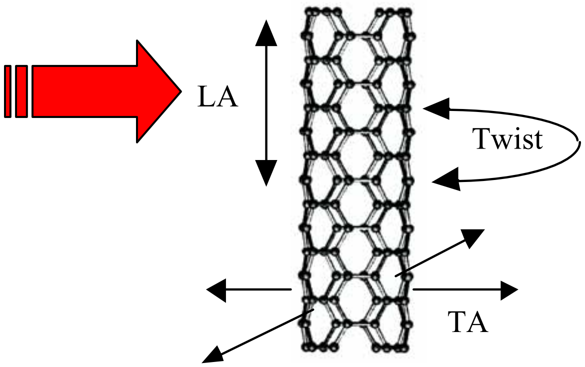
MWNT bundle, scalebar 1 μm

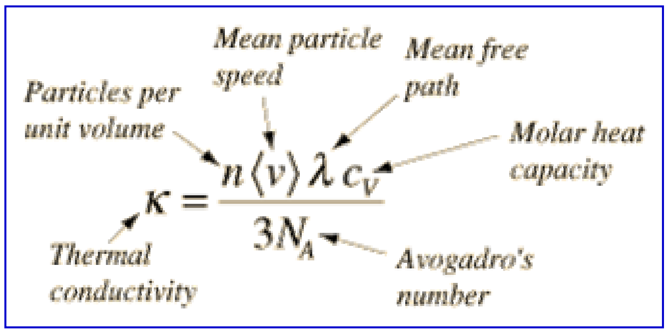
One MWNT, 10 μm scalebar

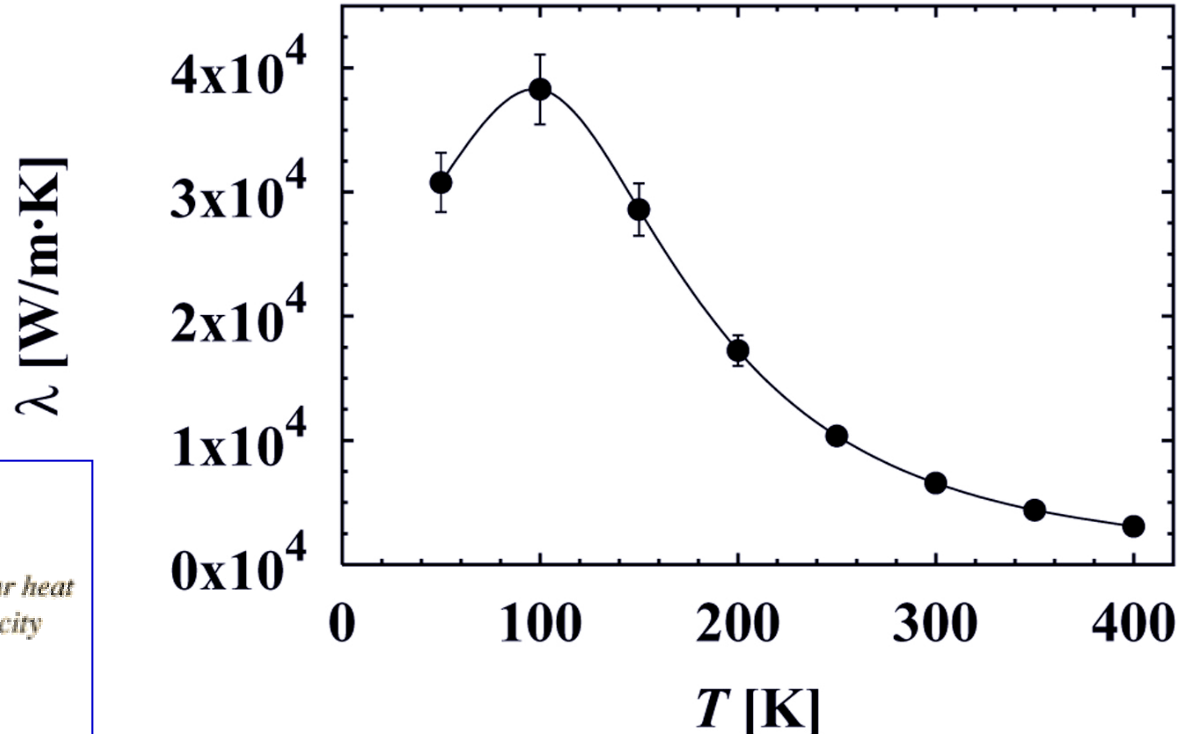
Multi-step optical or e-beam lithography; no control over tube selection.

P. Kim et al., PRL 87, 215502 (2001)

“Unusually high thermal conductivity of carbon nanotubes”







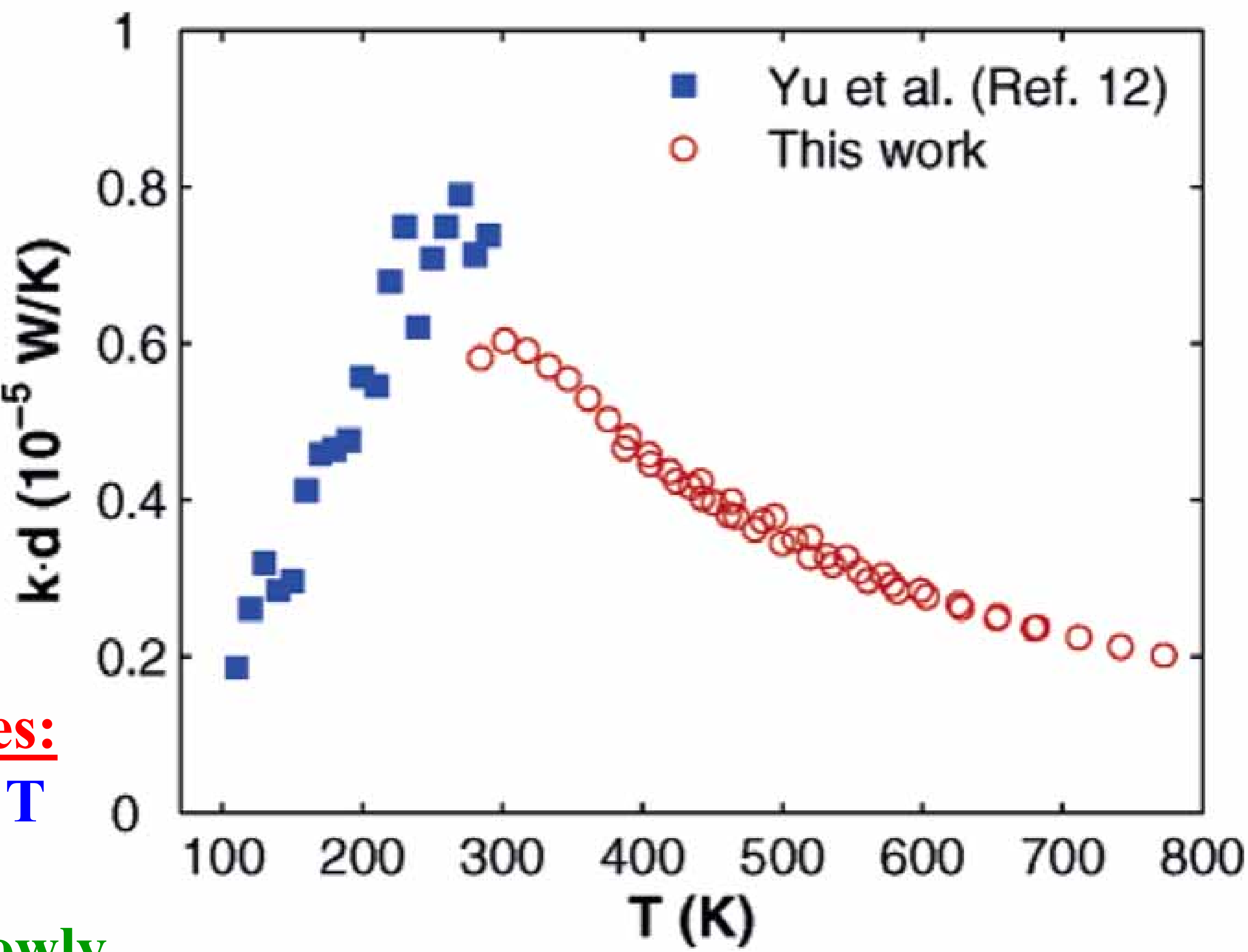
“ ……accurate carbon potentials to determine the thermal conductivity and its dependence on temperature. Our results suggest an unusually high value 6600 WmK for an isolated SWNT at 300K, …….”

“We believe these high values are associated with the **large phonon mean free paths** in these systems.”

Also stiff 1-D mechanical system, large V_s (JEF)

Berber et al., *PRL* **84** (2000)

Qualitative agreement between theory and experiment.



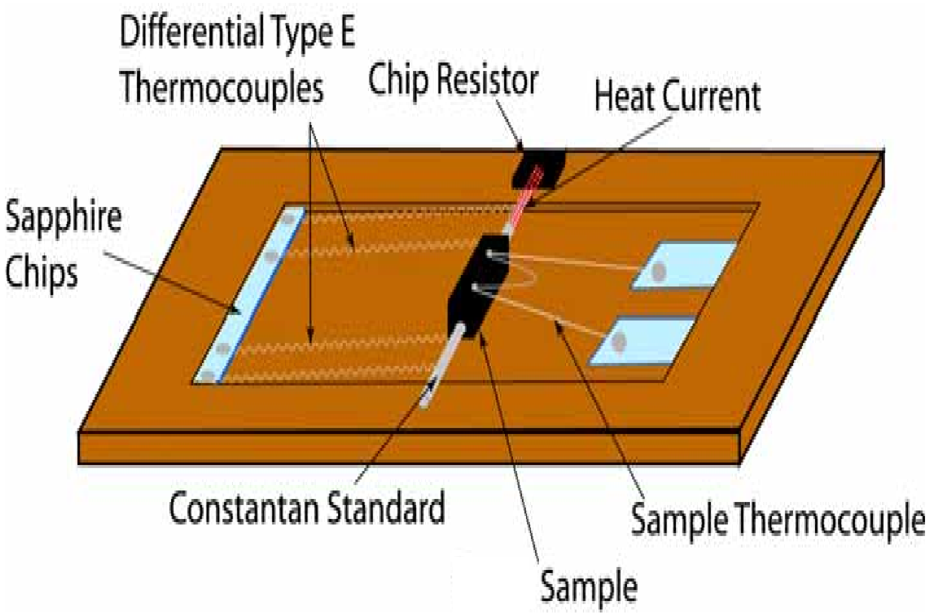
Notable differences:

peak κ at higher T than predicted

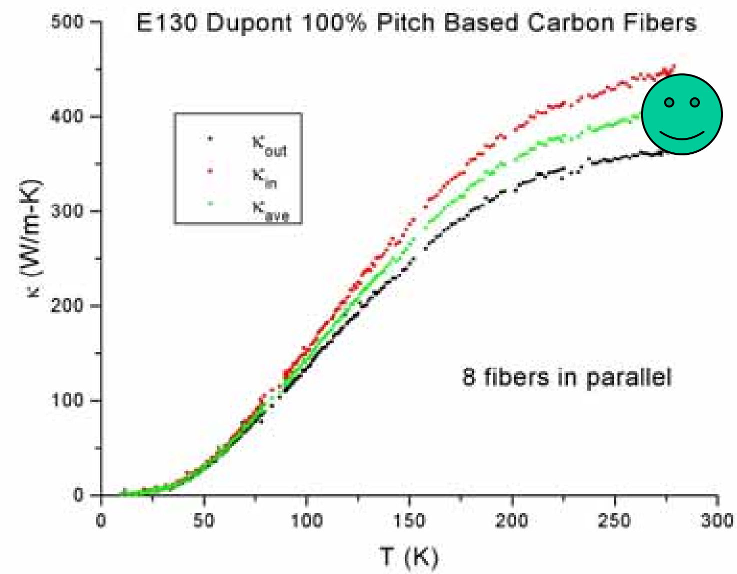
κ falls off more slowly with increasing T than predicted.

E. Pop *et al.*, *Nano Letters* **6**, 96-100 (2006)

How to measure kappa(T)?
"bulk" samples: comparator method

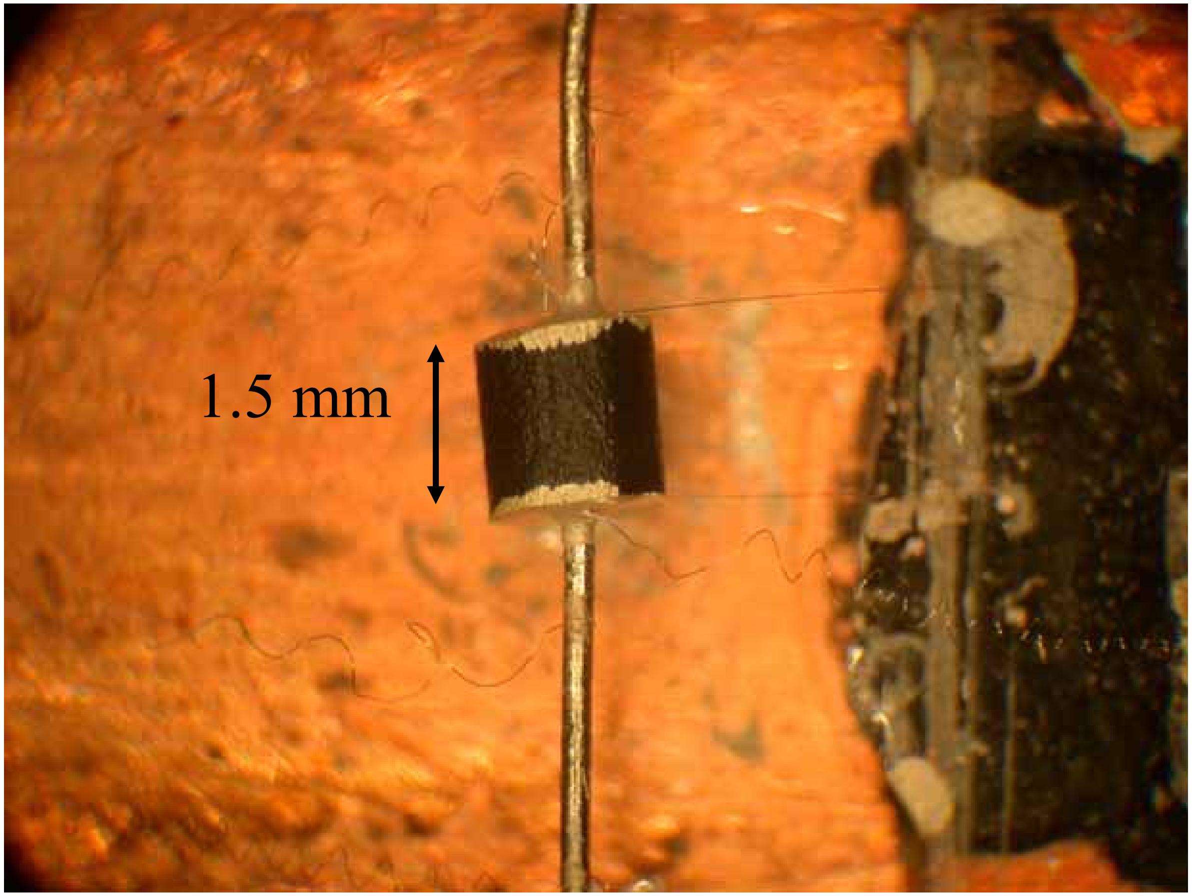


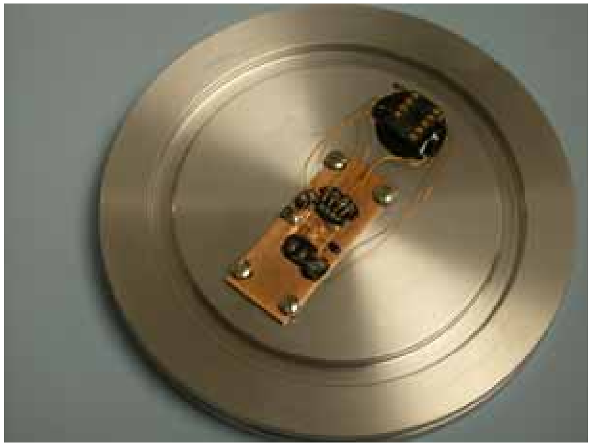
400 W/mK @ 270K



$$\frac{\kappa_{\text{sample}}}{\kappa_{\text{standard}}} \propto \frac{\Delta T_{\text{standard}}}{\Delta T_{\text{sample}}} \quad \text{if} \quad G_{\text{sample}} \approx G_{\text{standard}}$$

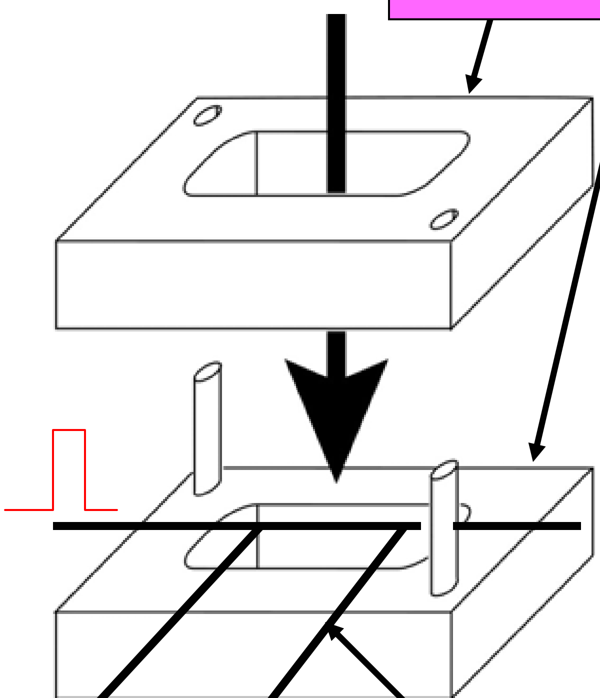
J. Hone *et al.*, *Applied Physics Letters* **77**, 666-668 (2000).


1.5 mm



How to measure kappa at fixed T?
Composites: transient hot-wire method

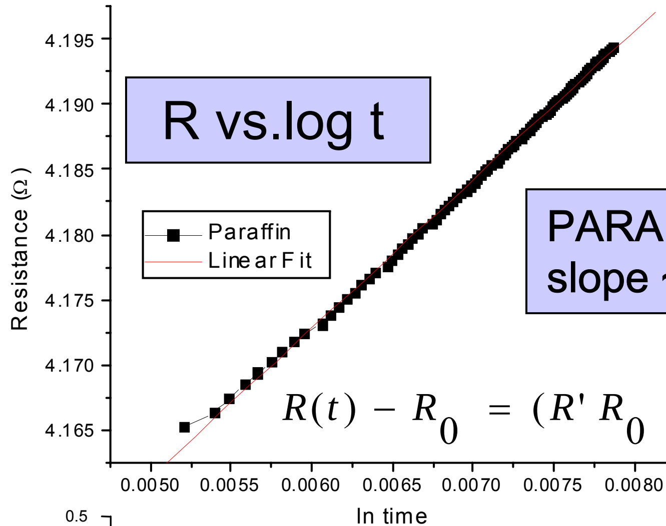
TEFLON split mold



$\Delta V \sim \Delta R \sim \Delta T$

25 μm Ni 4-wire heater + RTD

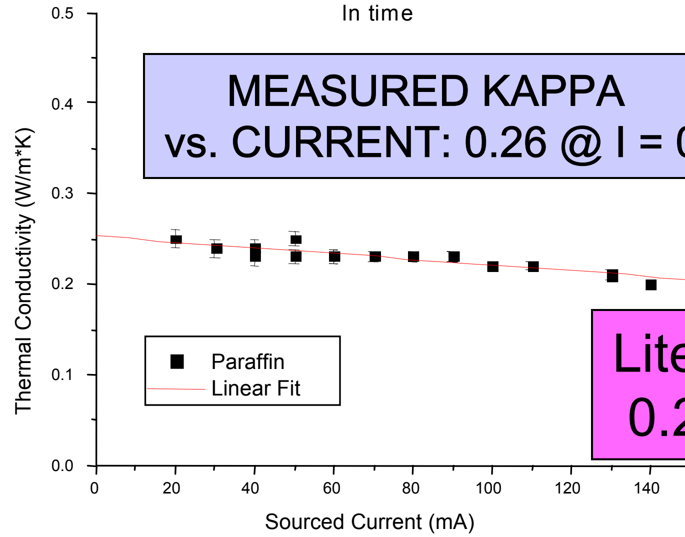
Current pulse @ t = 0; measure T(t) relaxation via TCR of Ni wire.



R vs.log t

PARAFFIN ~ 6 grams
slope ~ K, intercept ~ D

$$R(t) - R_0 = (R' R_0 / 4\pi L\kappa) I^2 \ln[(4D / r^2 c)t]$$



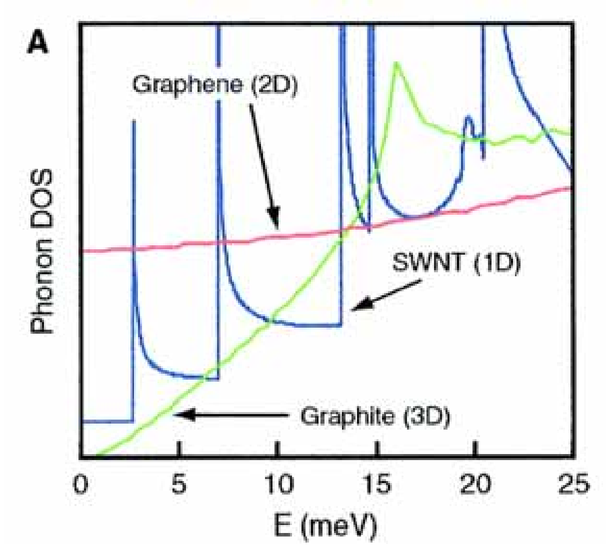
MEASURED KAPPA
vs. CURRENT: 0.26 @ I = 0

Literature value:
0.25 W/mK

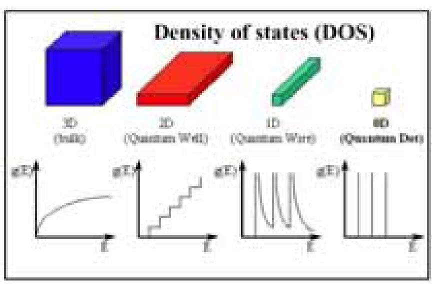
Pros and cons

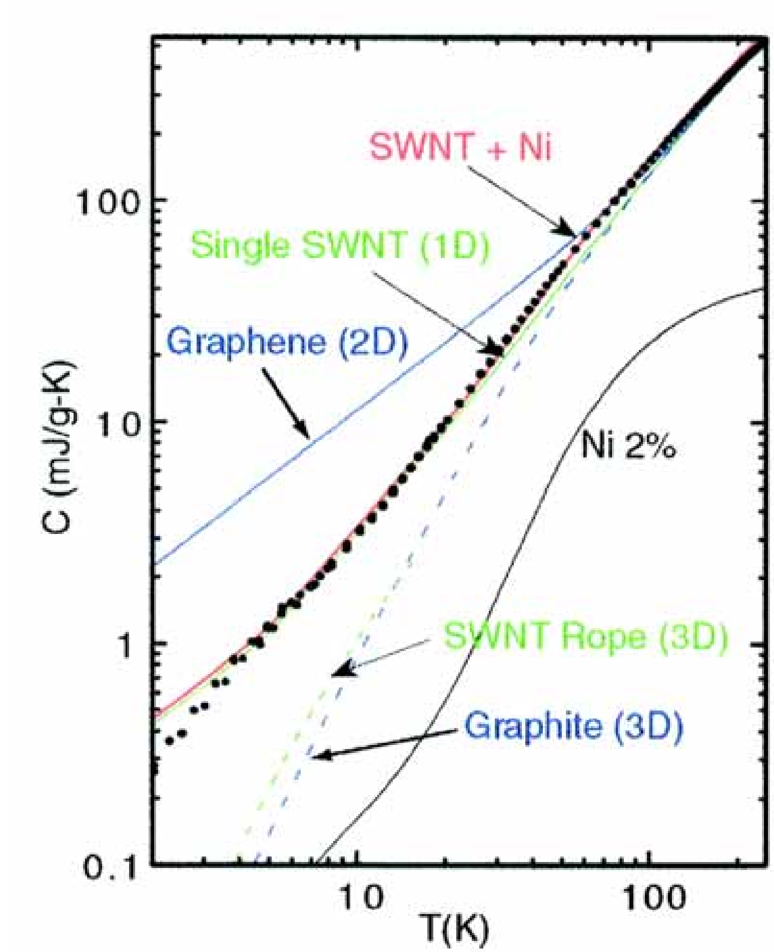
Attributes of methods for measuring thermal conductivity	Comparator	Hot-Wire	Three-Omega	Modulated Thermoreflectance
small samples (~ mg.)	✓	no	✓ ✓ ✓	✓
high spatial resolution (few μm)	no	no	no	✓
anisotropic samples	✓	no	✓	no
poor *electrical* conductors	✓	✓	difficult	✓
high accuracy for low κ samples	no	✓	no	✓
rapid screening	no	no	✓	✓
variable temperature (10-800 K)	✓	✓	✓	Above room temp.
thermal conductivity range (W/mK)	1 – 5000	0 – 2.0	0.1-1000	0-50

Assume all the T dependence in κ comes from $\mathbf{\underline{C_P}}$ …



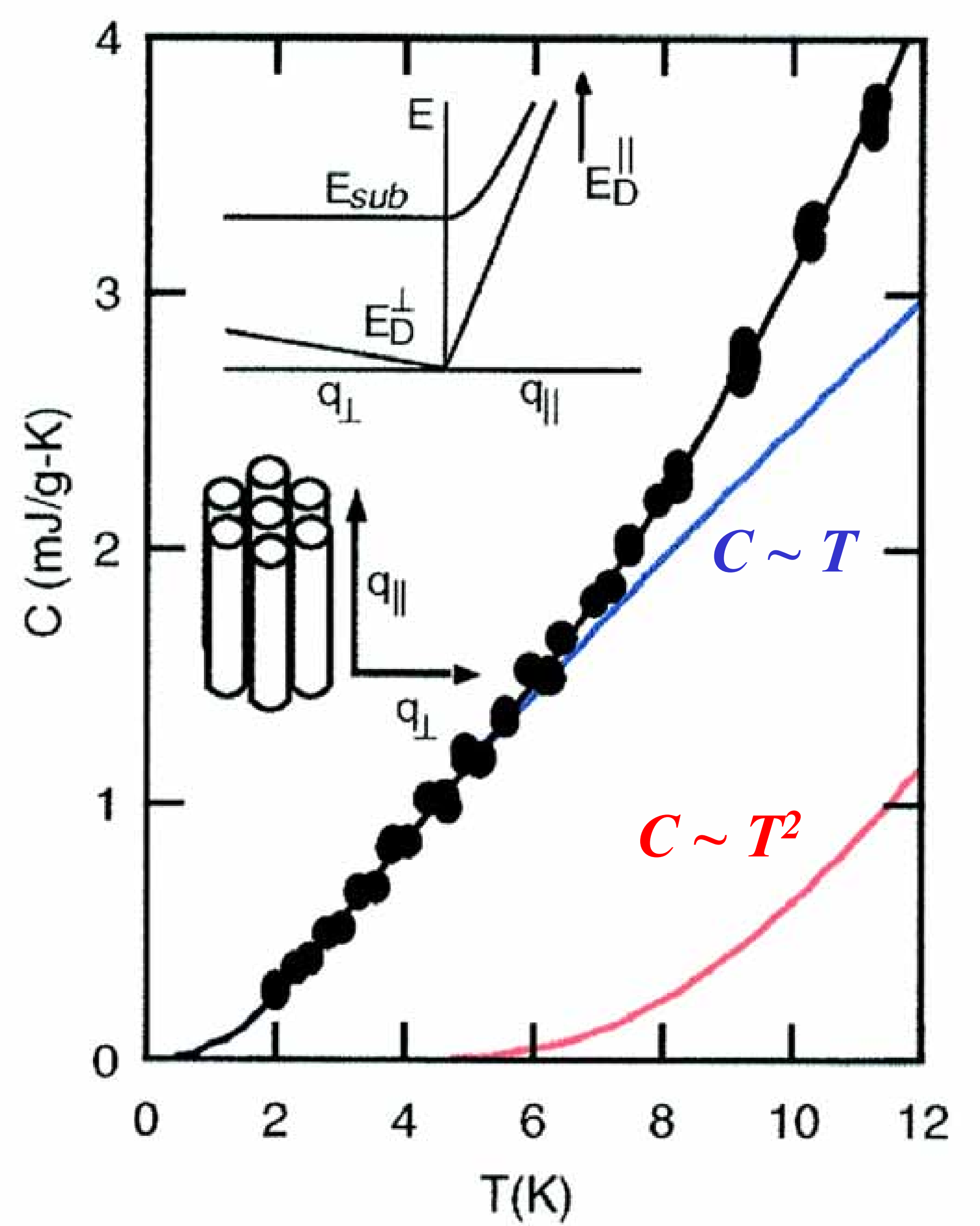
Theoretical phonon density of states for 2-D graphene, 3-D graphite, and an isolated 1.25-nm-diameter SWNT. Interlayer coupling in graphite shifts spectral weight from lower to higher energies.





In a real sample containing ropes, the phonons are 3-D at low temperature, crossing over to a 1-D regime at a T characterized by the transverse Debye energy E_D

J. Hone *et al.*, *Science* **289**, 1730 (2000).



Heat capacity data on an expanded (linear) scale (solid dots) and a fit to a two-band Debye model that accounts for weak coupling between SWNTs in a rope (black curve). The contribution from acoustic modes with large on-tube Debye energy E_D and small transverse Debye energy E_D gives the blue curve, which fits the data at low temperatures but lies below the data above 8 K. Including the first 1-D subband, approximated as a dispersionless optic branch at E_{SUB}, adds a contribution given by the red curve. These are combined in the black curve, which fits the data over the entire range.

So κ/T should go as const + AT………

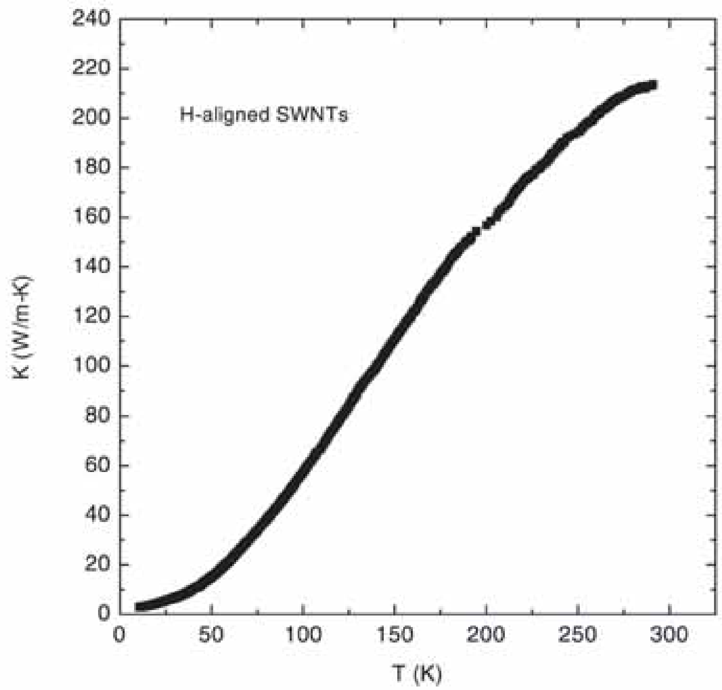


Fig. 7. Thermal conductivity of a bulk sample of SWNTs in which the tubes are aligned by filtration in a strong magnetic field [9]. The measurement is taken in the direction parallel to the tubes

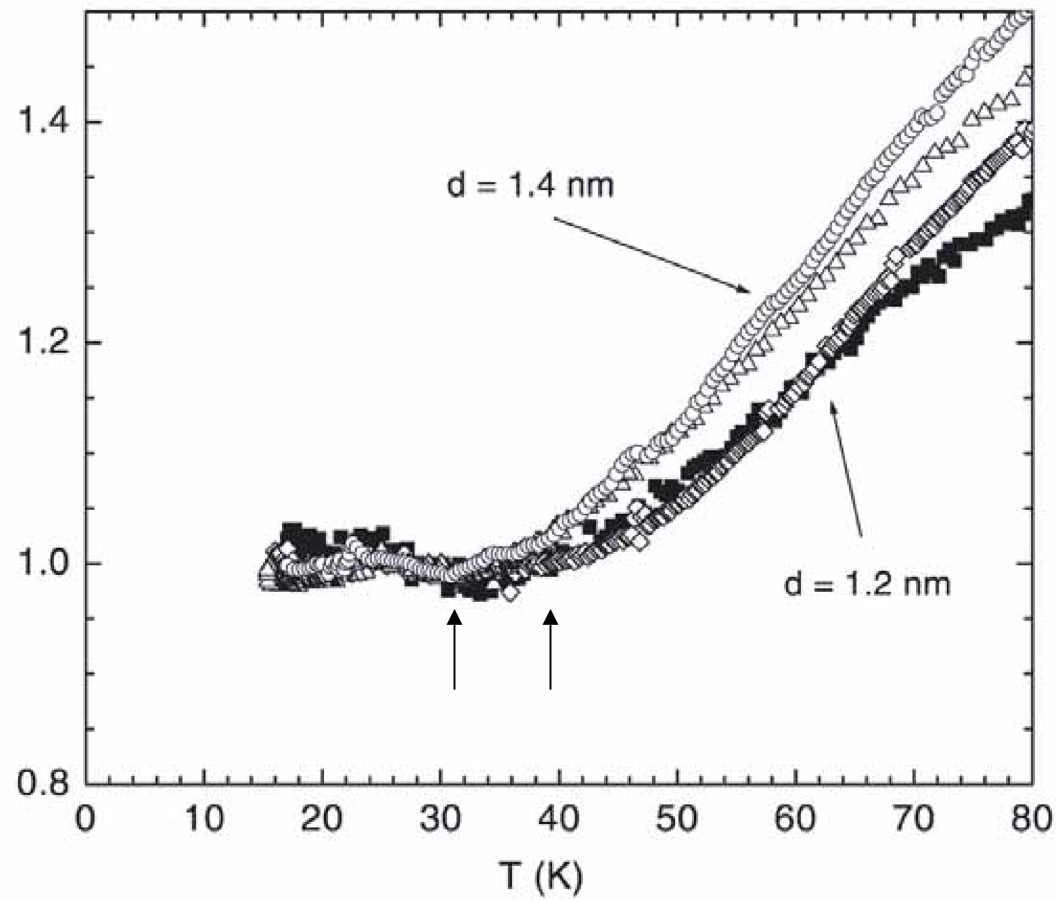


Fig. 8. Thermal conductivity divided by temperature, K/T, of SWNT samples with different average diameters [11]. The range of linear $K(T)$, i.e. constant K/T, extends to higher temperatures in samples with a smaller diameter, as would be expected for a scenario of 1D quantization of the phonon structure

J. Hone, M. Llaguno *et al.*, *Applied Physics A* **74**, 339 (2002).

Peapods: a case study
How do the peas affect σ and κ?

Pea and pod have different work functions - charge transfer doping?

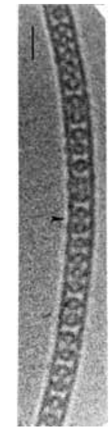
Pea-pod coupling – energy scale, coherent or incoherent? Peas may limit the electron mean free path.

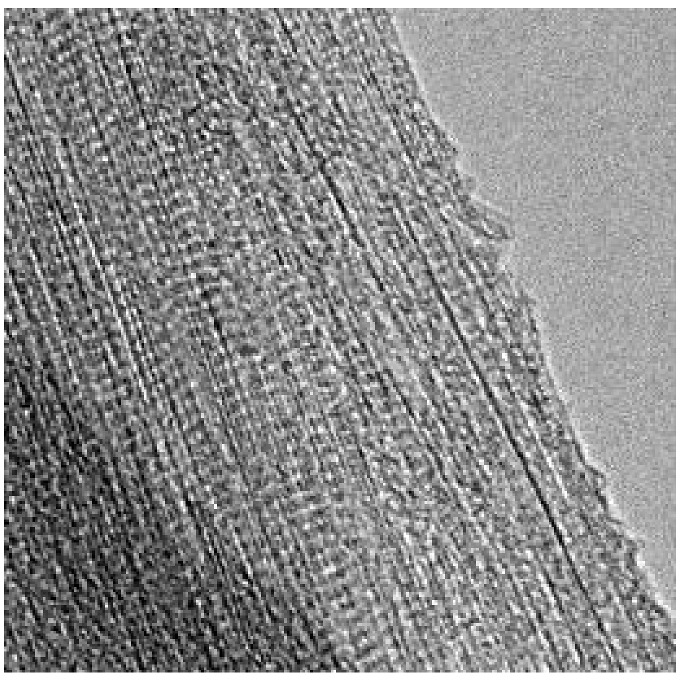
Random filling: more phonon scattering, κ goes down?

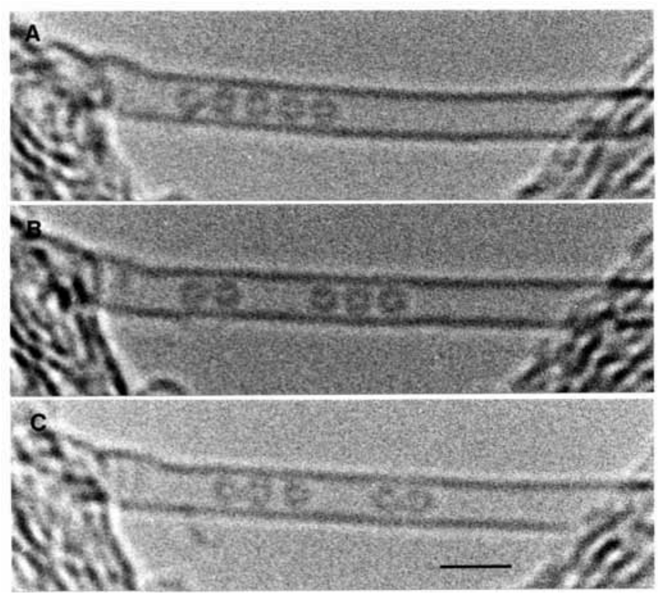
Ordered 1-D chains: new 1-D acoustic branch with small v_s

Partial filling: All tubes partly filled, or 2-phase filled + empty?

Does TEM tell us the right story of pea dynamics – beam heating?



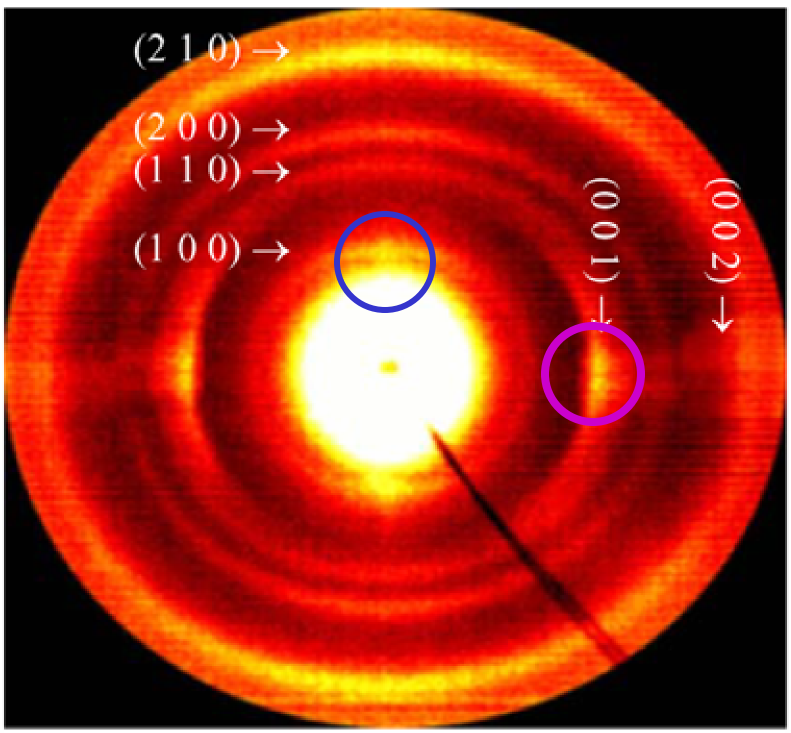


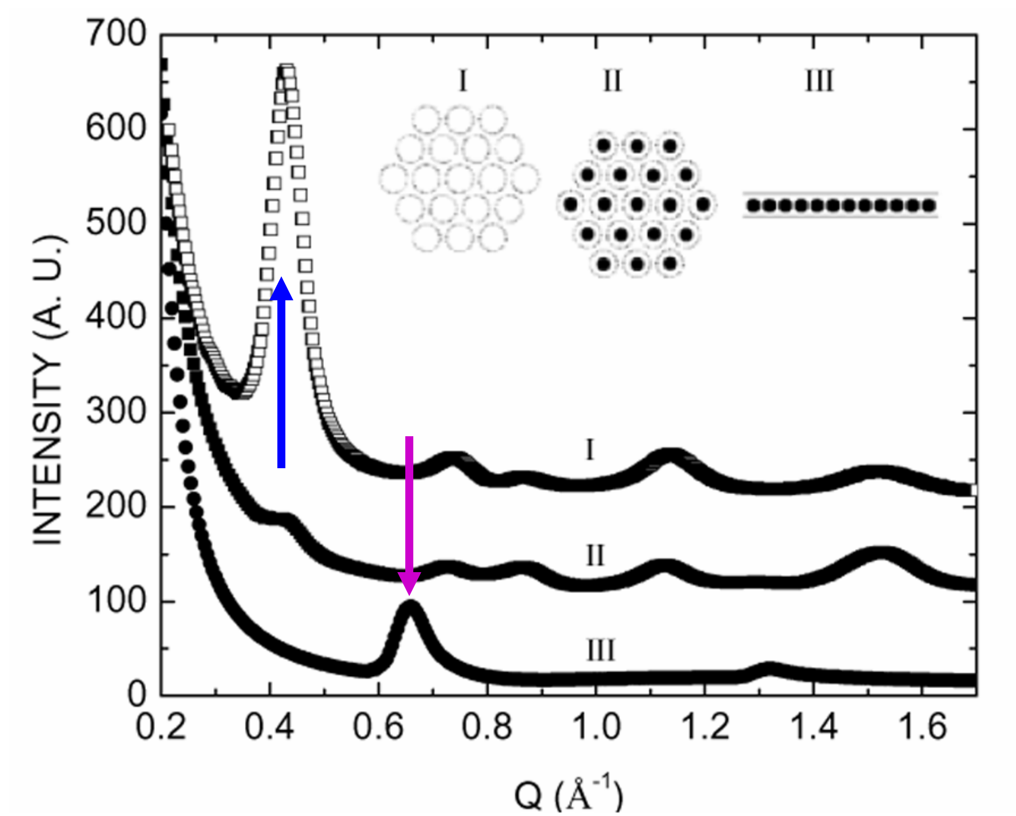


HRTEM images from B. Smith and Y. Kim, U. Penn

Characterization: xrd using 2-D detector and partially-oriented film

(100) Bragg peak from 2-D triangular lattice loses intensity
Due to destructive interference between pod and pea form factors.
(001) comes from ordered 1-D chain of peas; C_{60}-C_{60} = 0.978 nm

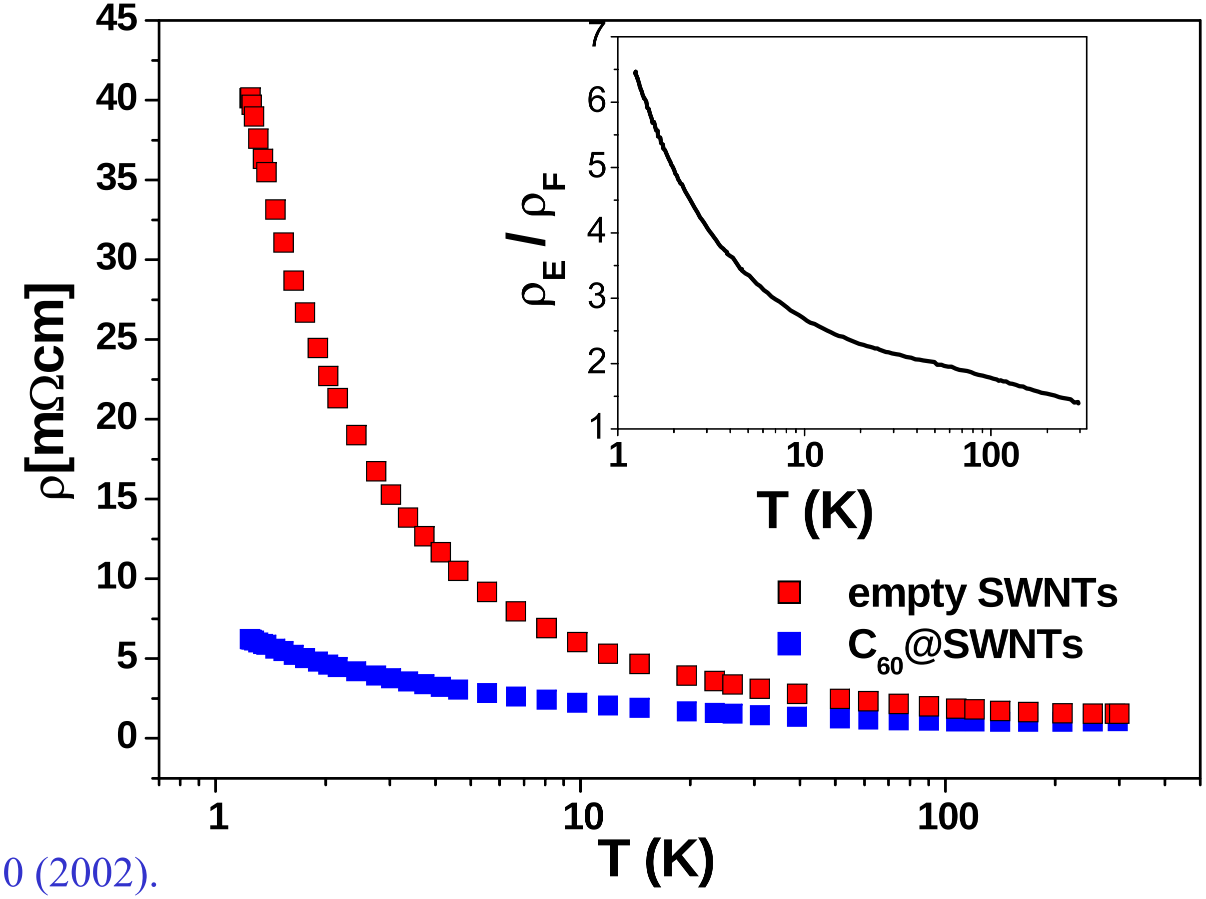




Appl. Phys. Letters **84**, 2172 (2004)

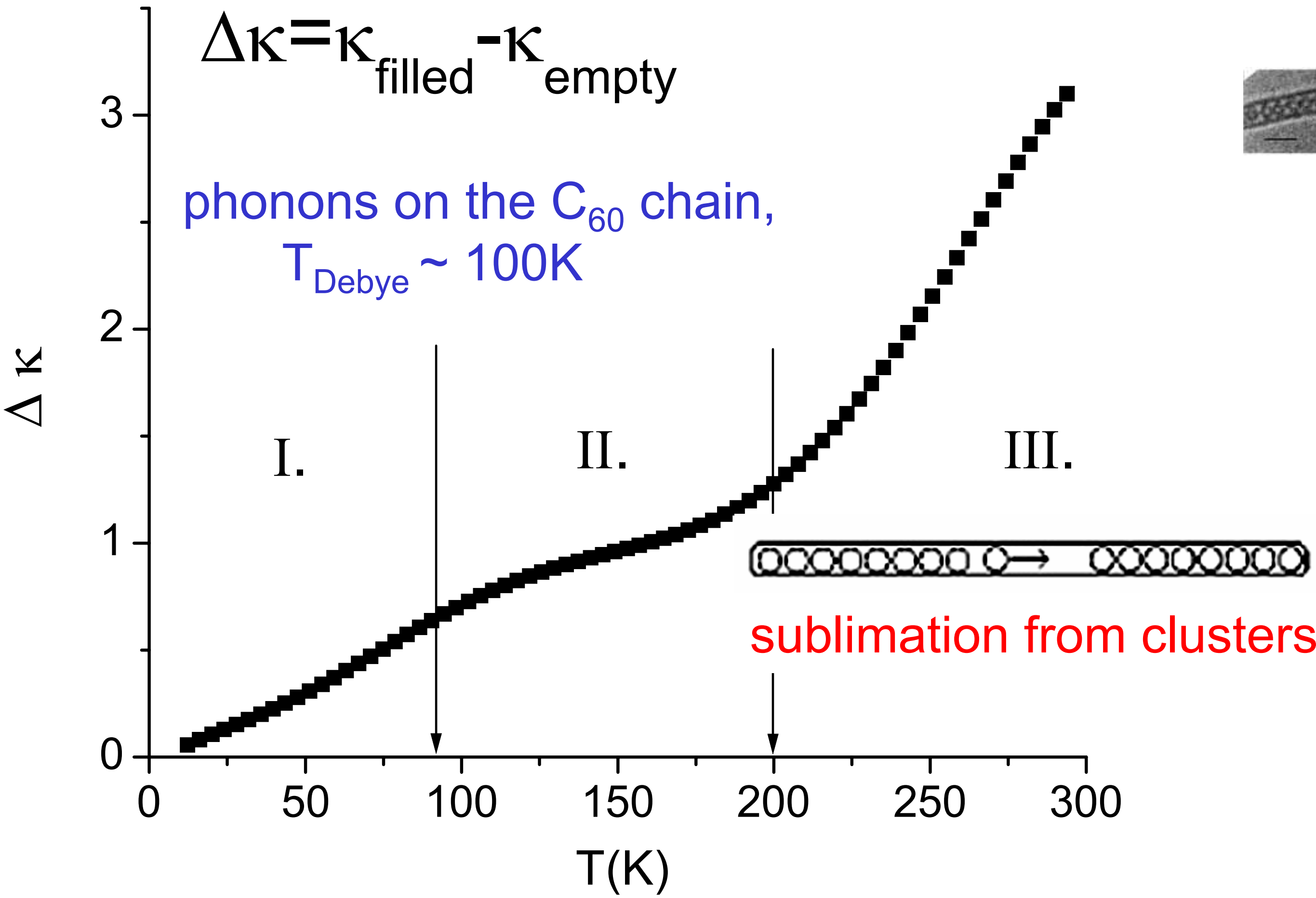
Electrical resistivity vs. T: Filled vs. empty

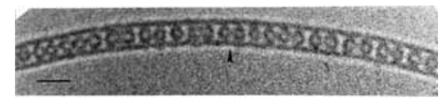
Peas have no effect on ρ(300K), but they suppress the resistivity divergence at low temperature. This suggests that any disorder associated with the filling has only a minor effect on electron transport; the modest temperature dependence suggests weak localization.



Appl. Phys. Letters **80**, 1450 (2002).

“Excess” thermal conductivity: peapods are better thermal conductors than SWNT at all T





Needs to be confirmed by varying the filling and establishing the distribution of “vacancies” – homogeneous or phase separation?

Summary and perspectives

- Electrical conductivity in CNT pretty well understood, for individual tubes, complex assemblies and composites.
- CNT already useful for high value added applications such as IC interconnects; major cost reductions required for large-scale applications, *e.g*. fillers in composites.
- Thermal conductivity also well understood for individuals. Results on assemblies and composites disappointing to date.
- The strong motivation to exploit high thermal conductivity of individual tubes in thermal management applications cannot be realized yet.