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ICTP 40th Anniversary

SMR 1564 - 18

SPRING COLLEGE ON SCIENCE AT THE NANOSCALE
(24 May - 11 June 2004)

ELECTRONIC / THERMAL TRANSPORT - Part II

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These are preliminary lecture notes, intended only for distribution to participants.

Electric and Thermal Transport in Nanoscale Materials –Part II

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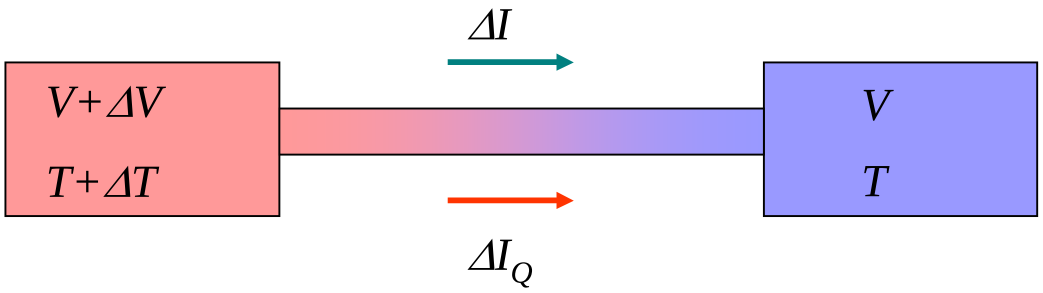
COLUMBIA UNIVERSITY
IN THE CITY OF NEW YORK

Columbia University and the National Science Foundation
Center for Electron Transport in Molecular Nanostructures

Outline

- Charge Transport and Energy Dissipation
- Mesoscopic Heat Transport Measurements
- Mesoscopic Thermoelectric Effects
- Field Effect Transport in 2D Crystallites (Thr)

Charge, Energy and Entropy Transport



Linear Response Regime

$$\Delta V = R\,\Delta I - S\,\Delta T$$

$$\Delta I_Q = \Pi\,\Delta I - K_{th}\,\Delta T$$

R : electric resistance (electron)

K_{th} : thermal conductance (electron&phonon)

S : Thermopower (electron+phonon)

Π : Peltier Coefficient

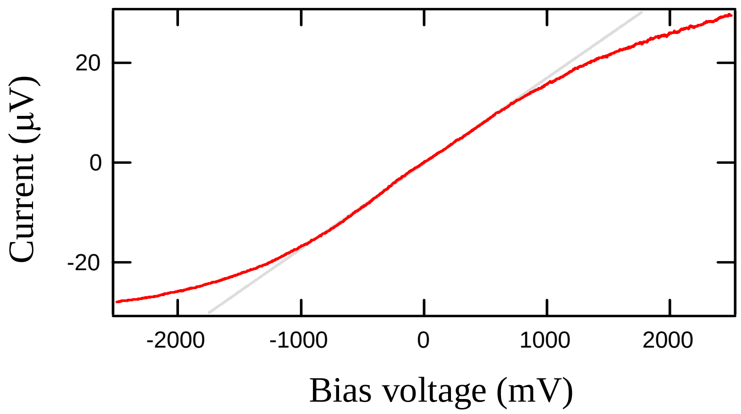
Ballistic to Diffusive Transport

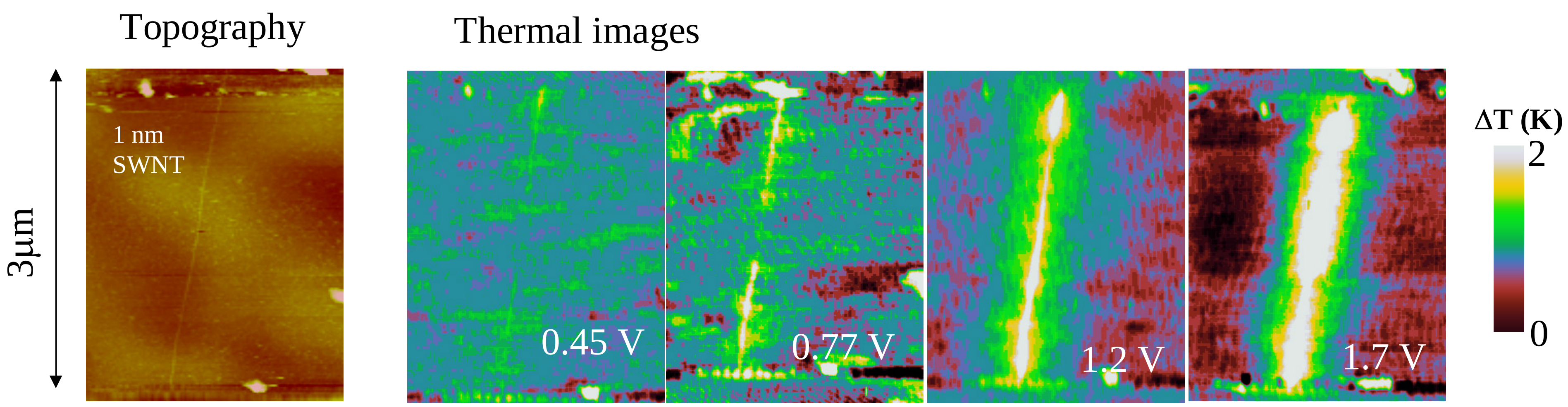
Low bias: ballistic

→ junction dissipation

High bias: diffusive

→ bulk dissipation





c

Measurement of Energy Flow

Thermal Conductivity

$$K_{th} = \frac{dQ}{dT}$$

Phonon Thermal Conductivity of Materials

Kinetic Theory

$$k = \frac{1}{3} C\, v_s\, l$$

thermal conductivity — specific heat — sound velocity — phonon mean free path

Specific heat :

If $T << \Theta$, $C \sim T^{d}$ (d:dimension)

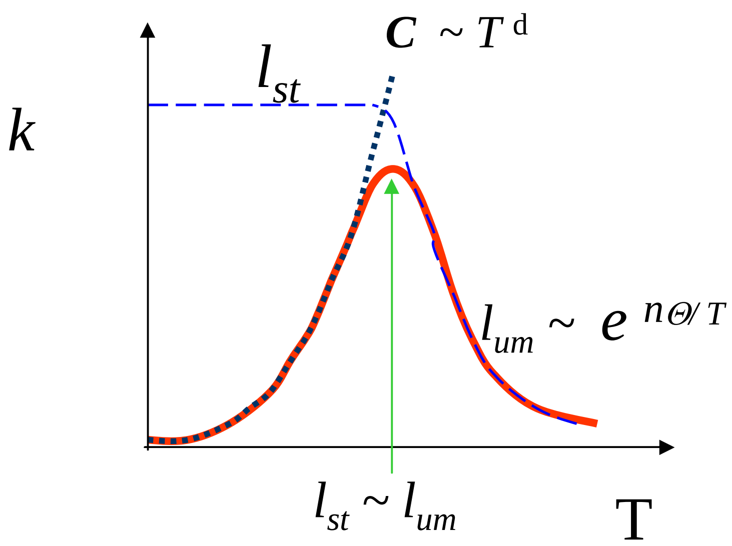
If $T > \Theta$, $C \sim constant$

Mean free path:

$$\frac{1}{l} = \frac{1}{l_{st}} + \frac{1}{l_{um}}$$

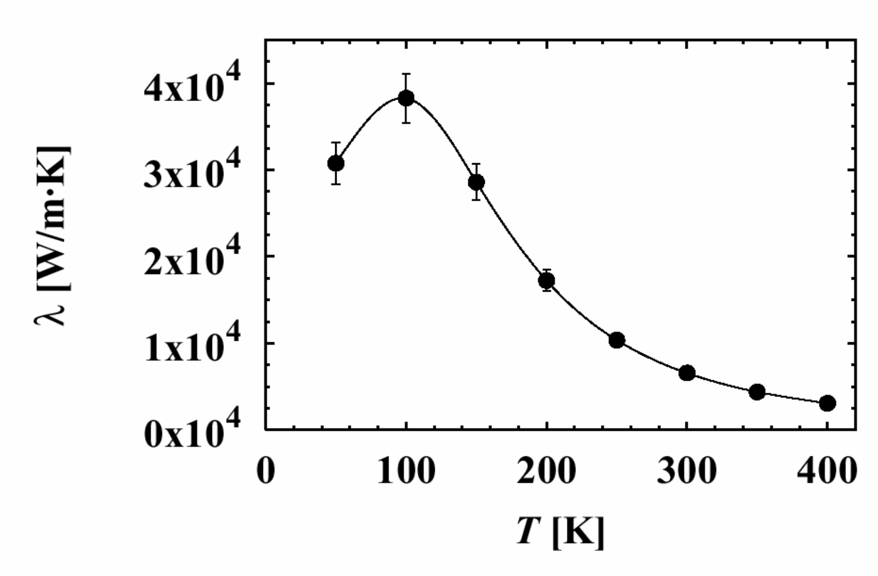
Static scattering: $l_{st} \sim constant$

Umklapp scattering: $l_{um} \sim e^{+n\Theta/T}$



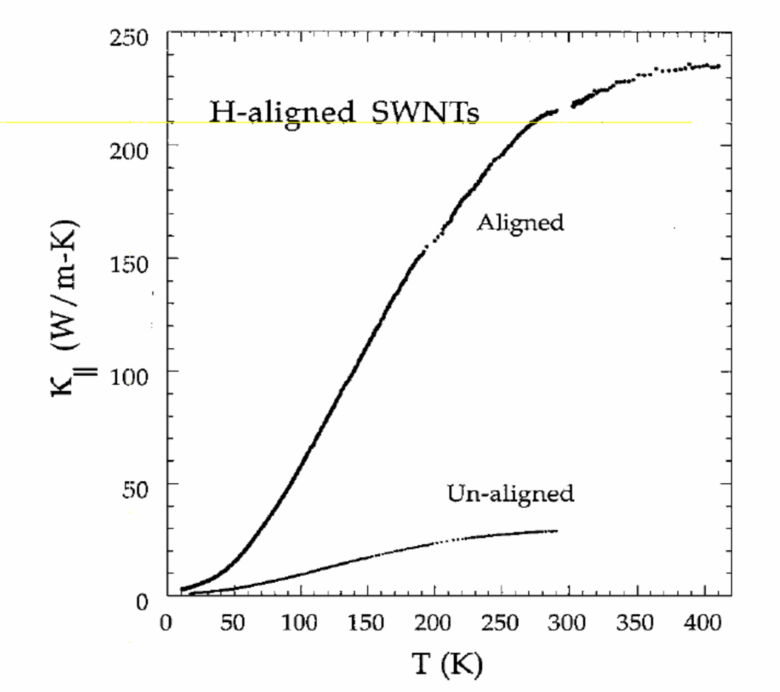
Thermal Conductivity of Carbon Nanotubes

Theoretical Expectation



S. Berber *et al.* PRL (2000)

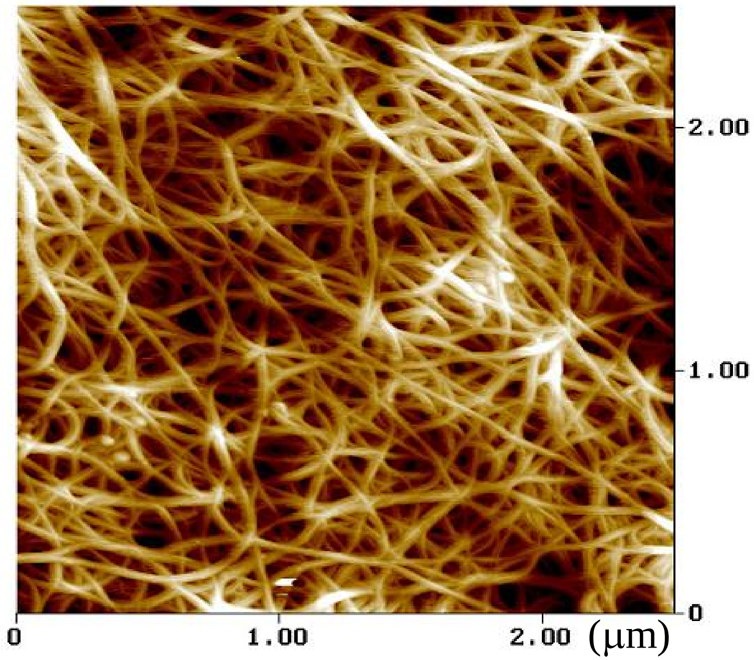
Experimental Measurement on ‘mat’



J. Hone *et al.* APL (2000)

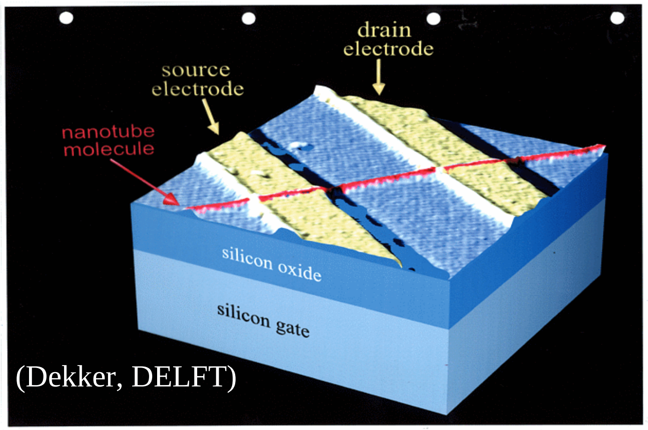
From Bulk To Individual SWNTs

Bulk Nanotube Sample

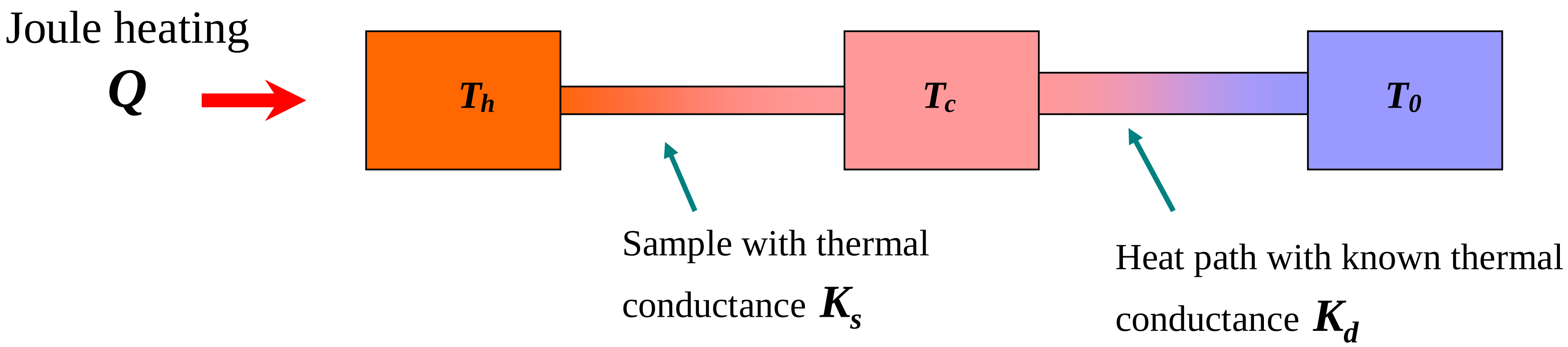


- Ensemble average over different tubes
- Uncontrolled tube-tube junctions

Mesoscopic Experiments (Individual SWNTs)

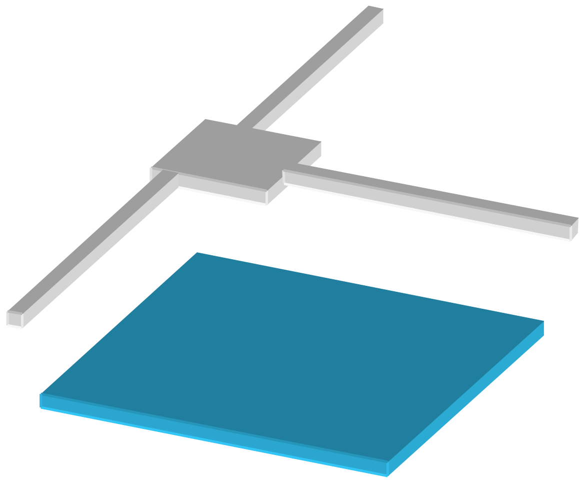


Thermal Conductivity Measurement



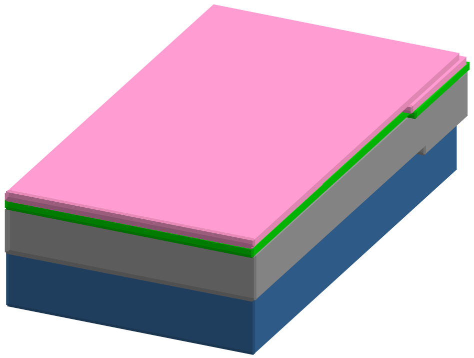
$$Q = K_s\,(T_h - T_c) = K_d\,(T_c - T_0)$$

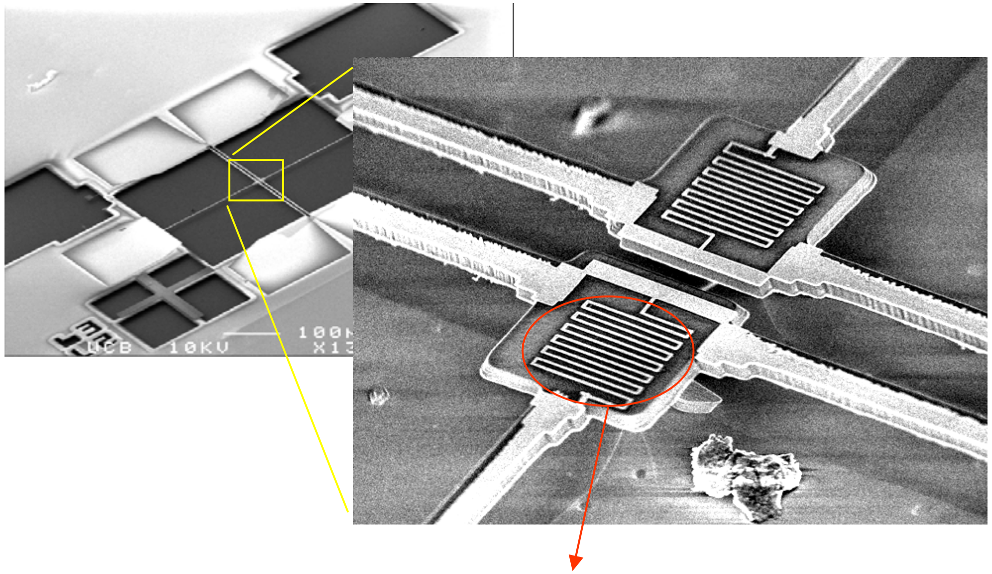
Requirement for mesoscopic measurement



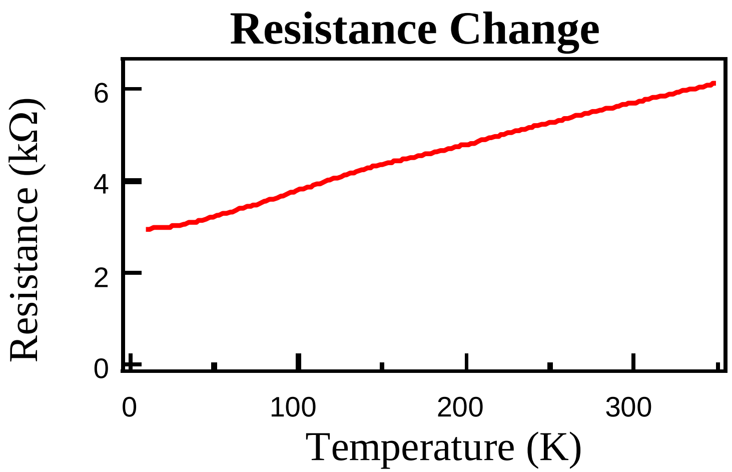
- Thermal isolation from environment ($Q < 1\ \mu W$)
- $K_d \sim K_s$ (single wall nanotube $K_s \sim 10^{-9}$ W/K)

Suspended Device For Thermal Measurement

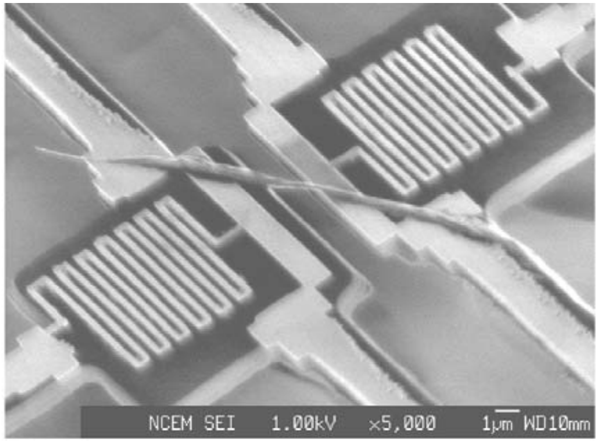




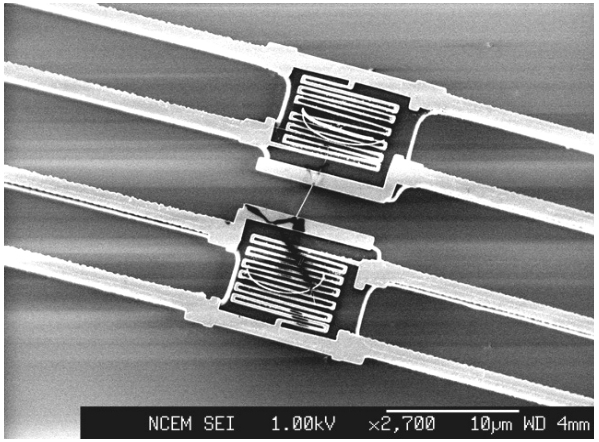
1. SiN/SiO/Si substrate
2. Pt metal structures (Electron beam lithography)
3. Spin coat photo resist
4. Etching mask definition (photolithography)
5. Reactive ion etching of SiN
6. SiO sacrificial layer etching



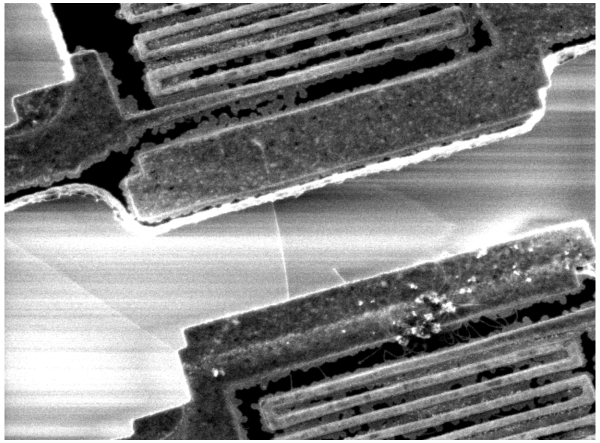
Nanotube MEMS Hybrid Device



Multiwall nanotube bundle
diameter 100 nm
mechanically manipulated



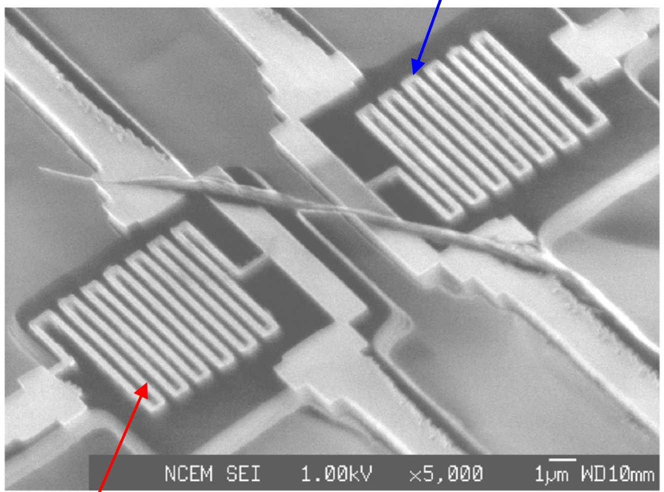
Single multiwall nanotube
diameter 14 nm
mechanically manipulated



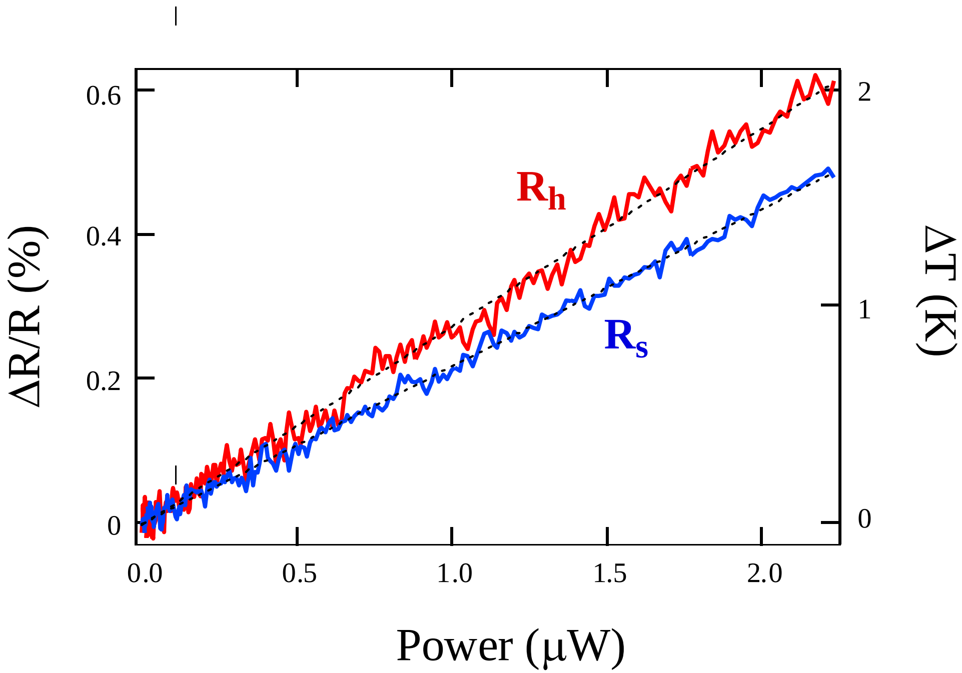
Single singlewall nanotube
diameter < 2nm
CVD grown

Mesoscopic Nanotube Thermal Transport

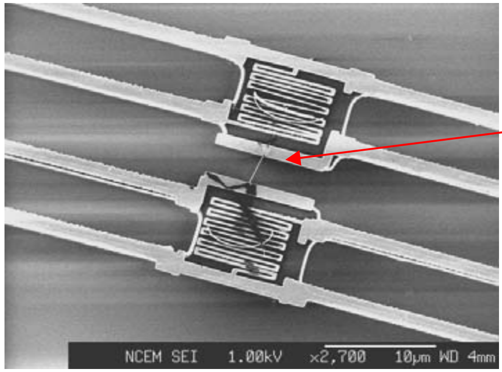
sensing resistor
R_h



heating resistor
R_h



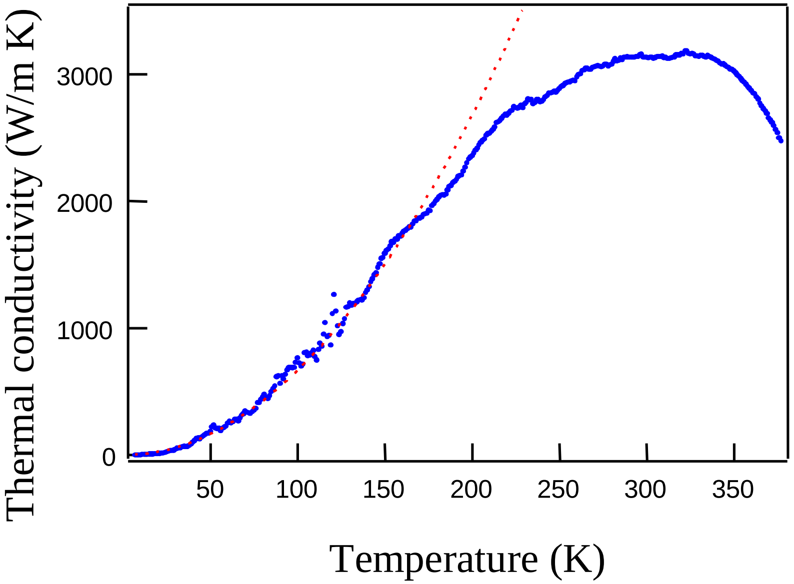
Thermal Conductivity of Single Multiwall Nanotube



A single multiwall nanotube

diameter ~ 14 nm

length ~ 2.5 μm



• Room temperature thermal conductivity ~ 3000 W/mK

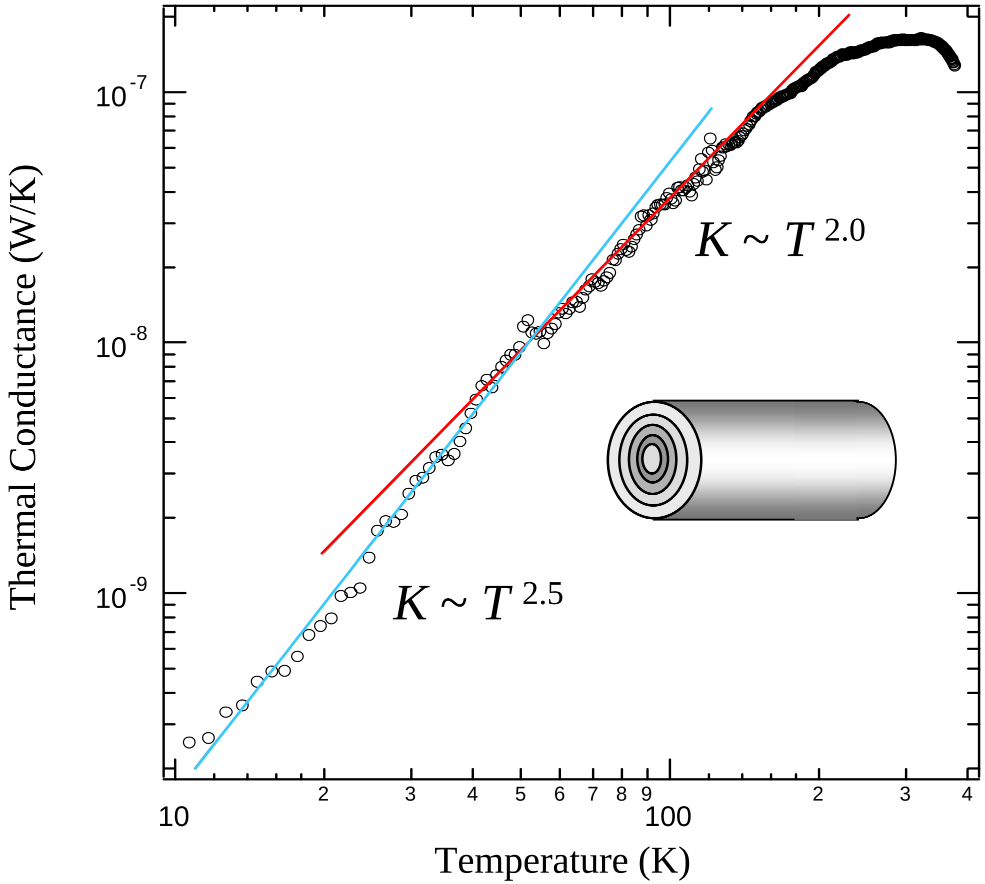
•Umklapp scattering above 320 K

$$k = \frac{1}{3} C\, v_s\, l$$

$l \sim 0.5$ μm

Kim *et al.* PRL (2001)

Low Temperature Thermal Conductance



In d dimension: $K \sim T^d$

Graphite: $K \sim T^{2.5}$

Strong anisotropy (weak layer coupling)

Graphene: $K \sim T^{2}$

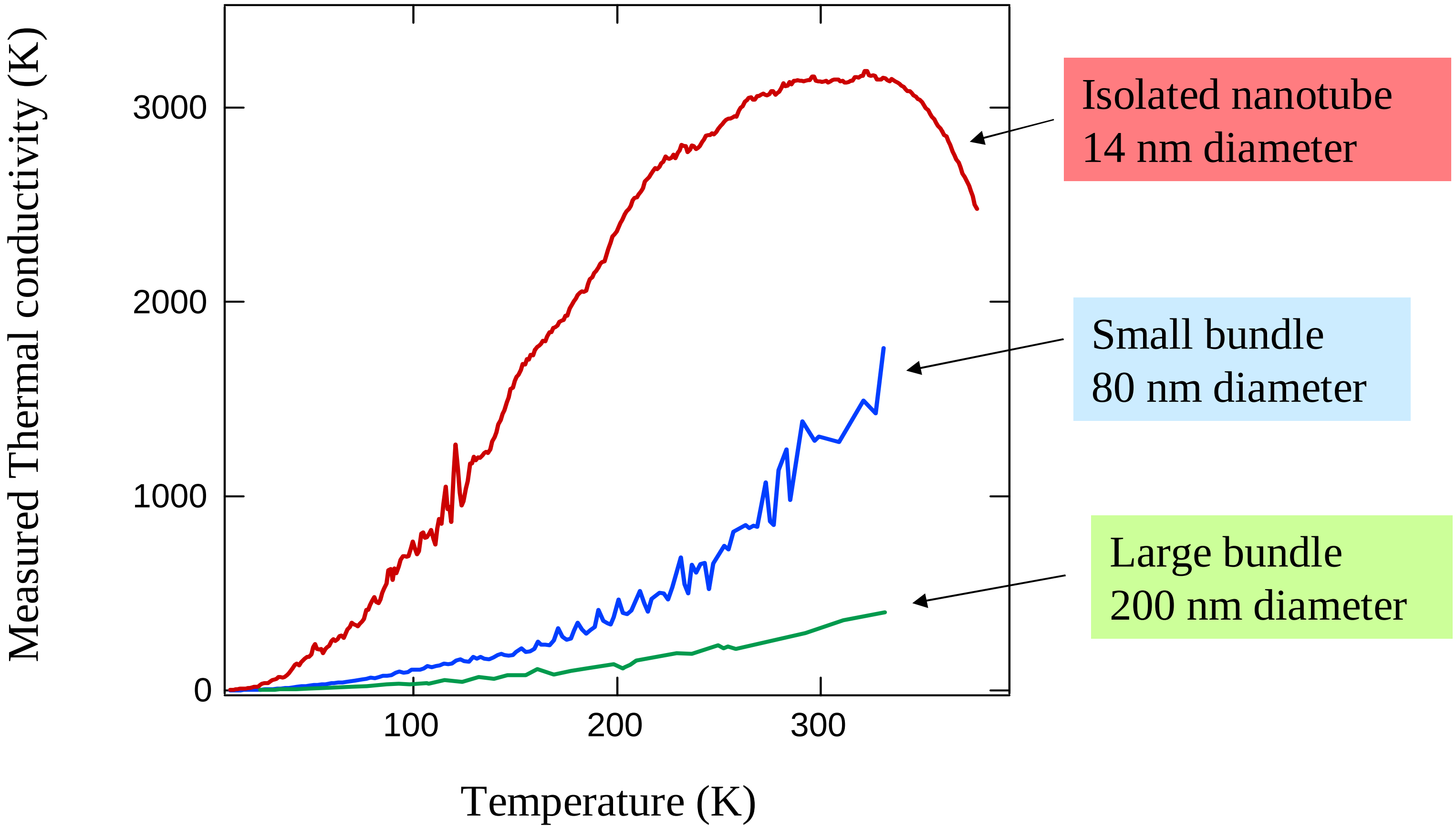
Strictly 2-dimensional

Out-of-plane Debye Temperature

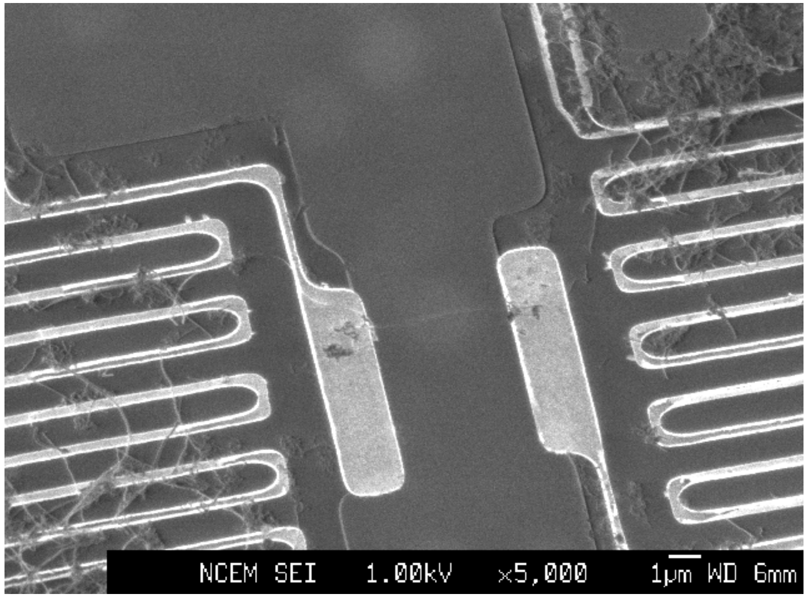
~ 50 K

c

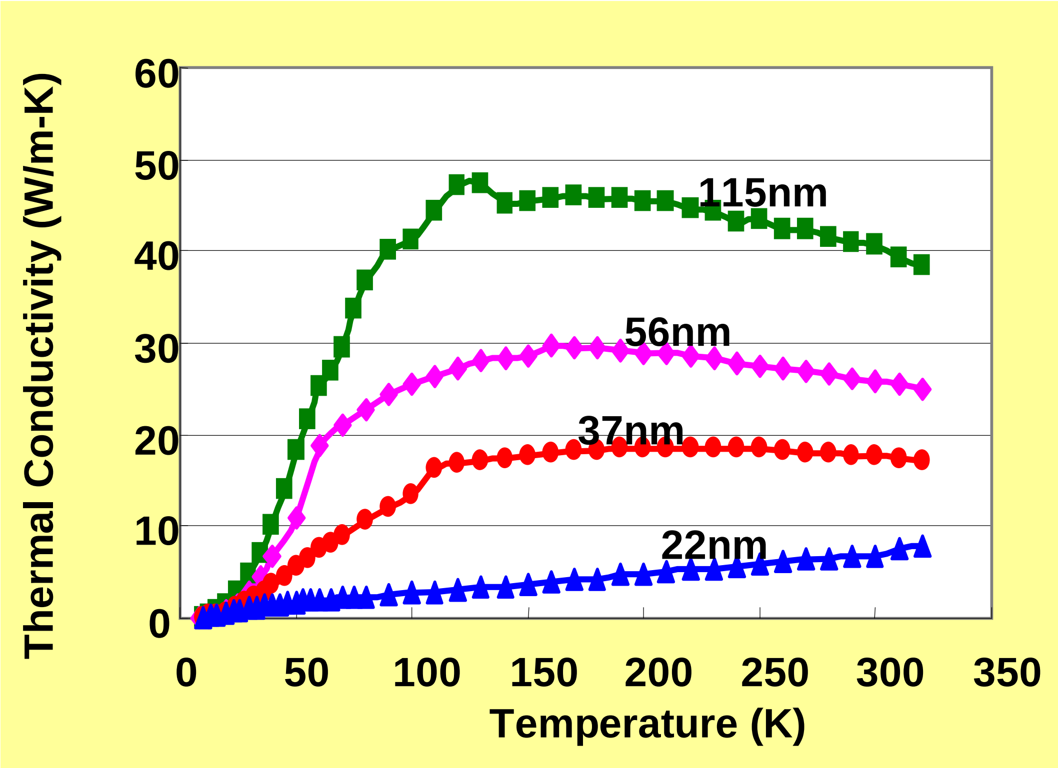
Bundles to isolated tubes



Silicon Nanowire



Drop deposited 30 nm diameter
Si nanowire (sample: Yang, UC Berkeley)

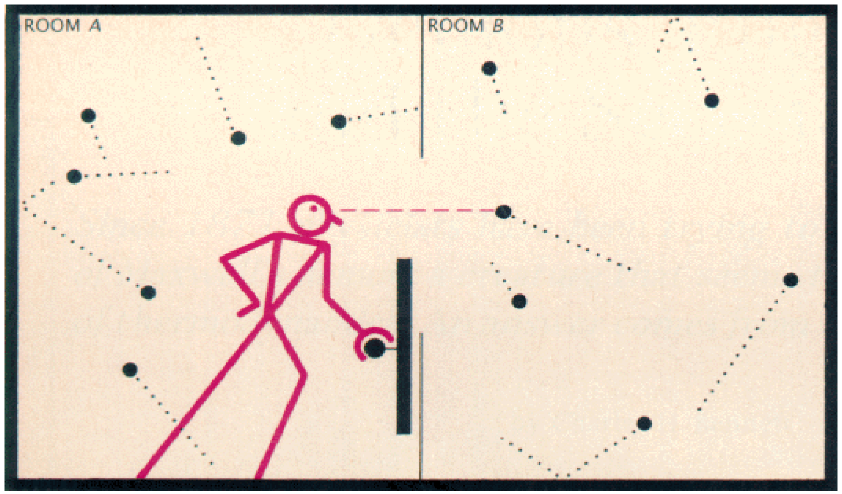


* Thermal conductivity is order of magnitude lower than bulk value.
* No Umklapp scattering peak → boundary scattering dominant, l_{ph} ~ diameter.

Li, Ying, Kim, Yang and Majumdar APL (2002)

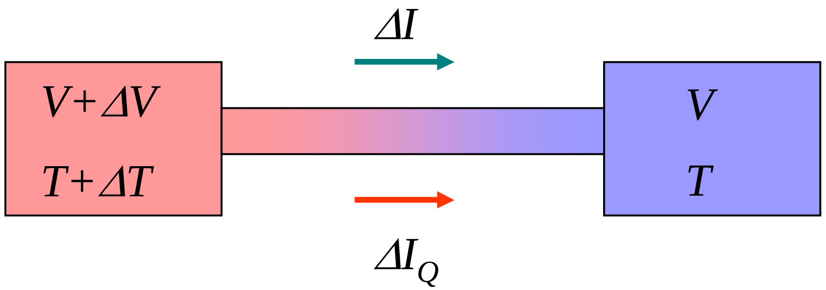
Measuring Entropy Flow

Thermo Electricity



Maxwell's demon

Thermoelectric Effects



Linear Response Regime

$$\Delta V = R\,\Delta I - S\,\Delta T$$

$$\Delta I_Q = \Pi\,\Delta I - K_{th}\,\Delta T$$

Energy transport per charge !

Peltier Coefficient: $\Pi = \Delta I_Q / \Delta I \quad (\Delta T = 0)$

Seebeck Coefficient (Thermopower) : $S = -\Delta V / \Delta T \quad (\Delta I = 0)$

Onsager relation

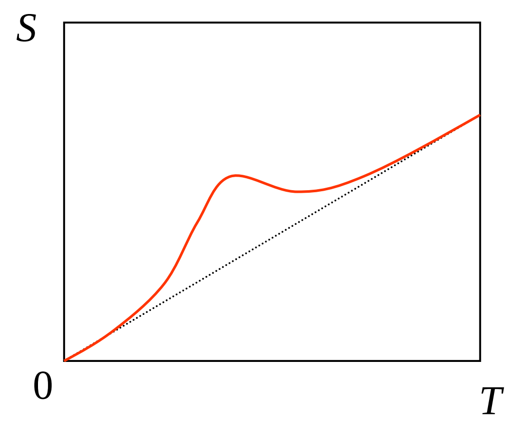
$$\Pi = S\,T$$

$$S = -\left(\frac{dV}{dT}\right)_{I=0} = \Pi / T$$

Entropy transport per charge!!

Thermopower of Bulk Systems

typical metal: $S \sim 5\ \mu V/K$ @ RT



$$S = S_d + S_{drag}$$

Electron diffusion

Phonon drag

Mott's formula **(Mott, 1969)**

$$S_d = \frac{-\pi^2 k_B{}^2 T}{3|e|} \frac{1}{G} \frac{dG}{dE}\bigg|_{E_f}$$

Bulk system: $G \sim n(E)\,\tau$

carrier density

scattering time

$$S_d = \frac{-\pi^2 k_B{}^2 T}{3|e|} \left(\frac{1}{\tau}\frac{d\tau}{dE} + \frac{1}{n(E)}\frac{dn(E)}{dE} \right)\bigg|_{E_F}$$

Sign of thermopower = Sign of major carrier

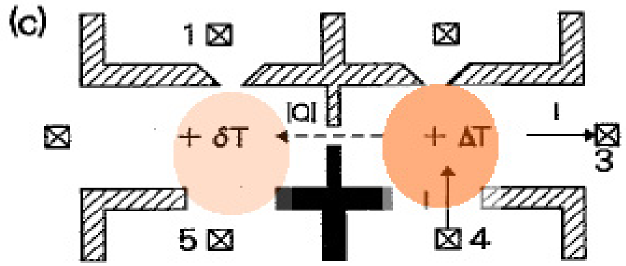
Thermopower in 1D Mesoscopic Systems

Landauer formula:

$$G = \frac{2e}{h} t_r \quad \longrightarrow \quad S_d = \frac{-\pi^2 k_B{}^2 T}{3|e|} \frac{1}{t_r} \frac{dt_r}{dE}\bigg|_{E_f}$$

Sivan and Imry (1986)

Quantum point contact

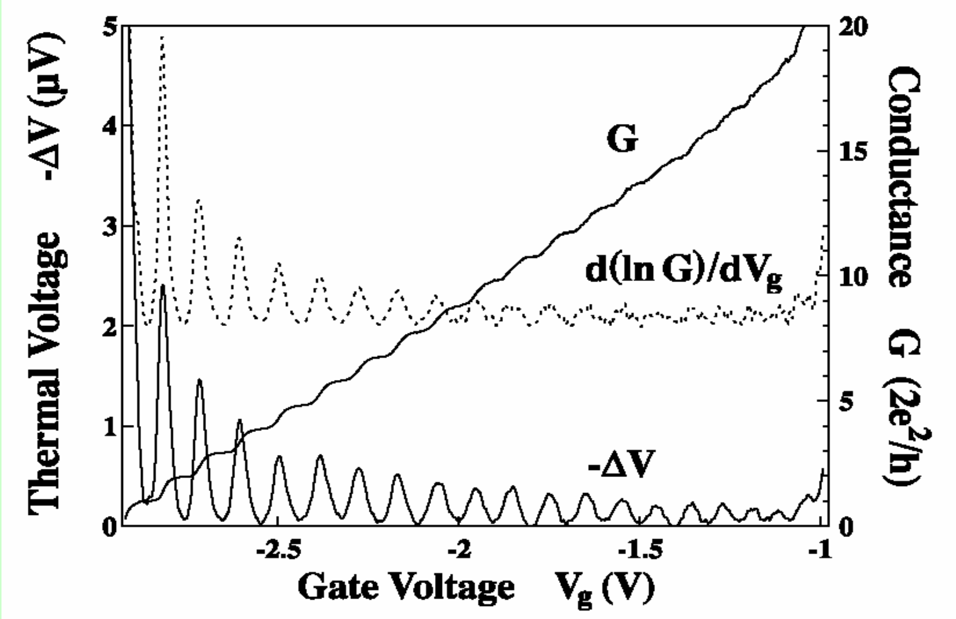


V_g

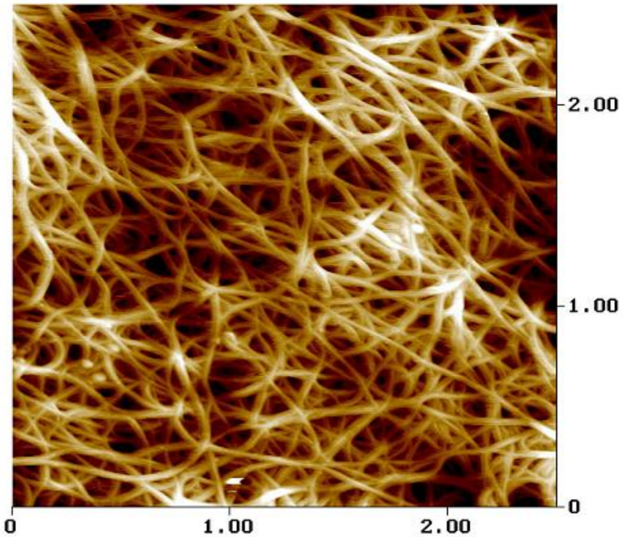
$$S_d = \frac{-\pi^2 k_B{}^2 T}{3|e|} \frac{1}{G} \frac{dG}{dE}\bigg|_{E_f} \sim -\frac{d\ln G}{dV_g}$$

Thermopower quantization

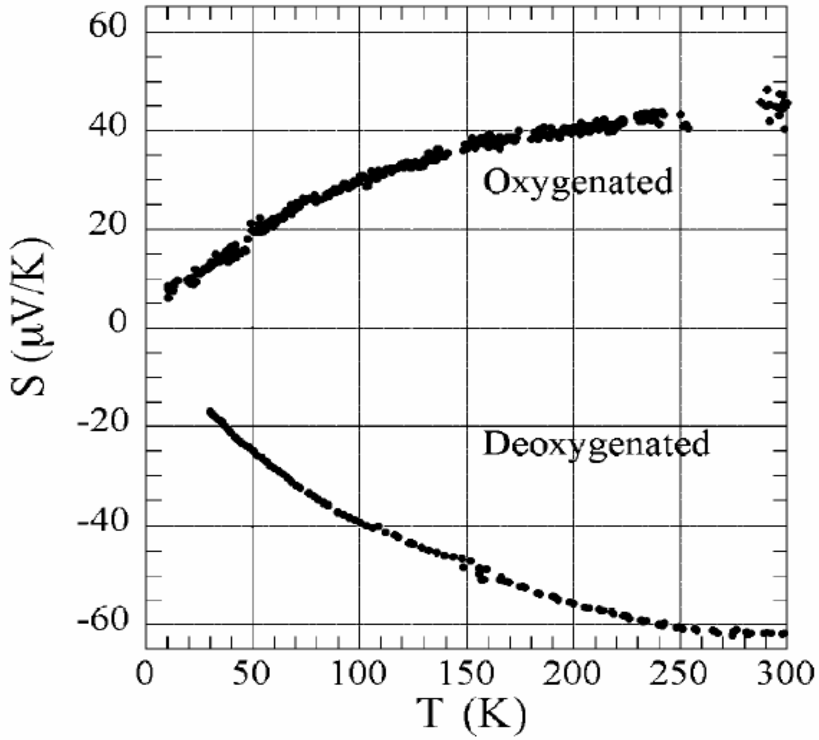
(Appleyard *et al.*, 1998)



Thermopower of Nanotube Bulk Samples



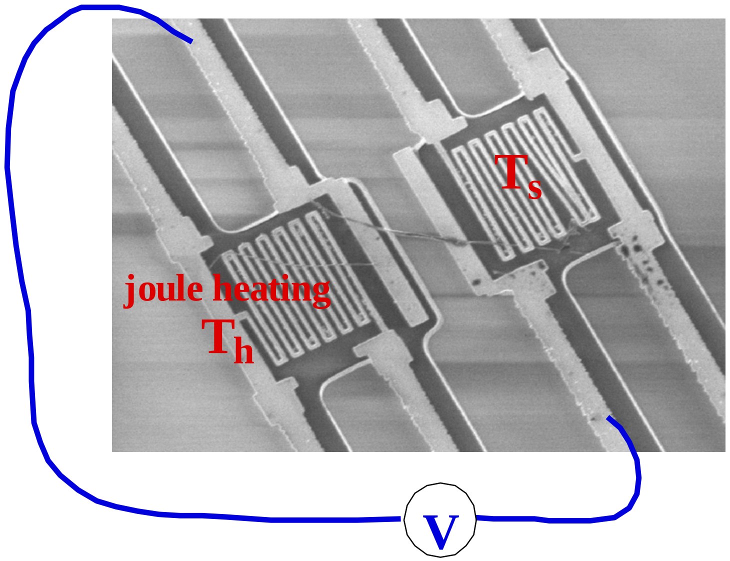
Bulk Nanotube Sample

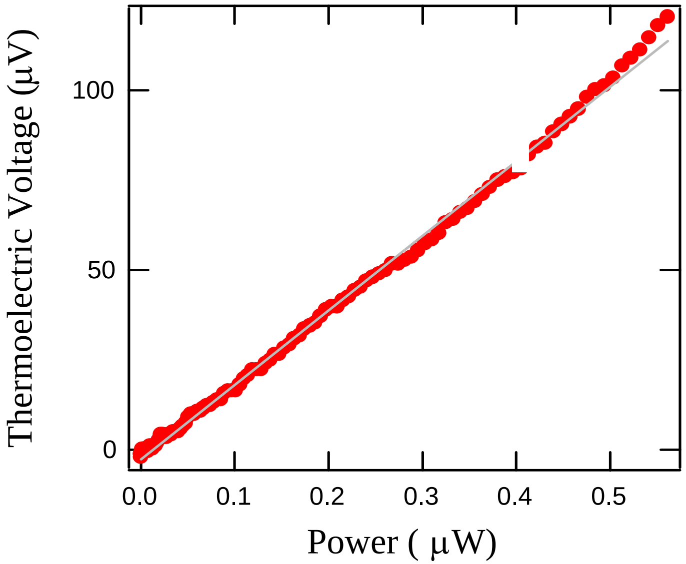


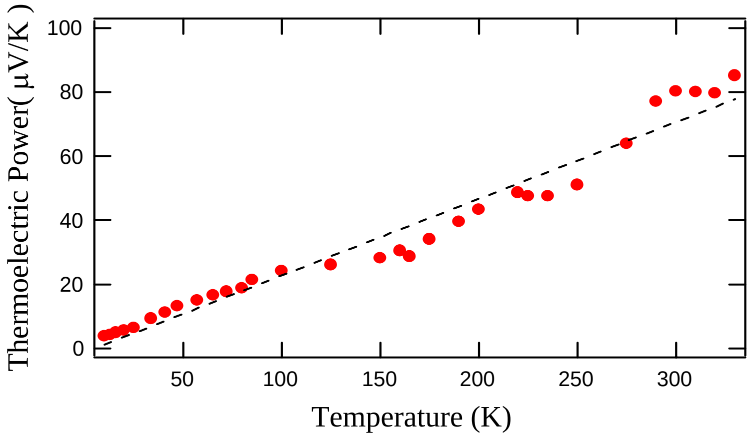
Bradley *et al*. PRL (2000)

In bulk materials, sign of S = sign of majority charge carrier.

Thermopower measurement in suspended device



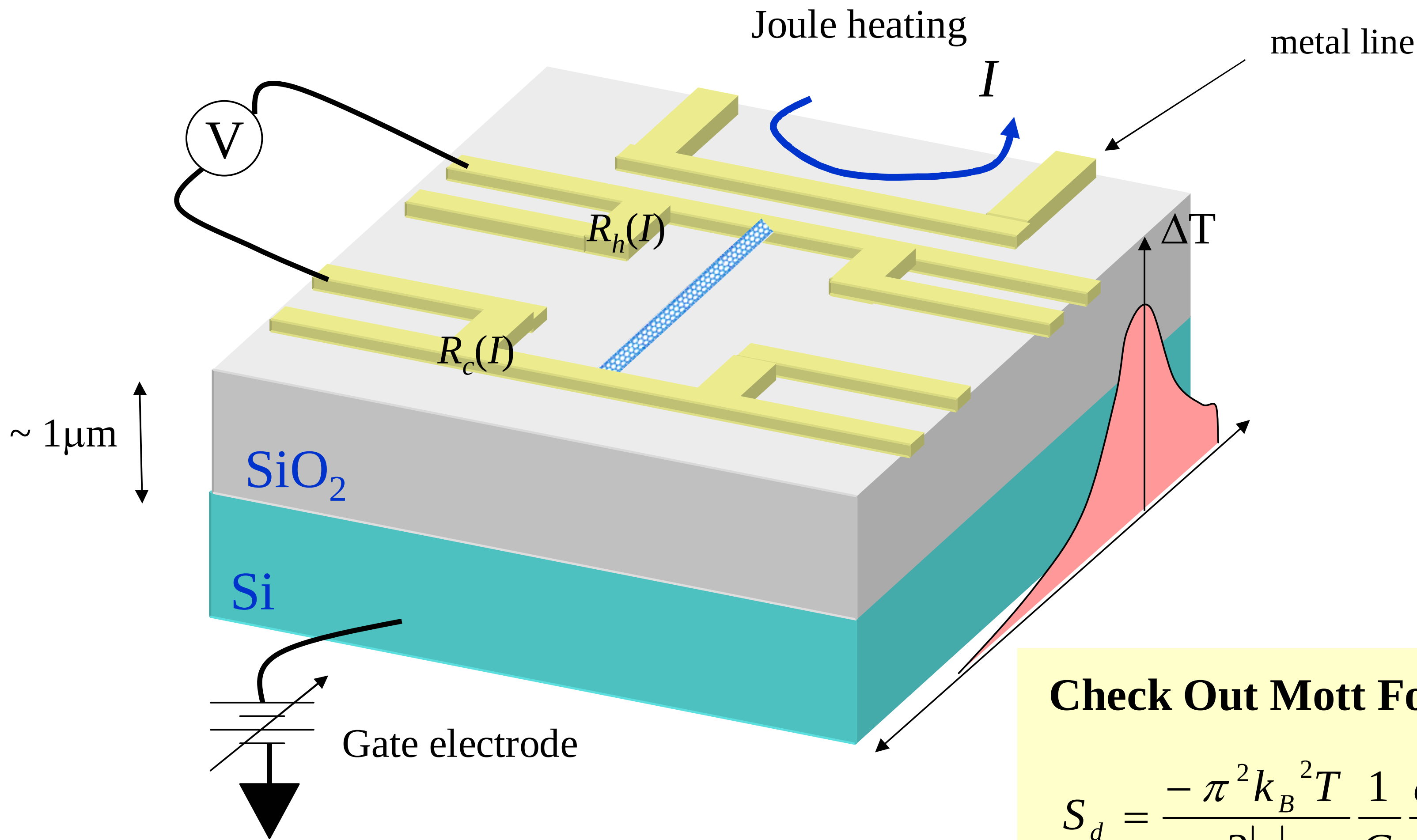




Small bundles of MWNTs
(diameter ~ 50 nm)

Kim *et al.* PRL (2001)

Thermopower measurement on silicon oxide substrate

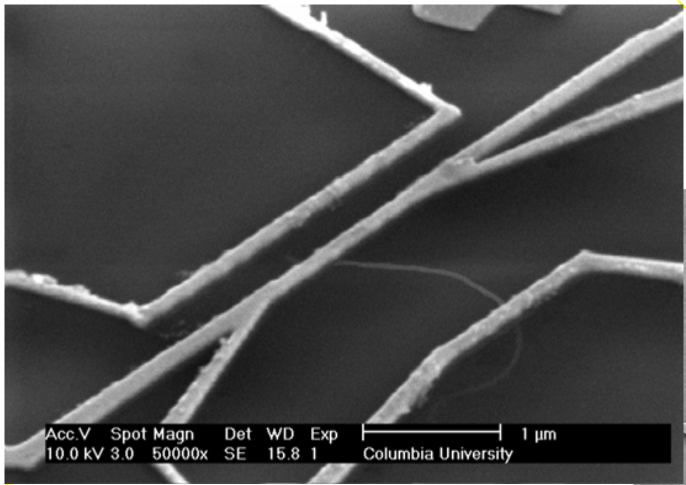


Check Out Mott Formula

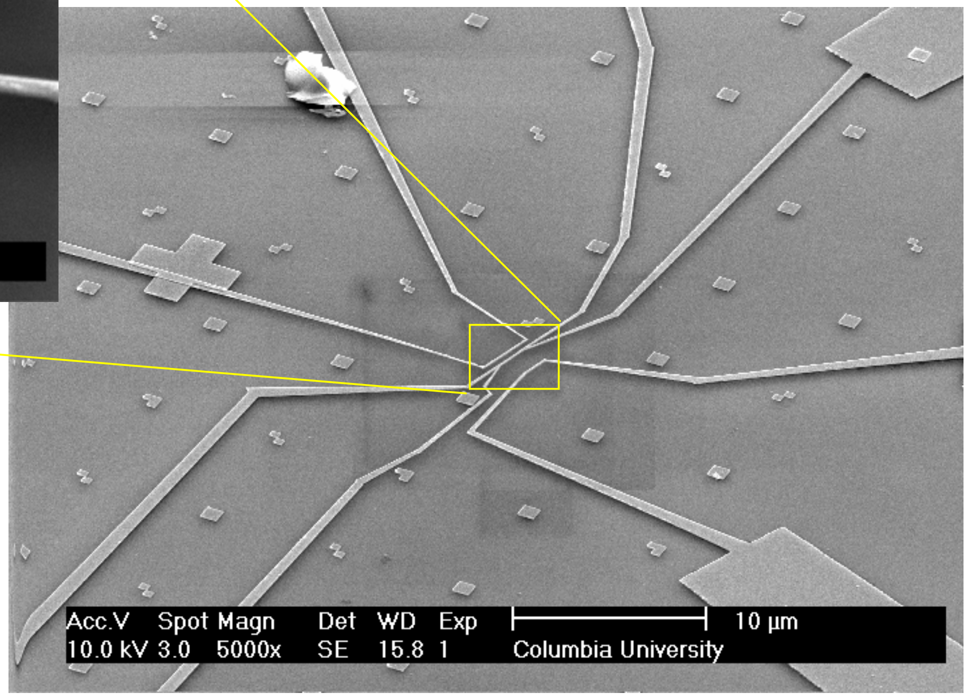
$$S_d = \frac{-\pi^2 k_B^2 T}{3|e|} \frac{1}{G} \frac{dG}{dE}\bigg|_{E_f}$$

Mesoscopic Thermopower measurement of Nanotube

Microfabricated devices for electric and thermal transport

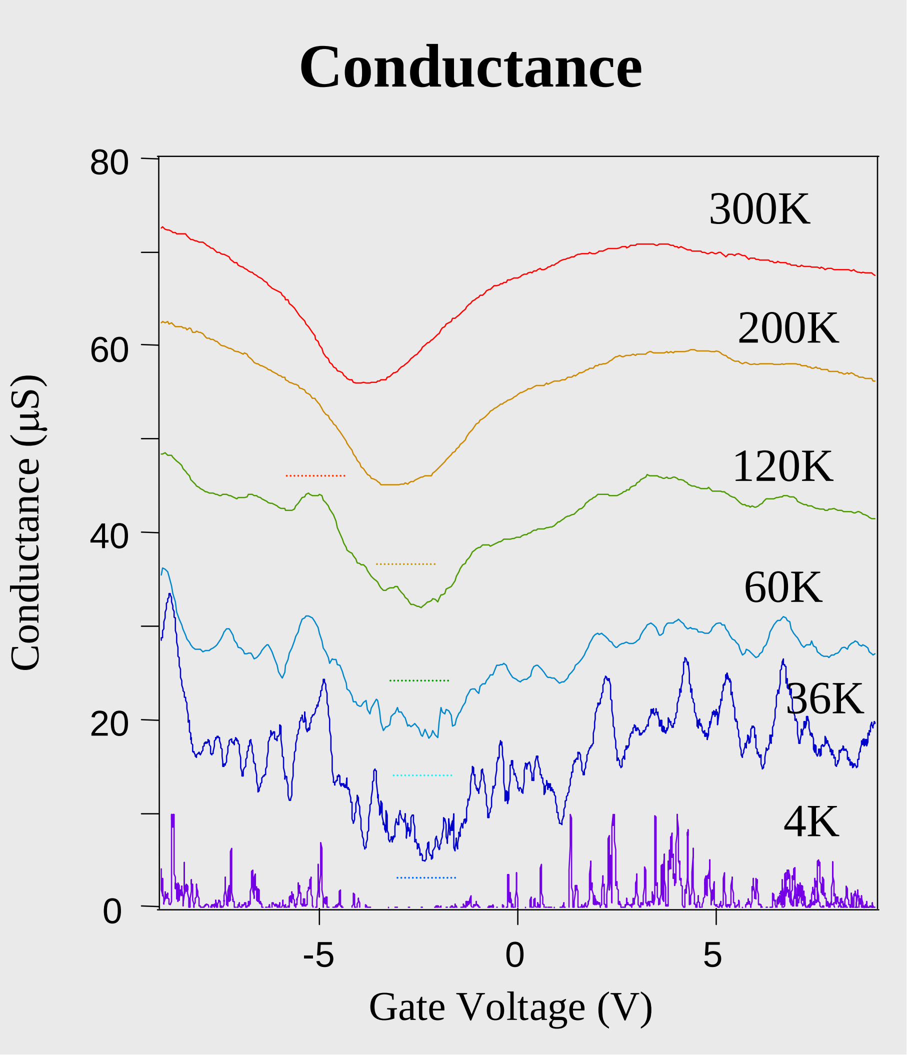


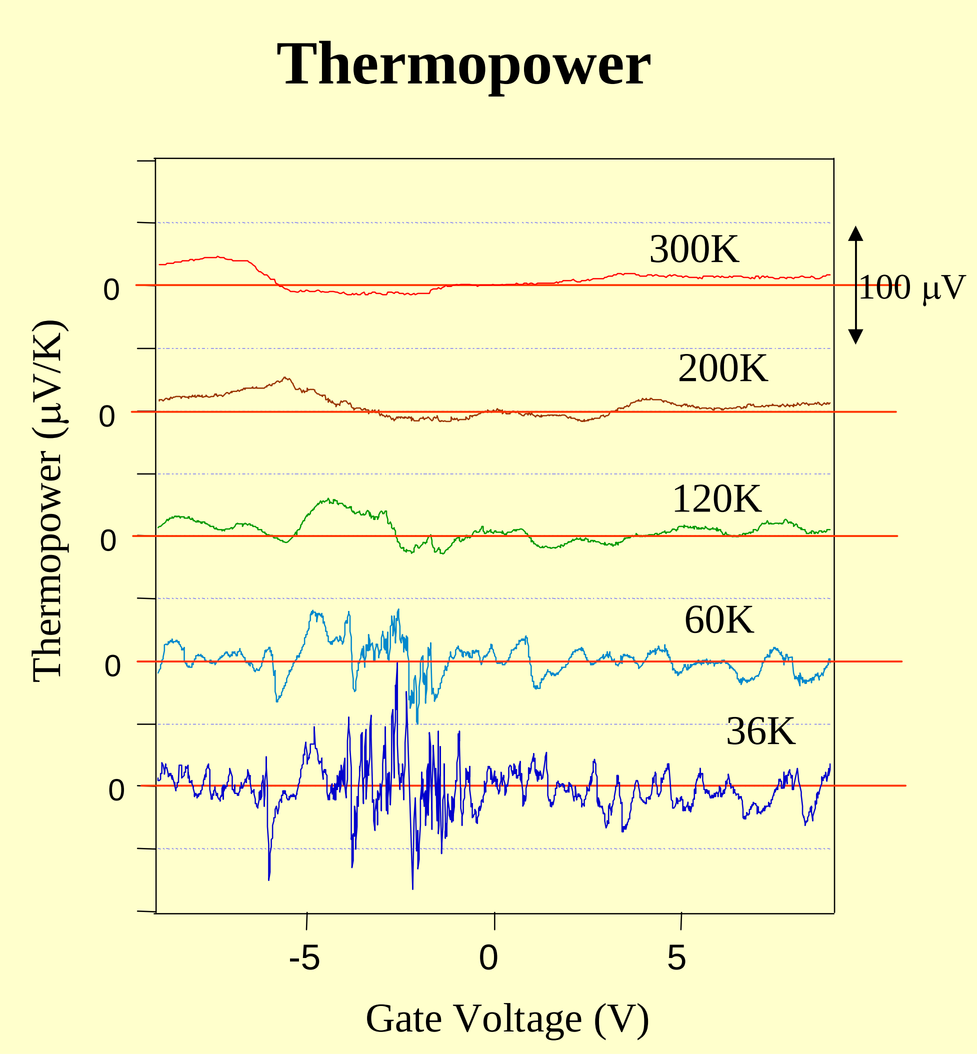
A device with CVD grown SWNT



Small and Kim, PRL (2003)

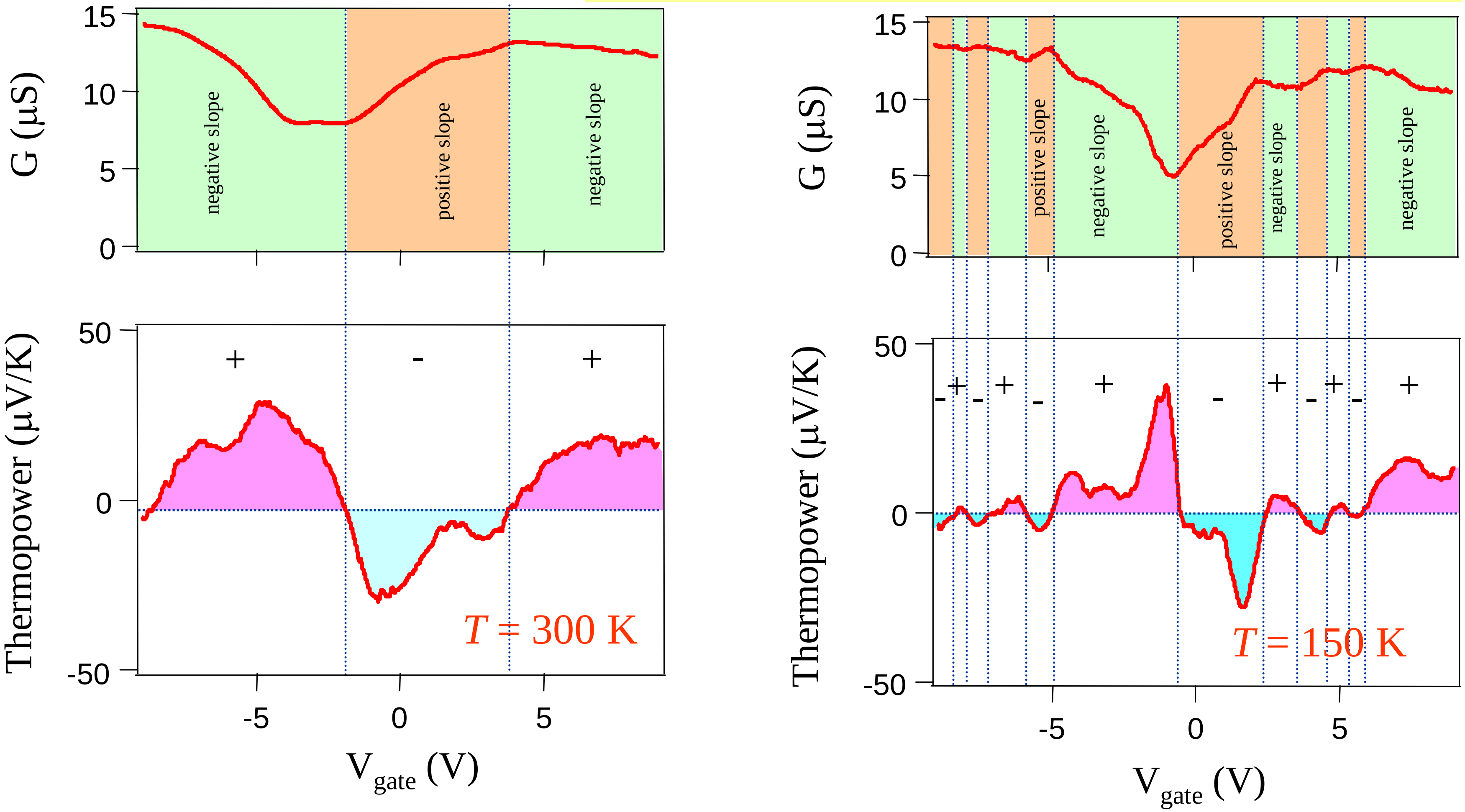
Conductance and Thermopower of Metallic Tube





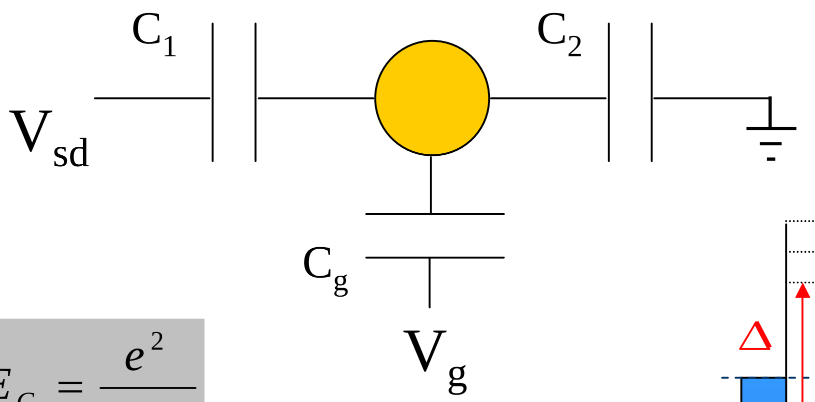
Electrical Conductance and TEP

Mott Formula: $$S_d = \frac{-\pi^2 k_B{}^2 T}{3|e|} \frac{1}{G} \frac{dG}{dE}\bigg|_{E_f}$$

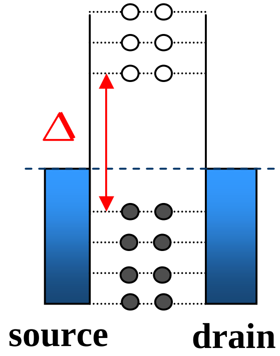


Coulomb Blockade Physics

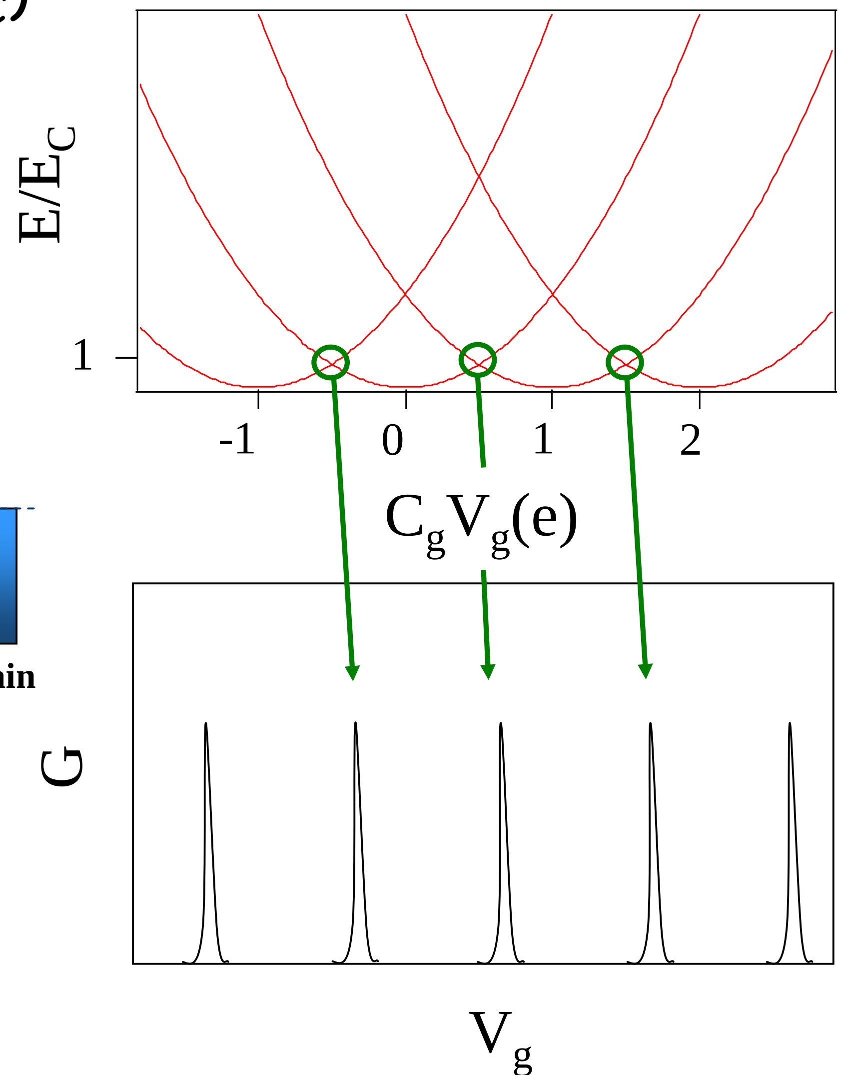
$(k_B T \ll E_C)$



$$E_C = \frac{e^2}{2C_\Sigma}$$



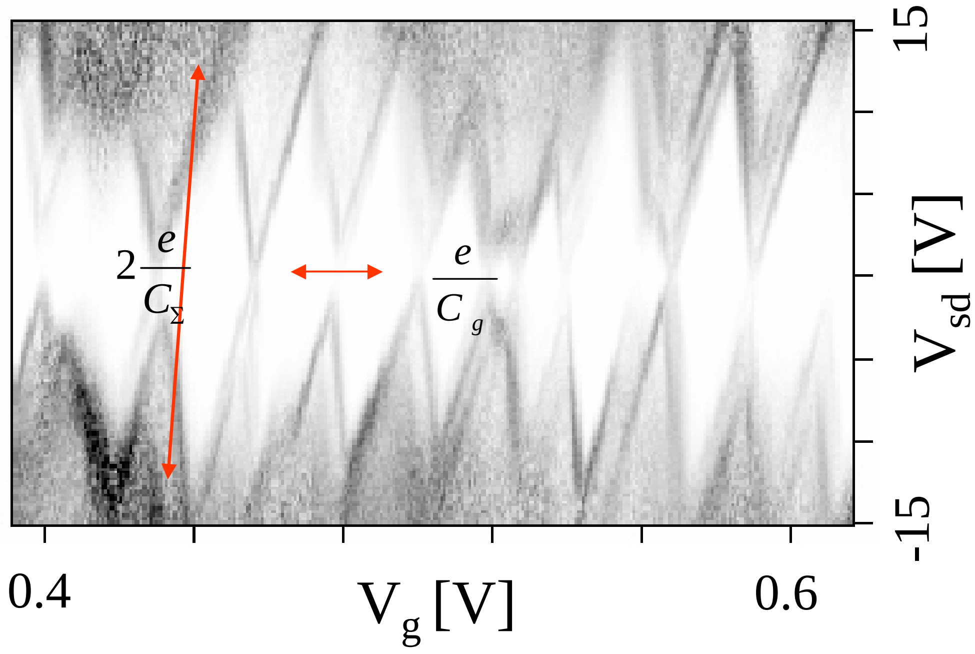
$$U = \frac{(Ne + C_g V_g)^2}{2C_\Sigma}$$

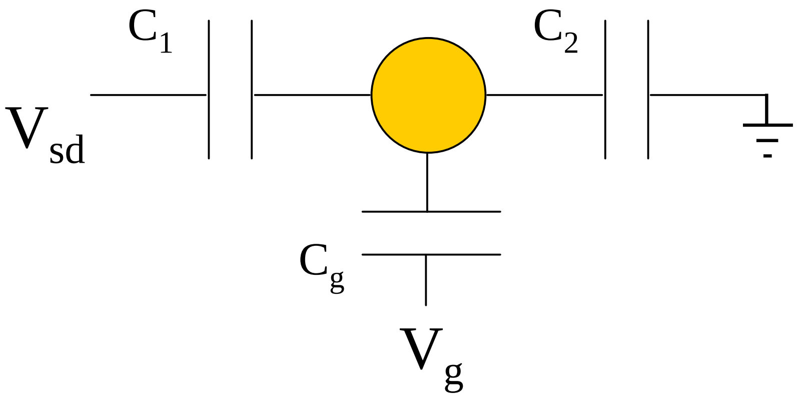


Electrostatics: Relation between E_f and V_g

Coulomb Blockade Regime

$(k_B T < E_C)$





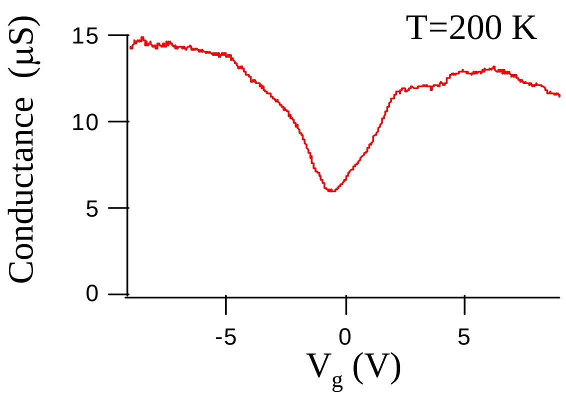
$$\rho \cdot \Delta E_F = C_g \Delta V_g$$

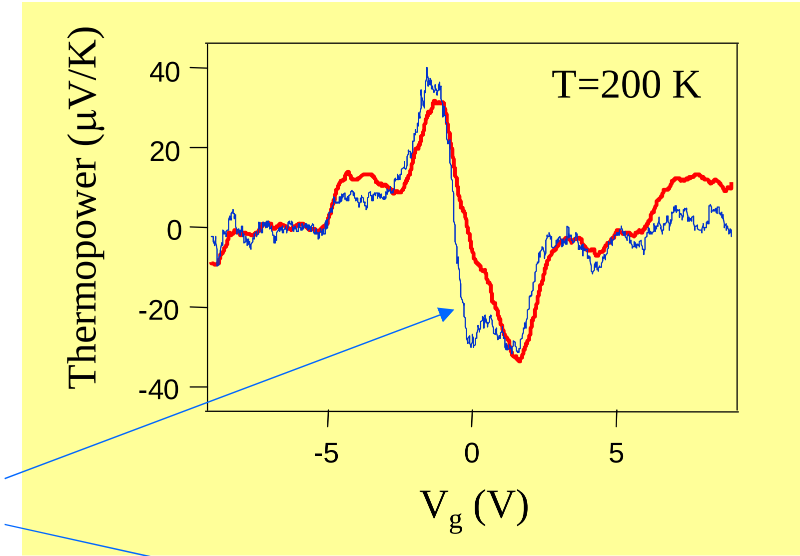
C_g=15 pF/m

$E_C = \frac{e^2}{2C_\Sigma}$ =6 meV

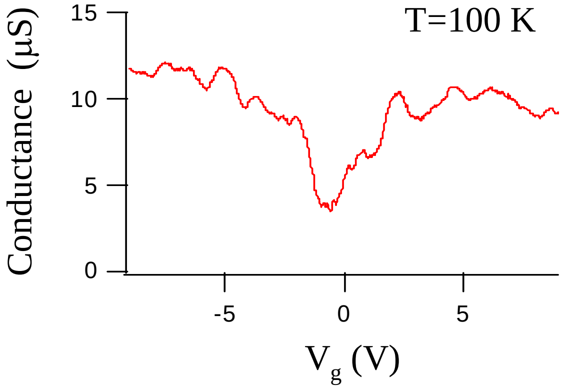
$dE_F/d(eV_g) = 0.05$

Quantitative Comparison with Mott Formula



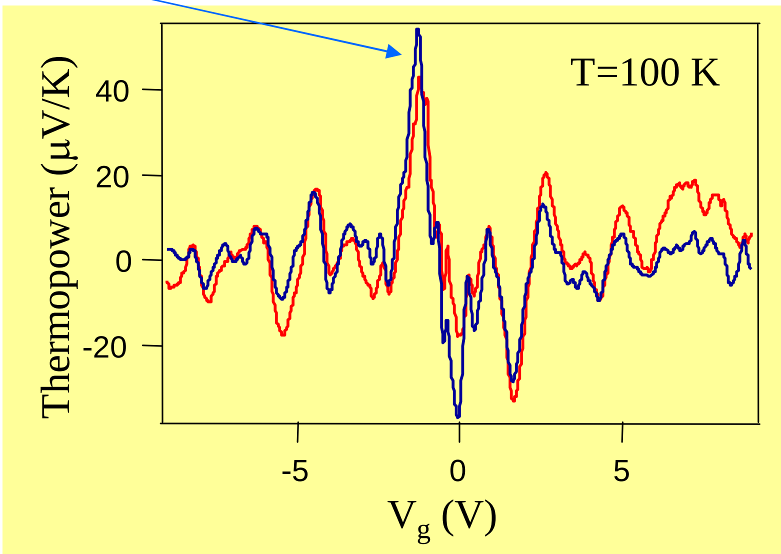


$$S_{Mott} = \frac{-\pi^2 k_B^2 T}{3|e|}\frac{1}{G}\frac{dG}{dE}\bigg|_{E_f}$$

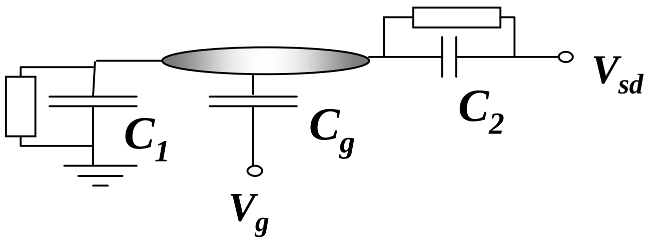


$$\Delta E_F = \frac{C_g}{DOS(E)} V_g$$

$$\approx 0.05\, V_g$$



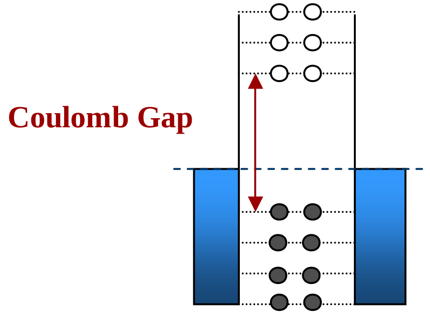
TEP in Quantum Dot (electron-electron interaction)

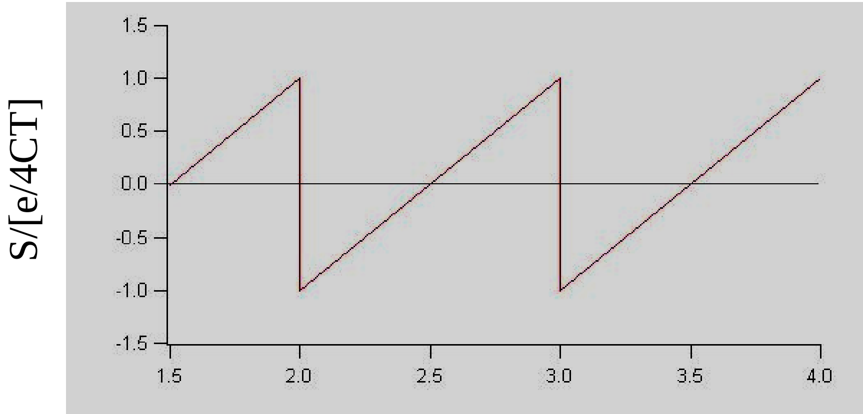


Coulomb Blockade Region

$$S = -\frac{1}{2eT}\left[\left(N_{\min} - \frac{1}{2}\right)\frac{e^2}{C} - e\phi_{ext}\right]$$

Beenakker, Staring PRB (1992)





$E_F/[e^2/2C]$

$$S \sim \frac{e}{2CT} = \left(\frac{k_B}{e}\right)\frac{E_c}{k_B T}$$

TEP Oscillation in Semicondutor Quantum Dot

VOLUME 81, NUMBER 23 PHYSICAL REVIEW LETTERS 7 DECEMBER 1998

Charging Energy of a Chaotic Quantum Dot

S. Möller, H. Buhmann, S. F. Godijn, and L. W. Molenkamp
2. Physikalisches Institut, RWTH-Aachen, Templergraben 55, D-52056 Aachen, Germany
(Received 30 June 1998)

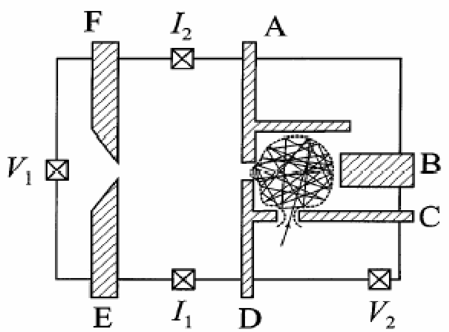
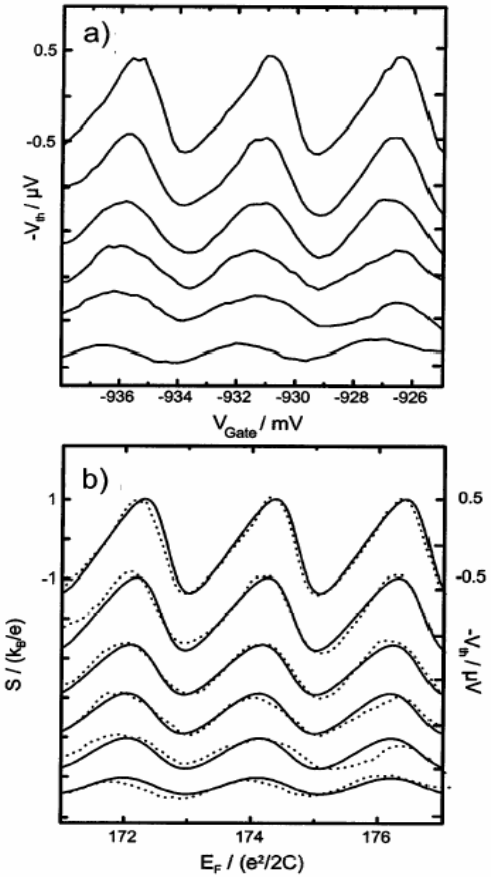


FIG. 1. Schematic top view of the sample structure. The hatched areas show the structure of the Schottky gates, the crosses denote Ohmic contacts. The heating current is passed between I_1 and I_2. The thermovoltage V_{th} is measured between V_1 and V_2. The chaotic electron trajectories are indicated in the gate-defined dot region (dashed line). An arrow points at the varied quantum-dot lead.

$$S \sim \frac{e}{2CT} = \left(\frac{k_B}{e}\right)\frac{E_c}{k_B T}$$



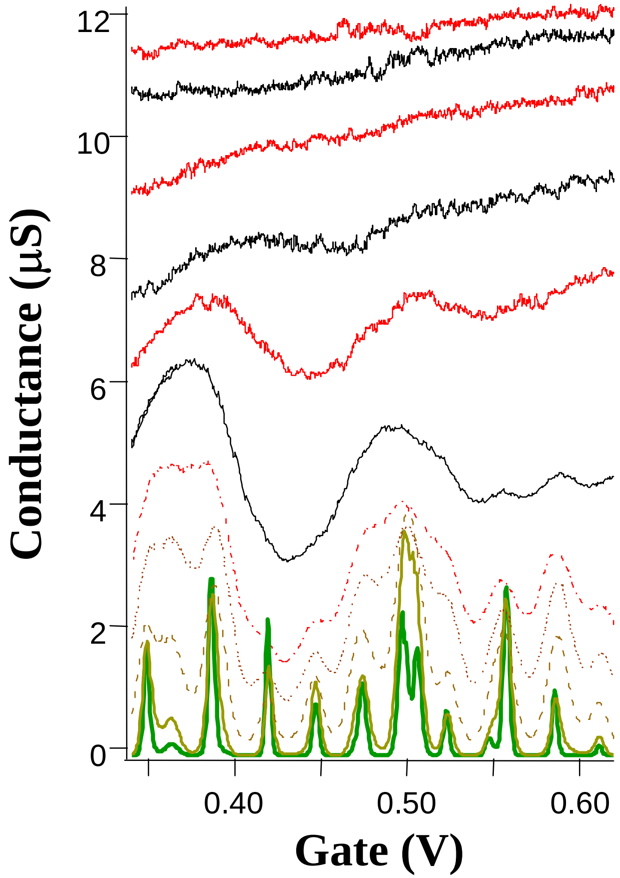
Charging energy

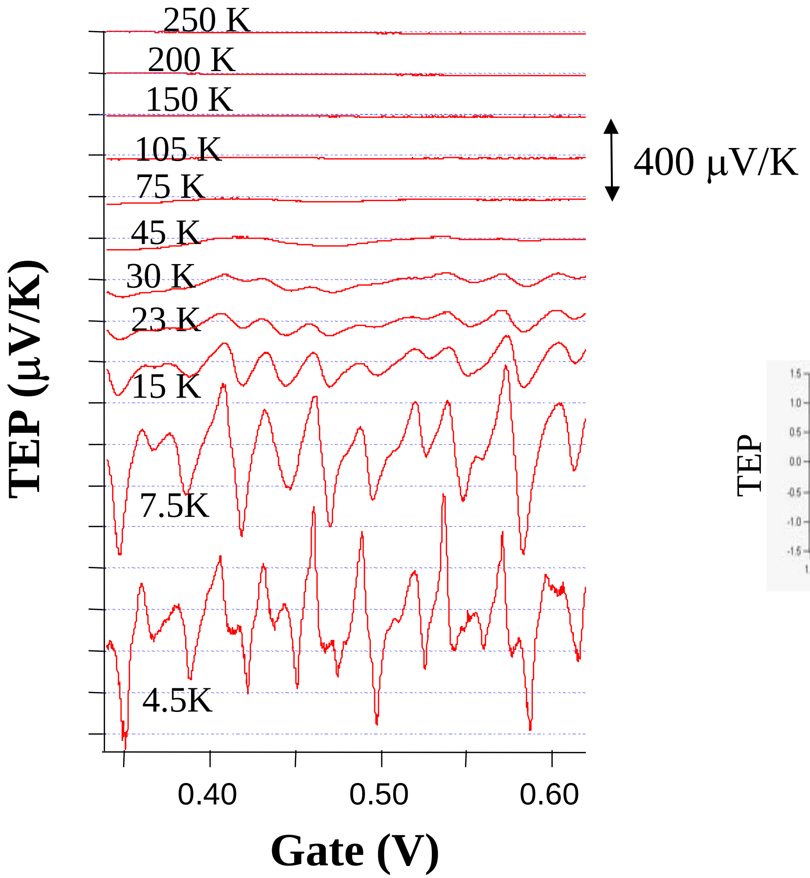
FIG. 2. (a) Experimental traces of the thermovoltage of the quantum dot for a heating current of 40 nA. The transmission probability of point contact *CD* was 0.06, 0.19, 0.29, 0.38, 0.43, and 0.82 from top to bottom. (b) Calculated curves of the thermopower of a quantum dot. The values of $k_B T/E_c$ are 0.22, 0.25, 0.30, 0.33, 0.37, and 0.45 from top to bottom (solid line). The experimental thermovoltage measurements from (a) are added as dashed lines.

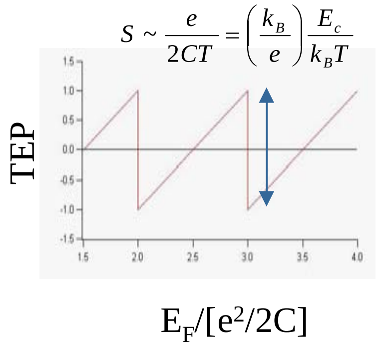
T = 40 mK : Lattice temperature

ΔT ~ 8 mK : indirect measurements

SWNT TEP in Coulomb Blockade Regime



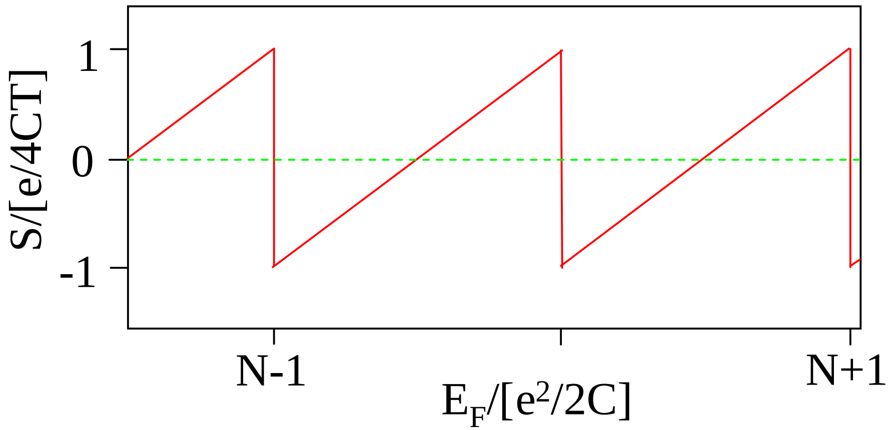


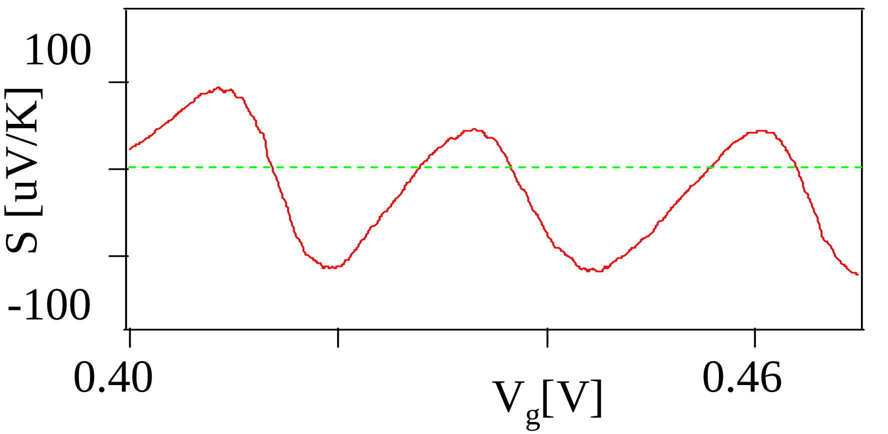


TEP with electron-electron interaction

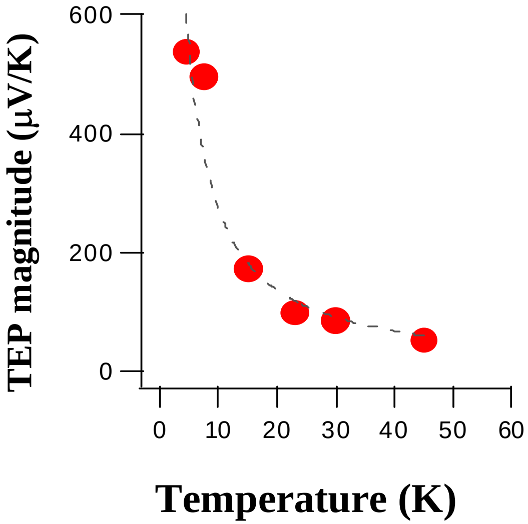
$$S = -\frac{1}{2eT}\left[\left(N_{\min} - \frac{1}{2}\right)\frac{e^2}{C} - e\phi_{ext}\right]$$

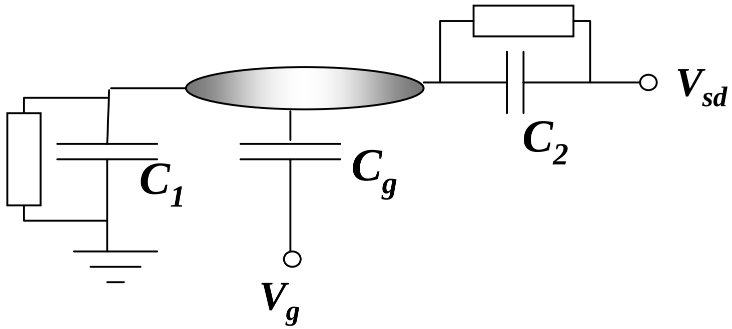
Beenakker, Staring PRB (1992)

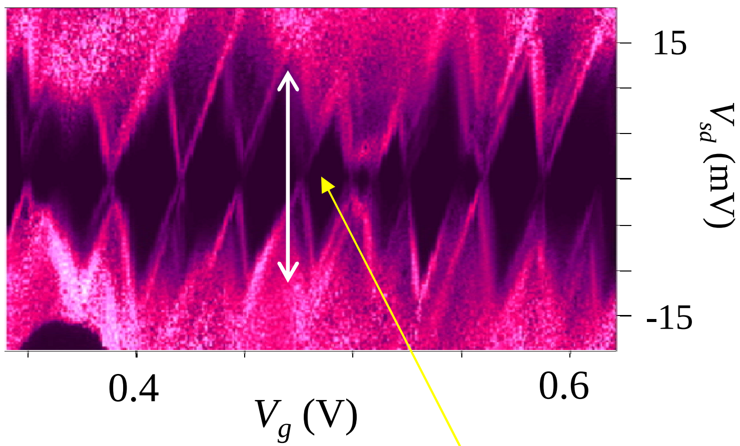




Charging Energy and TEP Oscillations







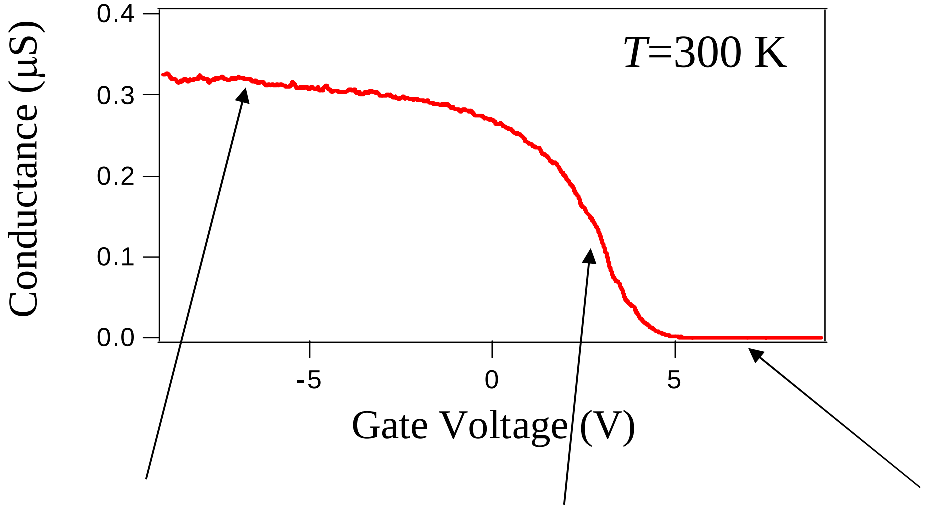
$$S \sim \frac{e}{2CT} = \left(\frac{k_B}{e}\right)\frac{E_c}{k_B T}$$

$$\frac{2e^2}{C} = 4E_c$$

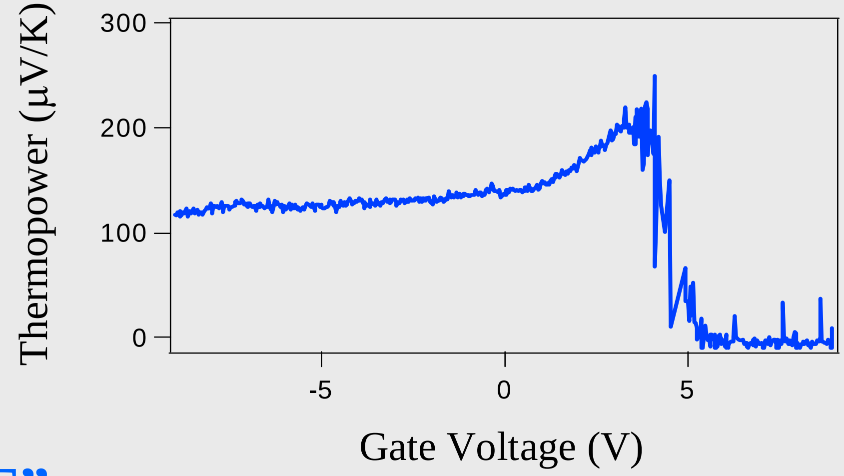
$E_c \sim 5$ meV

Thermopower in Semiconducting Nanotube

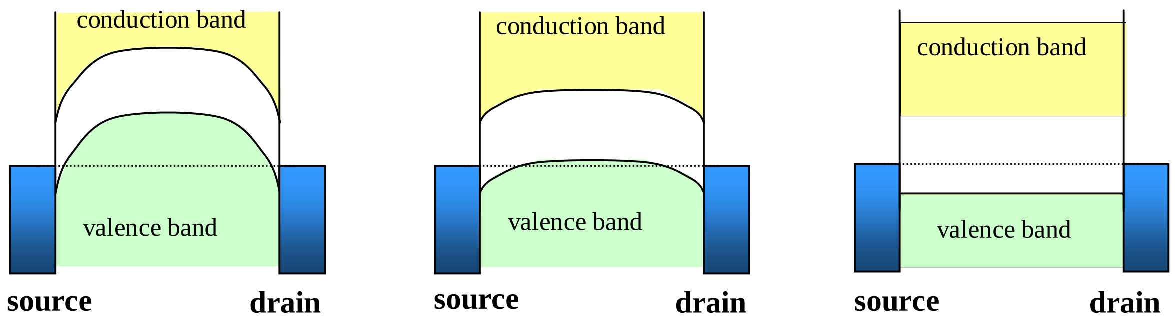
Schottky Barrier limited transport



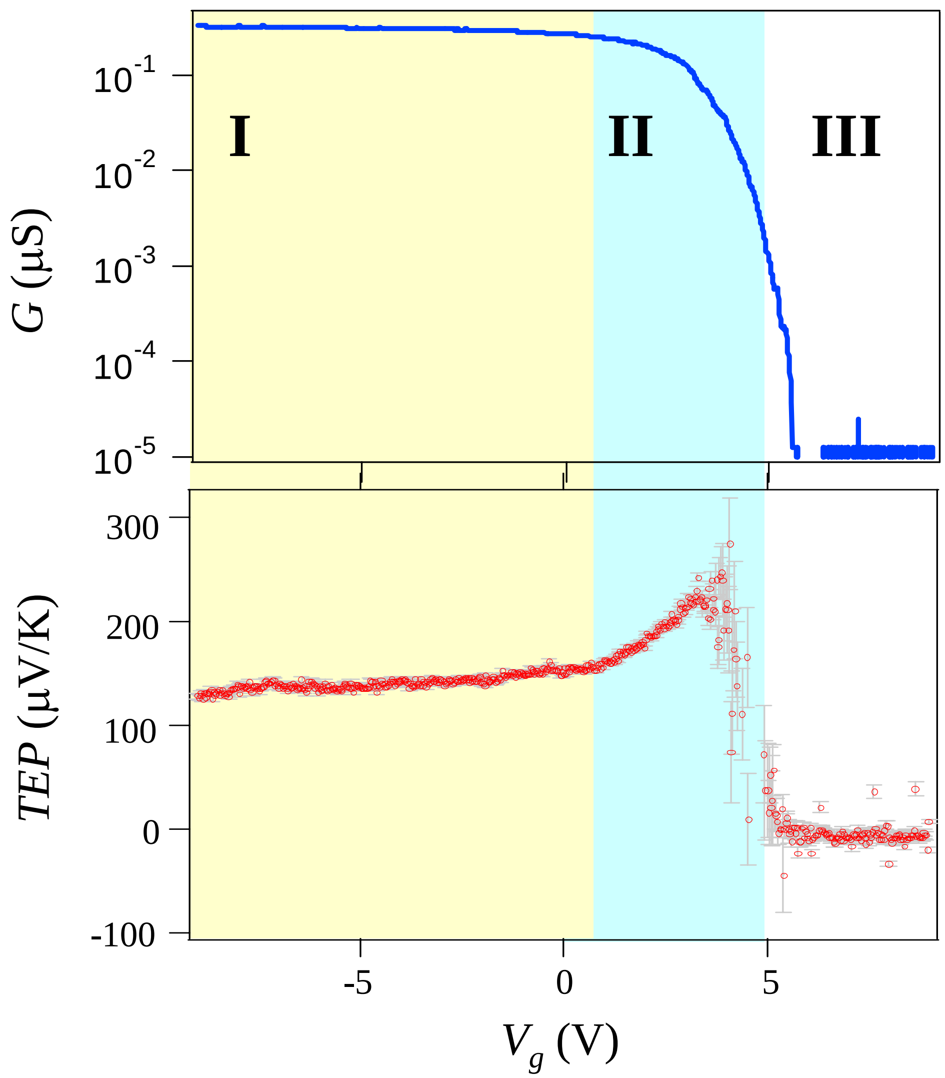
Very high valued & adjustable Thermopower



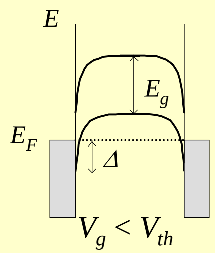
“ON” “subthreshold” “OFF”



Thermopower in Semiconducting Nanotube



I on-region

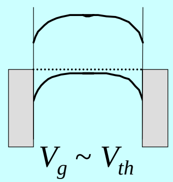


$$G(E) \approx \left(\frac{4e^2}{h}\right) Exp[-\alpha\sqrt{\Delta + E}]$$

$$S \approx -\frac{\pi^2}{6}\frac{k_B{}^2 T}{e\Delta}\ln[\frac{G_{meas}}{(4e^2/h)}]$$

$\Delta \sim 150$ meV

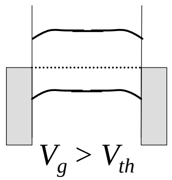
II subthreshold



$$G(E) \sim Exp[-(E-\Delta)/k_B T]$$

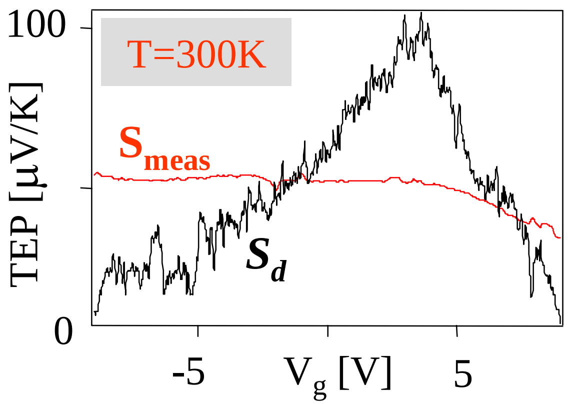
$$S \approx -\frac{\pi^2}{3}\frac{k_B}{e} = 284\ \mu v/K$$

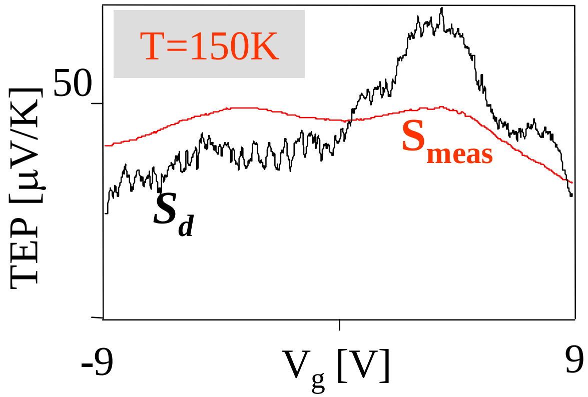
III off-region

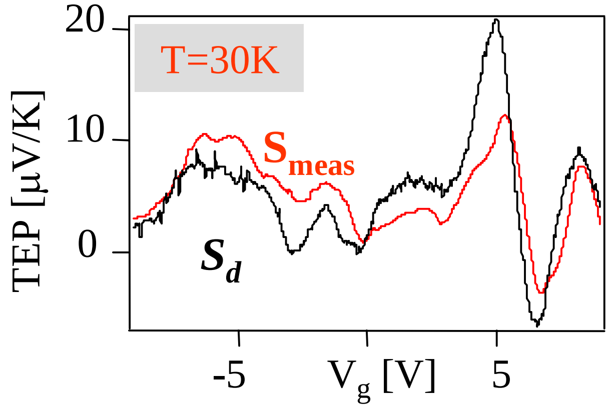


Multiwalled Nanotube Thermopower

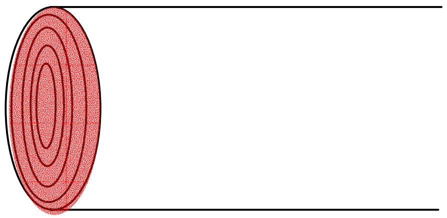
$$S_d = \frac{-\pi^2 k_B^2 T}{3|e|}\frac{d\ln G}{dE} = \frac{-\pi^2 k_B^2 T}{3|e|}\frac{d\ln G}{dV_g}\left(\frac{dV_g}{dE}\right)$$



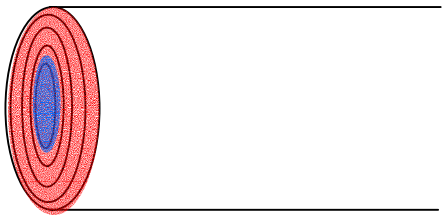




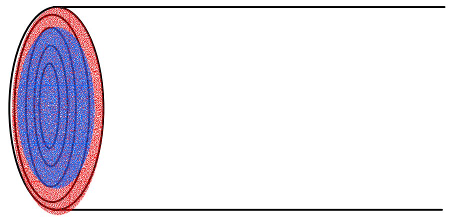
Current flows many shells…



inner tubes begin to freeze out…

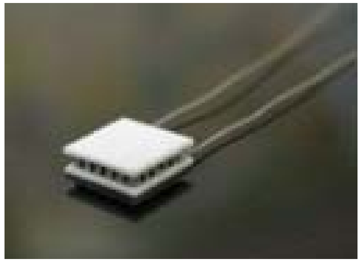


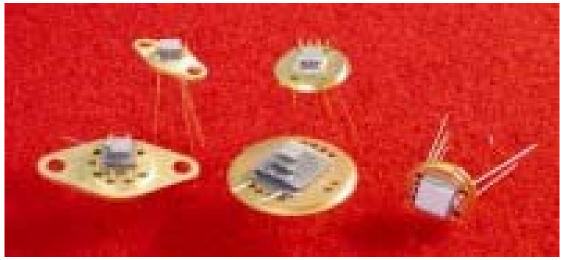
Current flows outter shell only



$$S_{tot} = \frac{G_1 S_1 + \alpha_2 G_2 S_2 + \alpha_2 G_3 S_3}{G_1 + \alpha_2 G_2 + \alpha_3 G_3}$$

Thermoelectric Cooling

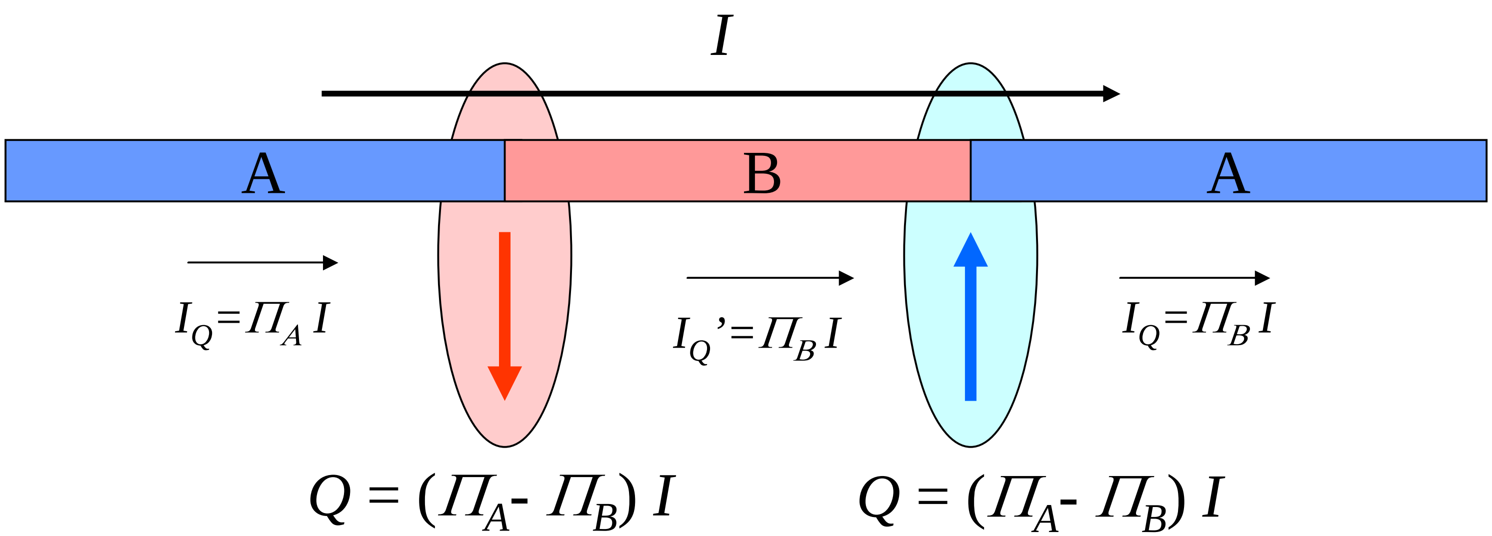




Solid state heat pump

$\Delta T_{max} \sim 70$ K

Peltier Effect



Thermodynamic Figure of Merit

Efficiency of Peltier Refrigerator

$$ZT = \frac{S^2 GT}{K_{th}} < 2 \quad \text{: Practical limit}$$

where $K_{th} = K^{e}_{th} + K^{ph}_{th}$

All Quantum limit transport:

$G = n\, g^{0}_{el}$ $K^{e}_{th} = n\, g^{0}_{th}$ $K^{ph}_{th} = p\, g^{0}_{th}$

(*n*, *p* :# of mode)

Wiedemann-Franz Law

$$\frac{g^{0}_{th}}{g^{0}_{el}} = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2 T$$

→ $ZT \sim n/(p+n)[S(\mu V/K)/100]^2$

High ZT materials at nanometer scale!

Conclusions

- Mesoscopic thermal conductance measurements in individual nanotubes
- Extremely high thermal conductivity
- Mesoscopic thermopower measurements in SWNTs
- Thermopower of SWNTs can be controlled by a gate electrode