Phonon Thermal Transport at Nanoscale

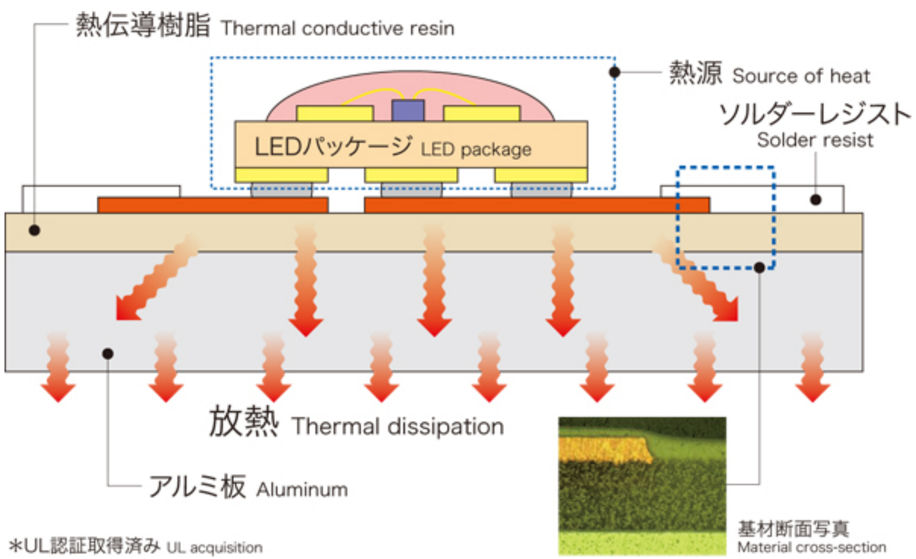
T. Yamamoto
Tokyo University of Science

CONTENTS

- Introduction
- Boltzmann Theory of Thermal Transport
- Landaur Theory of Thermal Transport
- Thermal Transport Simulations

Introduction

High thermal conductivity

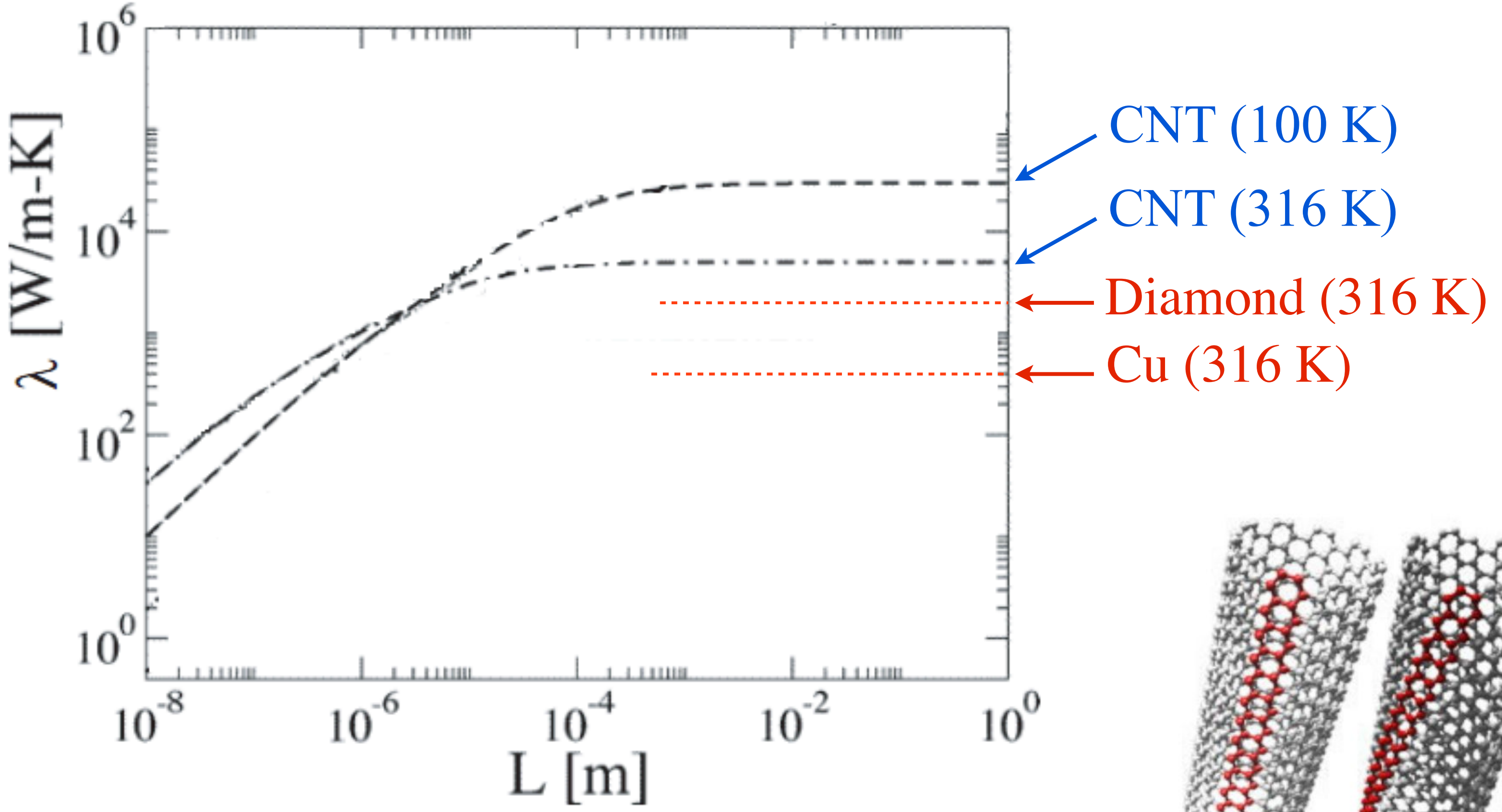


Heat Removal Materials

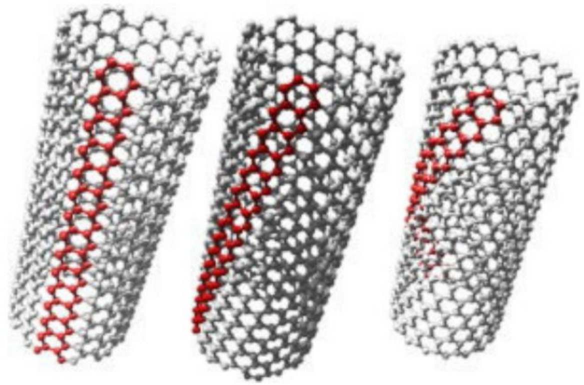
Low thermal conductivity

Thermoelectric Materials

High Thermal Conductivity of Carbon Nanotubes



Mingo & Broido, Nano Lett. **5,** 1221 (2005).

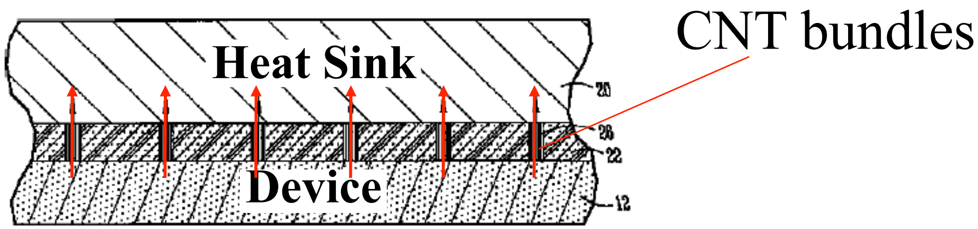


Thermal conductivity of CNTs is higher than that of diamond.

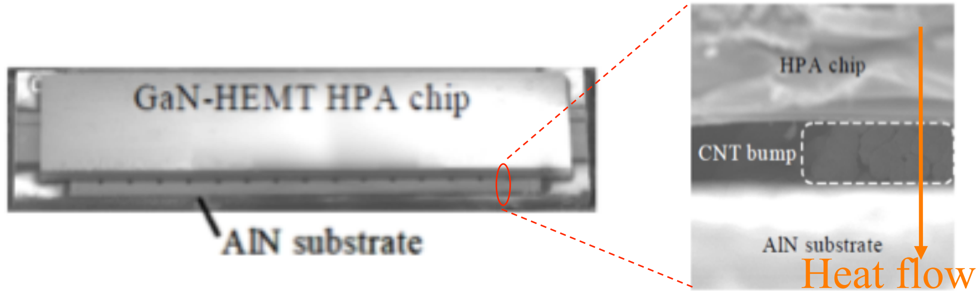
--> CNTs are potential candidates for heat removal materials.

High-Performance Devices using CNTs as Heat Removal

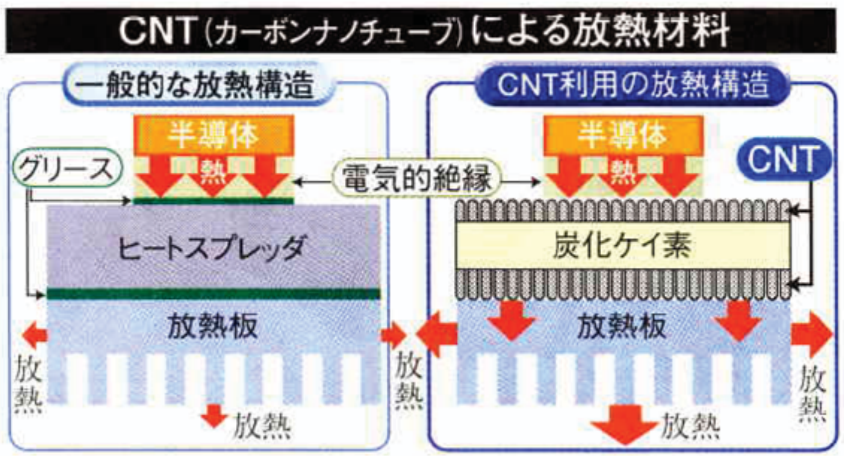
Intel (2003)



Fujitsu (2005)

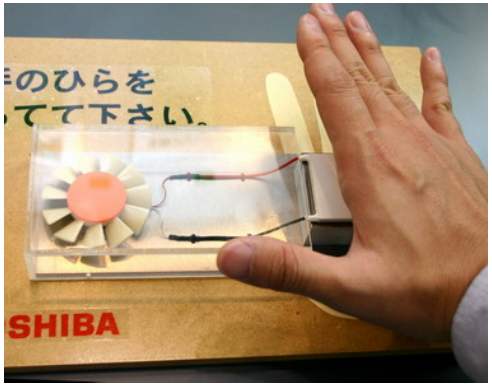


Nagoya Univ. (2008)



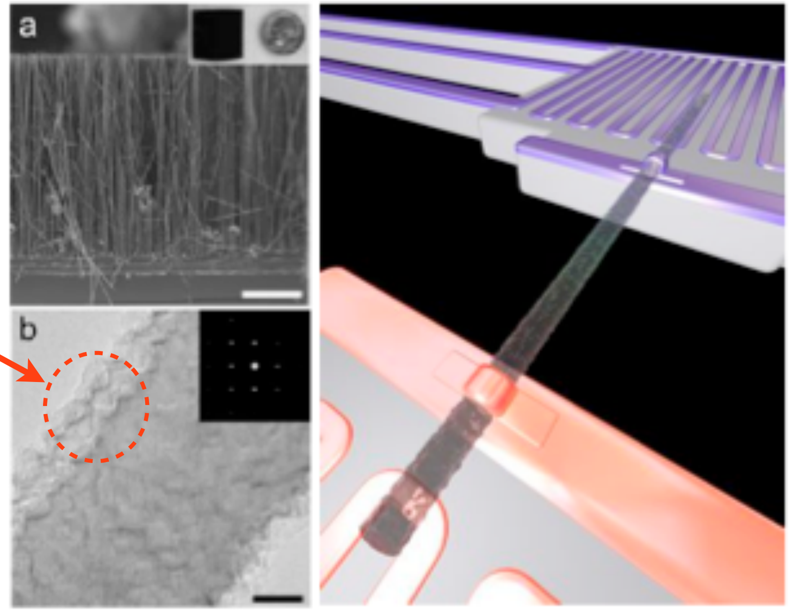
Low Thermal Conductivity of SiNWs

Energy conversion
from heat to electrical energy



Hochbaum et al., Nature 451, 163 (2007)

rough surface



Si nanowire (UC Berkeley)

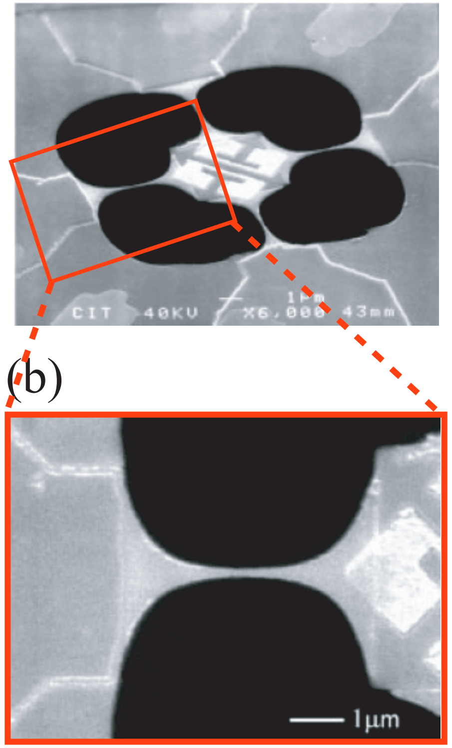
- Low Thermal Conductivity
- High Electrical Conductivity

New Thermal Transport Physics at Nanoscale

Quantization of Thermal Conductance!!

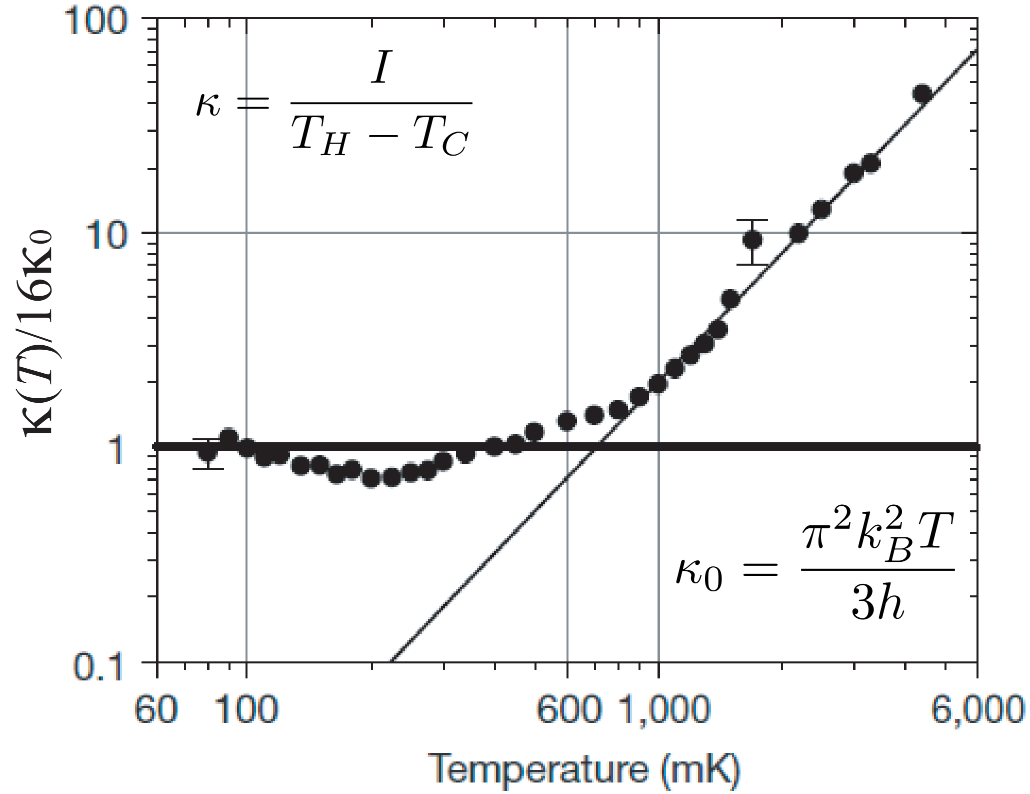
(a)

(b)



SiN nanowires

(c)

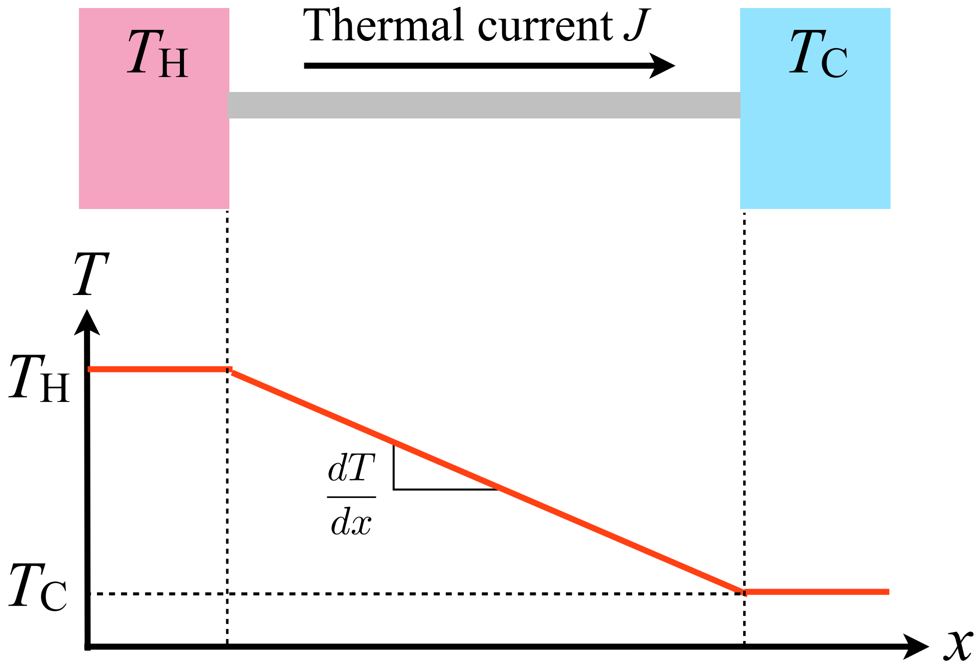


Schwab *et al.*, Nature (2000)

Theory of Thermal Transport at Macroscale

Phenomenological Theory: Fourier's law

Jean Baptiste Joseph Fourier
(1768 –1830, French)



Fourier's Law

$$\boxed{J = -\lambda \frac{dT}{dx}}$$

where λ is the thermal conductivity, which is independent of sample volume.

Boltzmann's Kinetic Theory

For simplicity, let us consider quasi-1D systems with volume $V(=LS)$.

The thermal current density is caused by a deviation from equilibrium:

$$\boxed{J = \frac{1}{V} \sum_{k>0,\nu} \hbar\omega_{k,\nu} \left(f_{k,\nu} - f_B(\omega_{k,\nu}, T)\right) v_{k,\nu}}$$

Thermal current density

where f_B is the Bose-Einstein distribution of phonons:

$$f_B(\omega_{k,\nu}, T) = \frac{1}{\exp\left(\hbar\omega_{k,\nu}/k_B T\right) - 1}$$

Bose-Einstein distribution

Boltzmann equation for phonon distribution function $f_{k,\nu}$

$$\boxed{\underbrace{\frac{df_{k,\nu}}{dt} + v_{k,\nu}\frac{\partial f_{k,\nu}}{\partial x}}_{\text{Drift term}} = \underbrace{\left[\frac{\partial f_{k,\nu}}{\partial t}\right]_{\mathrm{coll}}}_{\text{Collision term}}}$$

Boltzmann equation

For the steady states (d*f*/d*t*=0), Boltzmann equation becomes

$$\boxed{v_{k,\nu}\frac{\partial f_{k,\nu}}{\partial x} = \left[\frac{\partial f_{k,\nu}}{\partial t}\right]_{\mathrm{coll}}}$$

Steady-state Boltzmann equation

Two simple approximations:

(1) Relaxation time approximation

$$\boxed{\left[\frac{\partial f_{k,\nu}}{\partial t}\right]_{\mathrm{coll}} = -\frac{f_{k,\nu} - f_B(\omega_{k,\nu}, T)}{\tau_{k,\nu}}}$$

$\tau_{k,\nu}$: relaxation time

(2) Local equilibrium assumption

$$f_{k,\nu} \approx f_B(\omega_{k,\nu}, T(x))$$

$$\boxed{v_{k,\nu}\frac{\partial f_{k,\nu}}{\partial x} = v_{k,\nu}\frac{\partial f_B(\omega_{k,\nu}, T)}{\partial T}\frac{dT}{dx}}$$

Steady-state Boltzmann equation under two assumptions (1) & (2)

$$\underline{f_{k,\nu} - f_B(\omega_{k,\nu}, T)} = -\tau_{k,\nu} v_{k,\nu} \frac{\partial f_B(\omega_{k,\nu}, T)}{\partial T} \frac{dT}{dx}$$

Thermal current density under two assumptions (1) & (2) can be expressed as

$$J = \frac{1}{V} \sum_{k>0,\nu} \hbar\omega_{k,\nu} \boxed{(f_{k,\nu} - f_B(\omega_{k,\nu}, T))} v_{k,\nu}$$

$$= -\lambda \frac{dT}{dx}$$ Fourier's law

Here, λ is the thermal conductivity, which is given as

$$\boxed{\lambda = \frac{1}{V} \sum_{k>0,\nu} \hbar\omega_{k,\nu} |v_{k,\nu}| \Lambda_{k,\nu} \frac{\partial f_B(\omega_{k,\nu}, T)}{\partial T}}$$ Thermal conductivity

where $\Lambda_{k,\nu} = \tau_{k,\nu} |v_{k,\nu}|$ is the mean free path of phonons.

Thermal conductivity expression in frequency domain

$$\lambda = \frac{1}{S}\sum_{\nu}\int_{\omega_\nu^{\min}}^{\omega_\nu^{\max}} \hbar\omega \frac{D_\nu(\omega)}{2}|v_\nu(\omega)|\Lambda_\nu(\omega)\frac{\partial f_B(\omega,T)}{\partial T}d\omega$$

where $D_\nu(\omega)$ is the density of states (DOS), which is given as

$$D_\nu(\omega) = \frac{1}{L}\sum_k \delta(\omega_\nu - \omega_{k,\nu}) = \frac{1}{\pi|v_\nu(\omega)|}$$

Then, the thermal conductivity of quasi-1D system is expressed as

$$\boxed{\lambda = \frac{1}{2\pi S}\sum_{\nu}\int_{\omega_\nu^{\min}}^{\omega_\nu^{\max}} \hbar\omega \left[\frac{\partial f(\omega,T)}{\partial T}\right]\Lambda_\nu(\omega)d\omega}$$

The thermal transport behavior of quasi-1D systems is determined by the mean free path $\Lambda_\nu(\omega)$.

Breakdown of Fourier's Law

For a short system with $\Lambda_\nu(\omega) \ll L$

$$\frac{dT}{dx} = 0 \quad \Rightarrow \text{Thermal conductivity } \lambda \text{ cannot be defined!!}$$

Thermal Conductance

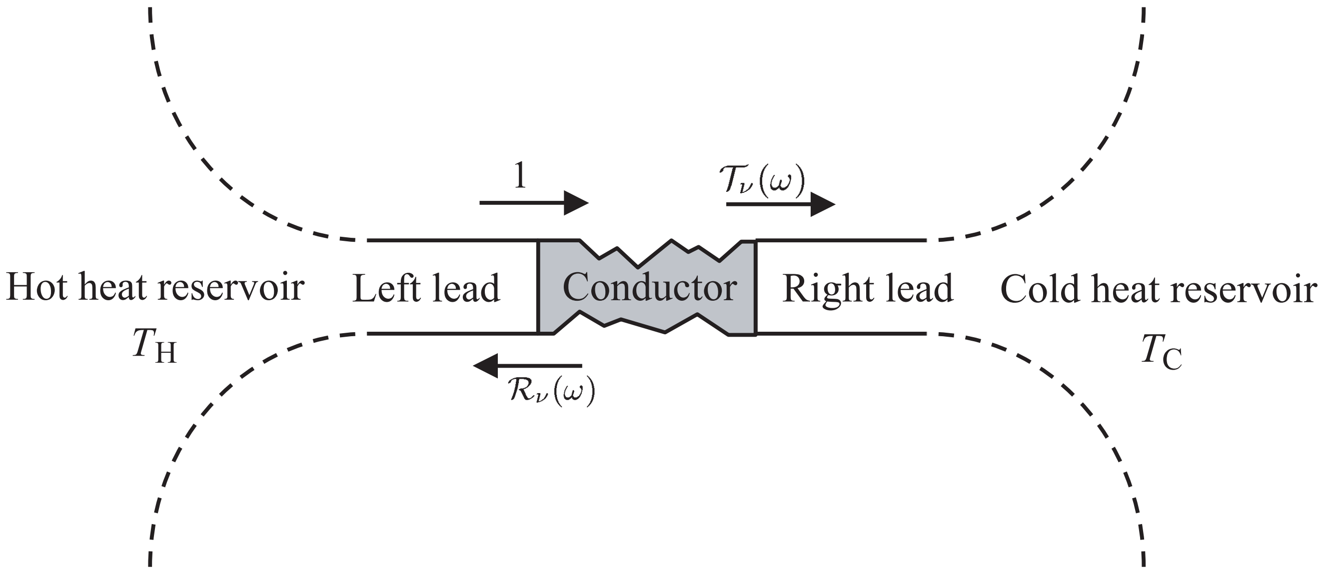
$$\boxed{\kappa = \lim_{T_H, T_C \to T} \frac{I}{T_H - T_C}}$$

T: Averaged temperature defined as $T=(T_H+T_L)/2$
I: Thermal current $I=JS$

Theory of Thermal Transport
at Nanoscale

Landauer Theory of Phonon Transport

Let us consider quasi-1D systems whose length L is much shorter than the mean free path of phonon Λ.



Thermal current from the left lead to the center

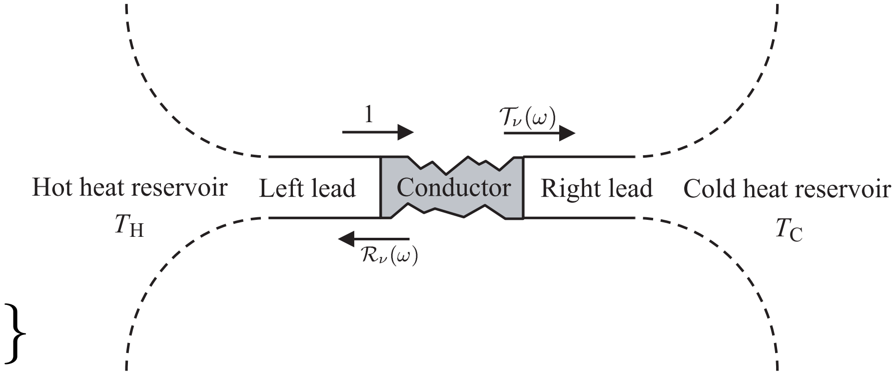
$$
\begin{aligned}
i_\nu^L(\omega) &= \hbar\omega|v_\nu(\omega)|D_\nu^+(\omega)f(\omega, T_H) \\
&= \frac{1}{2\pi}\hbar\omega f(\omega, T_H)
\end{aligned}
$$

Thermal current from the right to the center

$$
\begin{aligned}
i_\nu^R(\omega) &= \hbar\omega|v_\nu(\omega)|D_\nu^-(\omega)f(\omega, T_C) \\
&= \frac{1}{2\pi}\hbar\omega f(\omega, T_C)
\end{aligned}
$$

Net thermal current flowing through the left lead, which is carried by phonons with mode ν

$$
\begin{aligned}
i_\nu(\omega) &= i_\nu^L(\omega)\{1-\mathcal{R}_\nu(\omega)\} - i_\nu^R(\omega)\mathcal{T}_\nu(\omega) \\
&= \mathcal{T}_\nu(\omega)\{i_\nu^L(\omega) - i_\nu^R(\omega)\} \\
&= \frac{1}{2\pi}\hbar\omega\mathcal{T}_\nu(\omega)\{f(\omega,T_H)-f(\omega,T_C)\}
\end{aligned}
$$



Thus, the thermal current is given as

$$
\begin{aligned}
I &= \sum_\nu \int_{\omega_\nu^{\min}}^{\omega_\nu^{\max}} i_\nu(\omega)d\omega \\
&= \frac{1}{2\pi}\sum_\nu \int_{\omega_\nu^{\min}}^{\omega_\nu^{\max}} \hbar\omega\{f(\omega,T_H)-f(\omega,T_C)\}\mathcal{T}_\nu(\omega)d\omega
\end{aligned}
$$

The thermal conductance

Thus, the thermal conductance for the coherent phonon transport is given by

$$\boxed{\kappa = \frac{1}{2\pi}\int_0^{\infty} \hbar\omega \left[\frac{\partial f(\omega, T)}{\partial T}\right] \mathcal{T}(\omega) d\omega}$$

Landauer formula of Thermal conductance

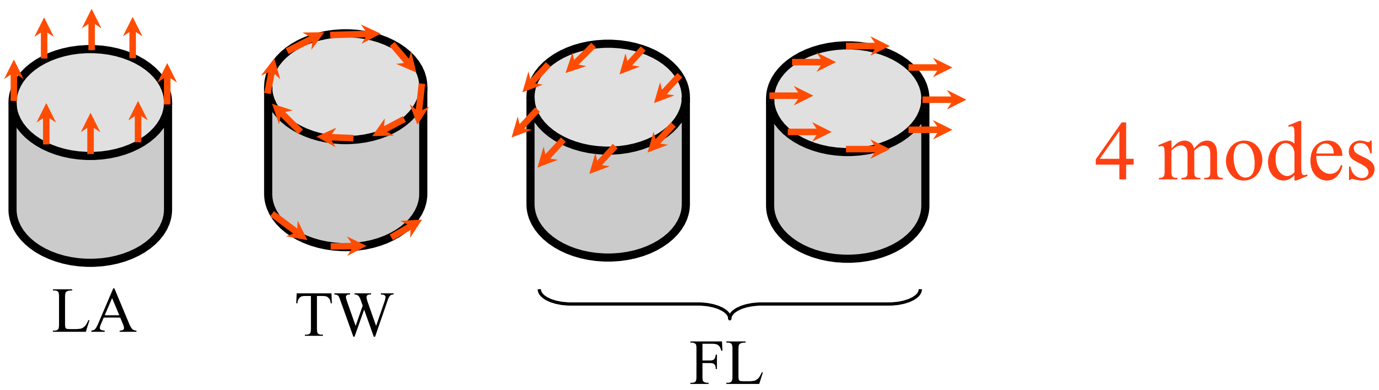
Rego and Kirczenow, Phys. Rev. Lett. **81** 232 (1998)

The coherent phonon transport behavior of quasi-1D systems is determined by the phonon transmission function $T(\omega)$.

Ballistic Phonon Transport

Let us consider low-T limit where the optical phonons are not excited.

Acoustic phonon modes of quasi-1D systems:



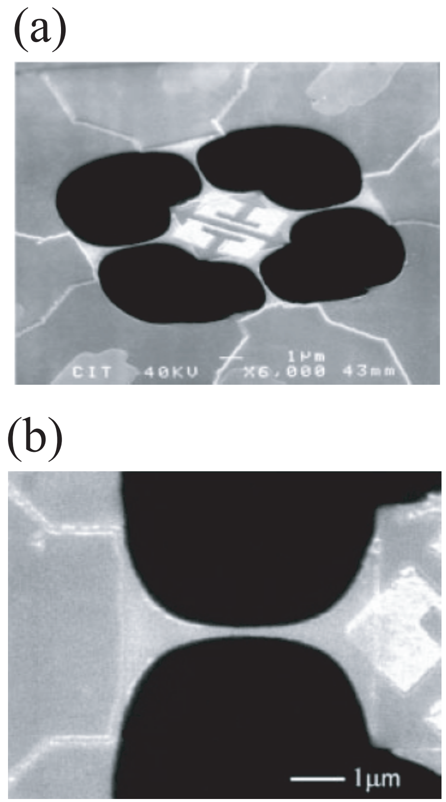
Thermal conductance of quasi-1D systems at low-T

$$\kappa = 4 \times \frac{k_B^2 T}{h} \int_0^\infty \frac{x^2 e^x}{(e^x - 1)^2} dx = 4\kappa_0$$

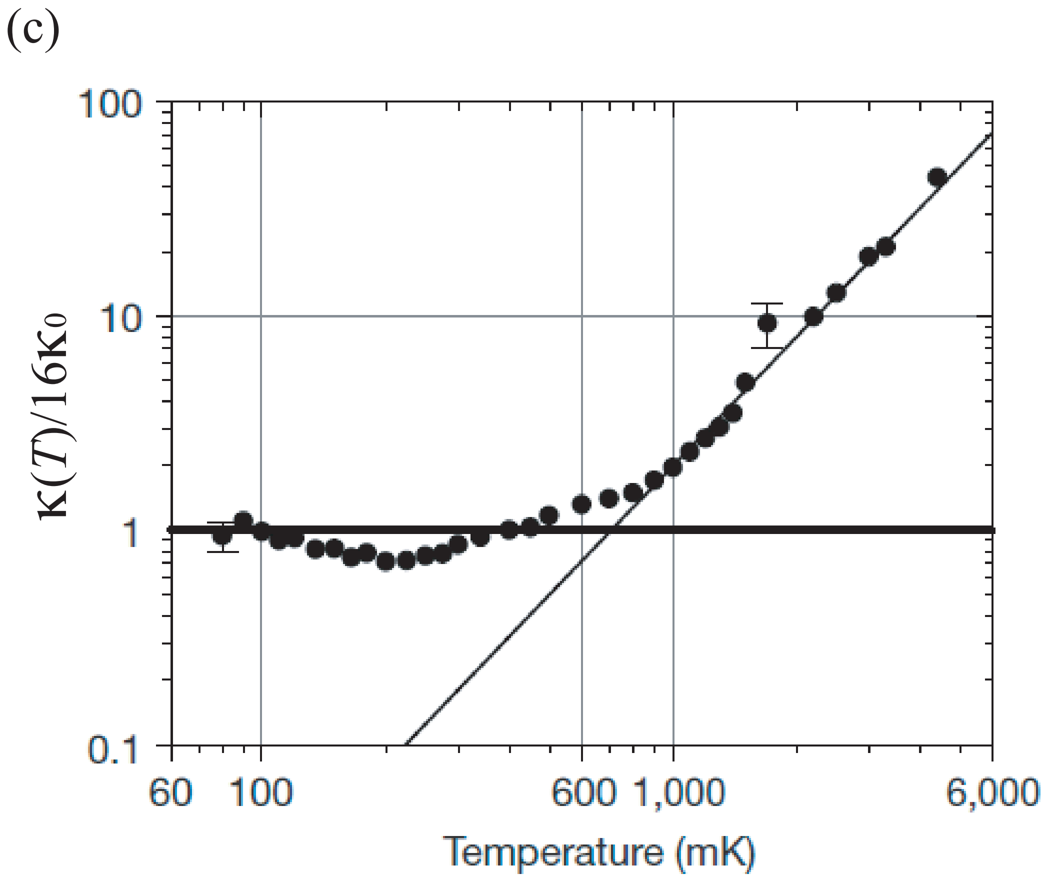
$$\boxed{\kappa_0 = \frac{\pi^2 k_B^2 T}{3h}} \equiv g_0 T \qquad (g_0 = 9.4 \times 10^{-13}\ \mathrm{W/K^2})$$

Thermal conductance quantum

Experimental Observation of Thermal Conductance Quantum



SiN nanowires



Schwab *et al.*, Nature (2000)

The quantum of thermal conductance is observable at less than 0.8K

Experiments: Carbon Nanotubes

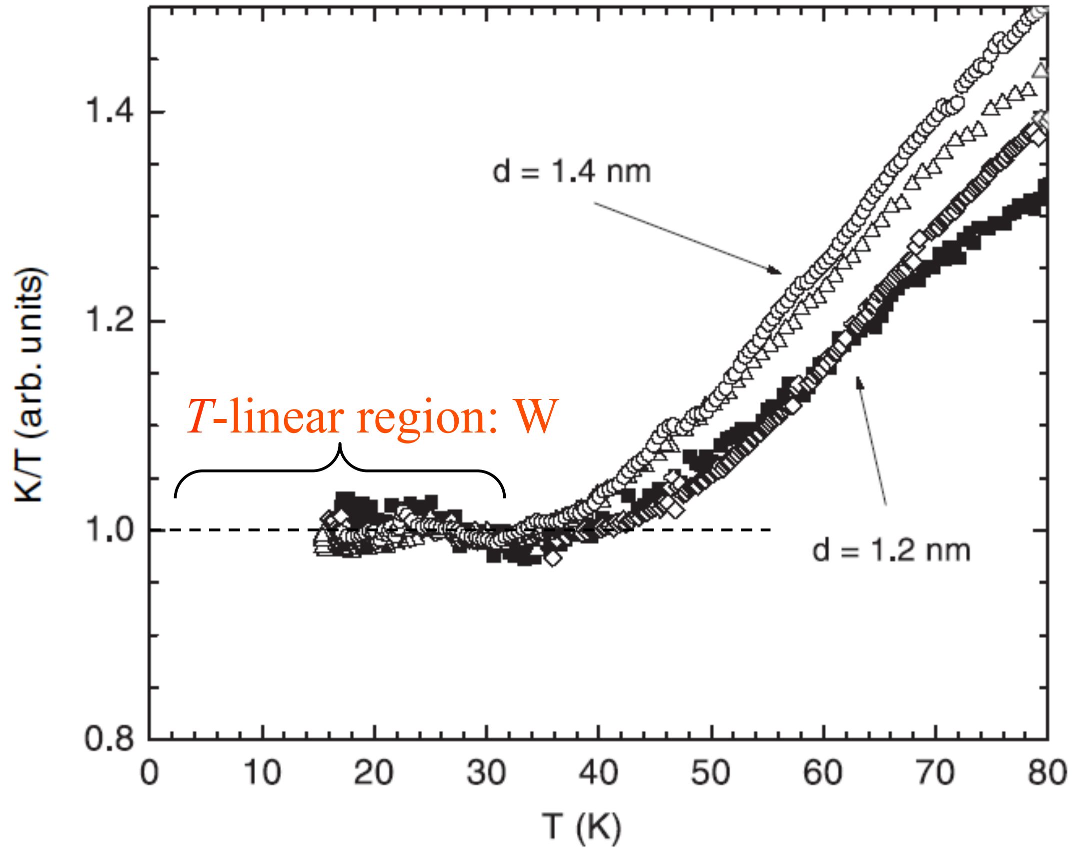
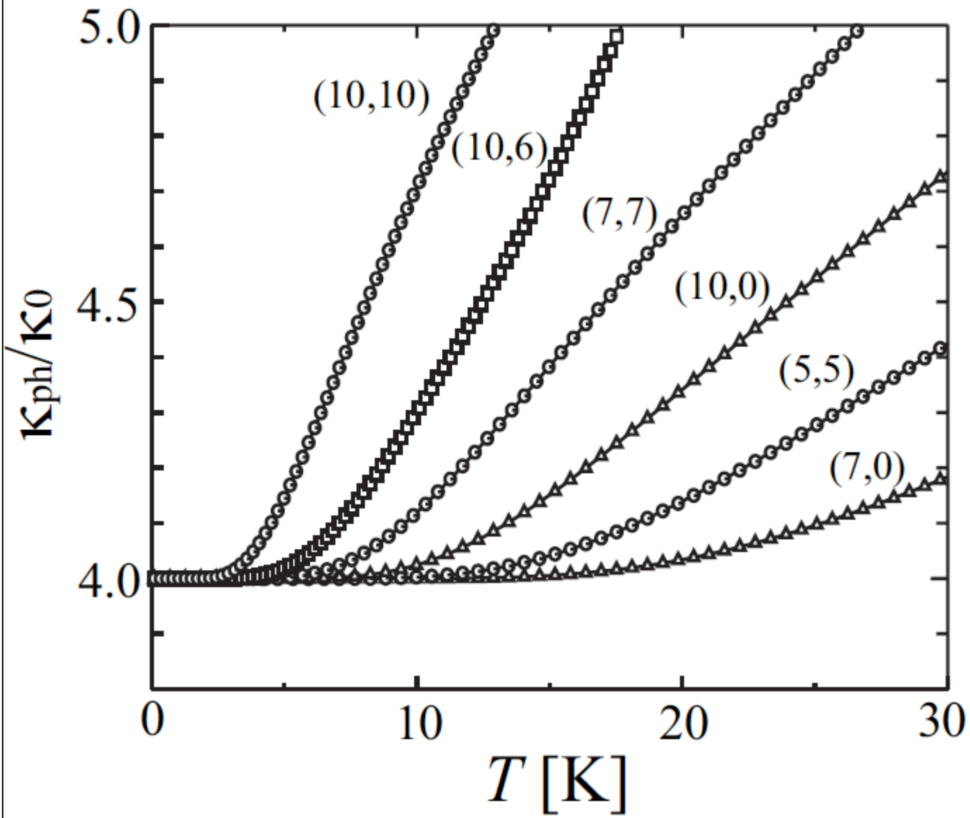


Fig.: Thermal conductance of single-walled CNTs with diameter d=1.2nm and d=1.4nm.

Hone *et al.*, Appl. Phys. A **74**, 339 (2002)

Low-T Thermal Conductance of Pristine SWNTs



Yamamoto *et al*., PRL **96**, 255503 (2004)

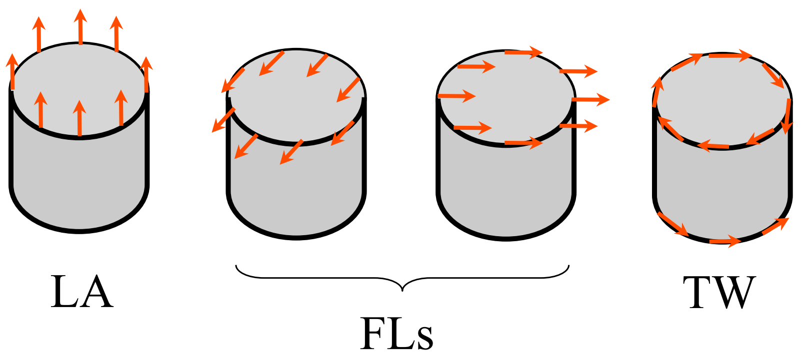
■ Quantized Thermal Conductance

$$\kappa_0 = \frac{\pi^2 k_B^2}{3h} T = g_0 T$$

$$g_0 = 9.4 \times 10^{-13}\ [\mathrm{W/K^2}]$$

■ At Extremely Low T

$$\kappa_{ph} = 4\kappa_0$$



■ Quantization Plateau Width

Plateau width increases with decreasing the tube diameter.

(Excitation energy of opt. phonons $\propto 1/d$)

Summary of Phonon Landauer Formula

+ System configuration (Landauer-type model)

+ Thermal conductance of Landauer-type model

$$\boxed{\kappa(T) = \int_0^\infty \frac{d\omega}{2\pi} \hbar\omega \frac{\partial f_B(\omega, T)}{\partial T} \zeta(\omega)}$$

Rego & Kirczenow: PRL **81**, 232 (1998)

T : Averaged temperature of the hot and cold heat baths

$\hbar\omega$: Energy of a phonon shot from a heat bath

$f_B(\omega, T)$: Bose-Einstein distribution function of a heat bath

$\zeta(\omega)$: Phonon transmission function

+ Two typical methods for the phonon transmission calculation

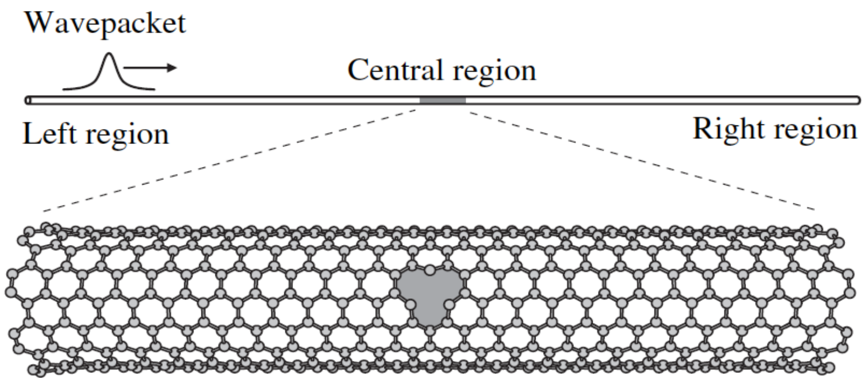
- Phonon wavepacket scattering method

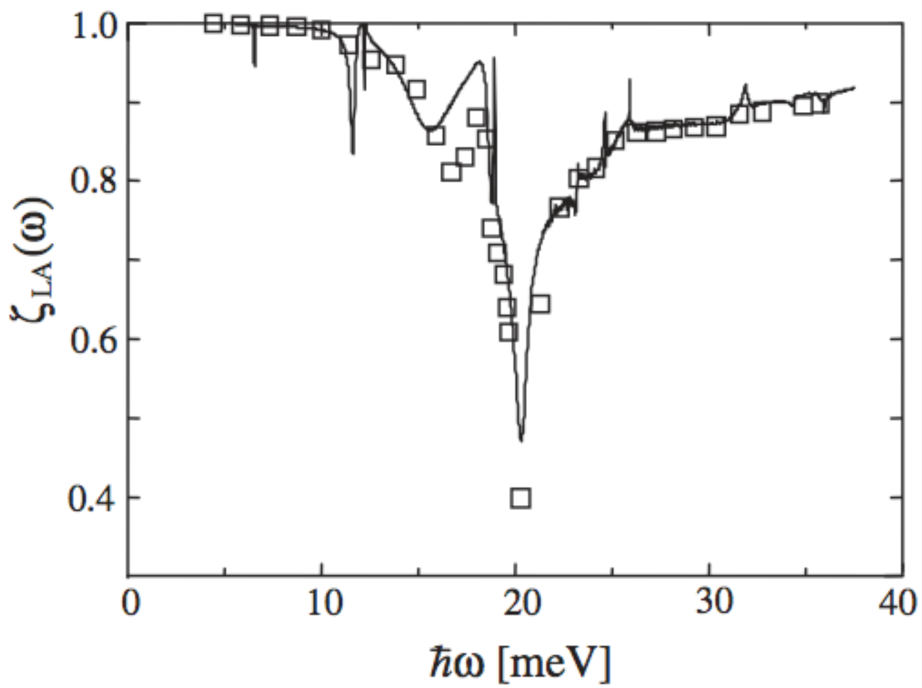
Kondo, Yamamoto, Watanabe: JJAP, **45**, L963 (2006)

- Nonequilibrium phonon Green's function method

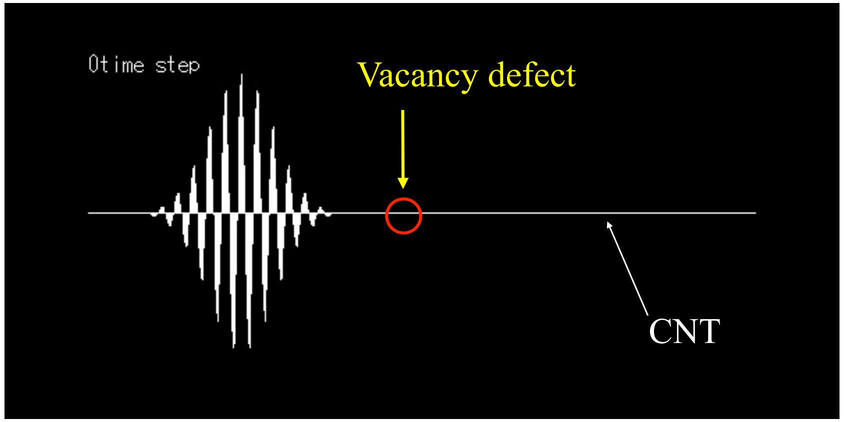
Yamamoto & Watanabe: PRL **96**, 255503 (2006)

Phonon Wave-Packet Scattering Method





Kondo, Yamamoto, Watanabe, JJAP, **45**, L963 (2006)



Energy of incident phonon wavepacket: 11.6 meV

Advantage

Easy to visualize dynamics of phonon scattering

Disadvantage

Limit of energy resolution due to the uncertain principle

NEGF Method

+ Green's function expression of the transmission function

$$\zeta(\omega) = \mathrm{Tr}\left[\mathbf{\Gamma}_L(\omega)\mathbf{G}(\omega)\mathbf{\Gamma}_R\mathbf{G}^\dagger(\omega)\right]$$

Yamamoto & Watanabe: PRL **96**, 255503 (2006)
Mingo: PRB **74**, 125402 (2006)
Wang, Wang & Zheng: PRB **74**, 033408 (2006)

$\mathbf{G}(\omega)$: Retarded Green's function

$\mathbf{\Gamma}_{L/R}(\omega)$: Level-broadening function

+ Retarded Green's function

$$\mathbf{G}(\omega) = \left[(\omega^2 + i\delta)\mathbf{M} - (\mathbf{D} + \mathbf{\Sigma}(\omega))\right]^{-1}$$

$\mathbf{M}$: Diagonal mass matrix with elements $M_{ij} = m_i\delta_{ij}$ (m_i is mass of *i*th atom)

$\mathbf{D}$: Dynamical matrix of a scattering region

$\mathbf{\Sigma}(\omega)$: Self-energy matrix due to the left and right leads

+ Dynamical Matrix: D

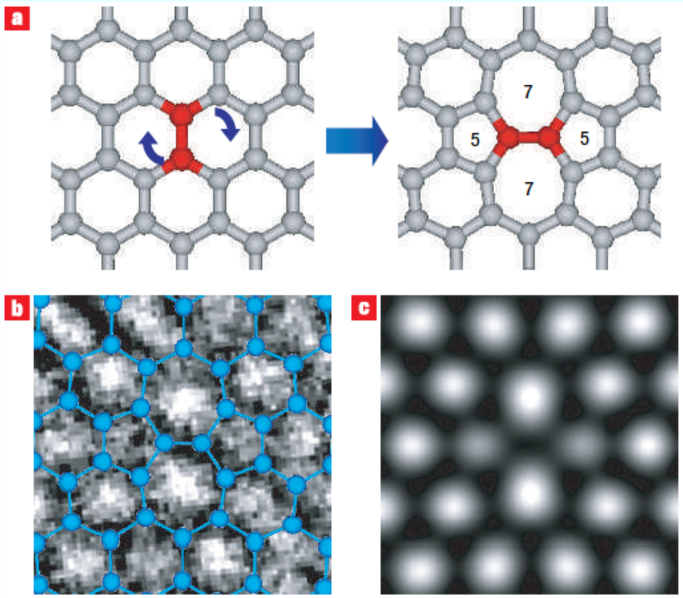
$$D_{ij}(\omega) = \frac{\partial^2 E_{\mathrm{tot}}}{\partial r_{i\alpha}\partial r_{j\beta}} \quad (i, j \in \text{Scattering region}, \alpha, \beta = x, y, z)$$

The total energy calculation with high accuracy is needed to obtain the phonon states.

Simulation on Thermal Transport in Carbon Nanotube

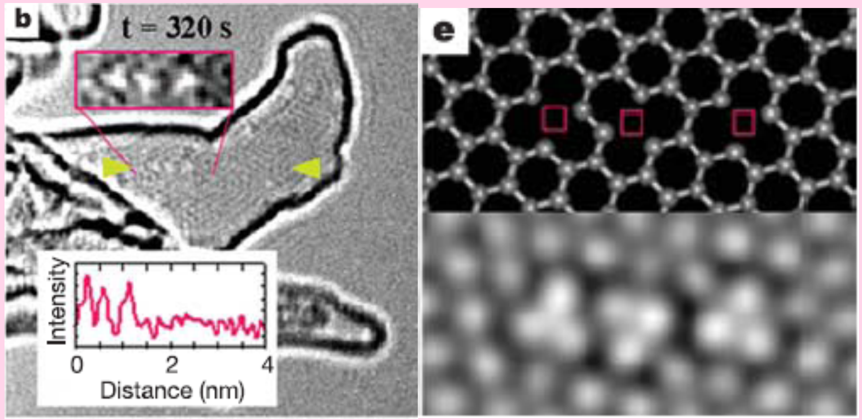
Influence of Defects on Thermal Transport in CNTs

Topological defects



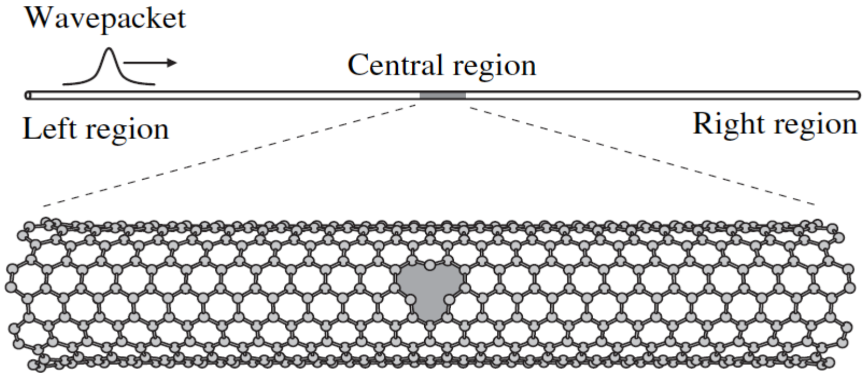
Suenaga, et al., Nature Nanotec. **2**, 358 (2007)

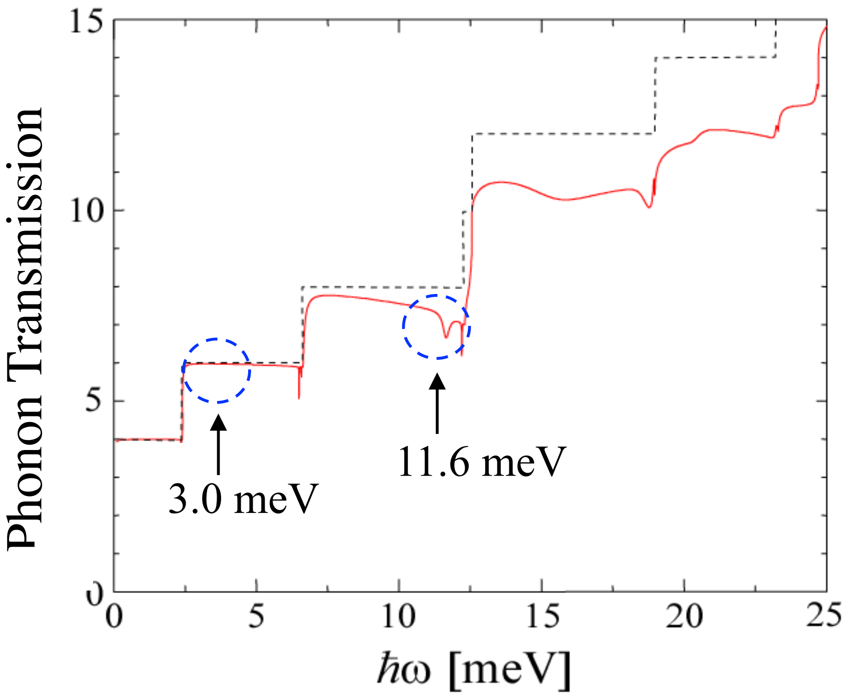
Vacancy defects



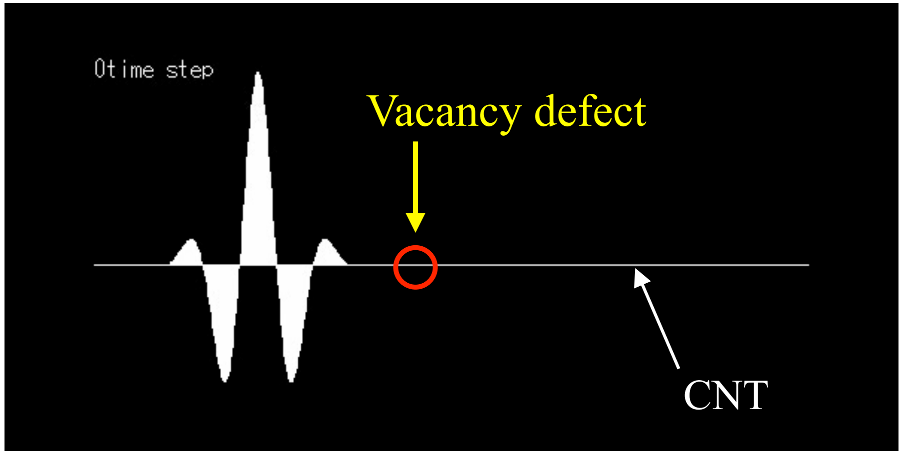
Hashimoto, *et al.*, Nature **430**, 870 (2004)

A Single Vacancy

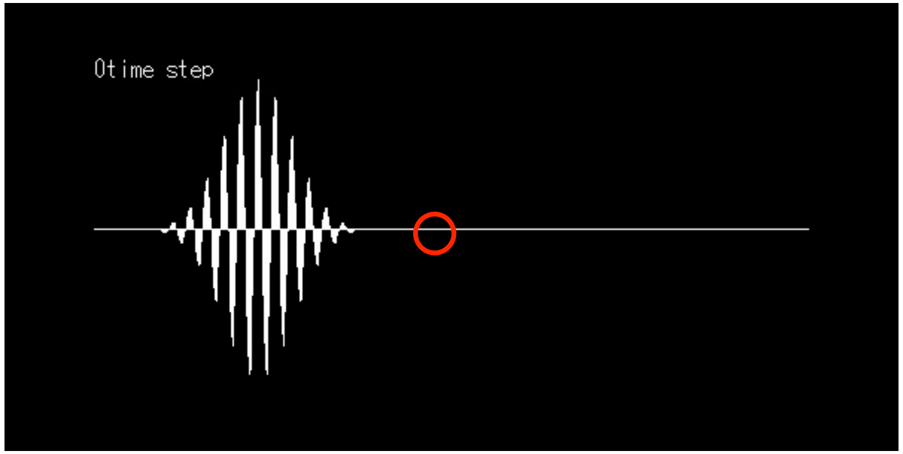




@ 3.0 meV

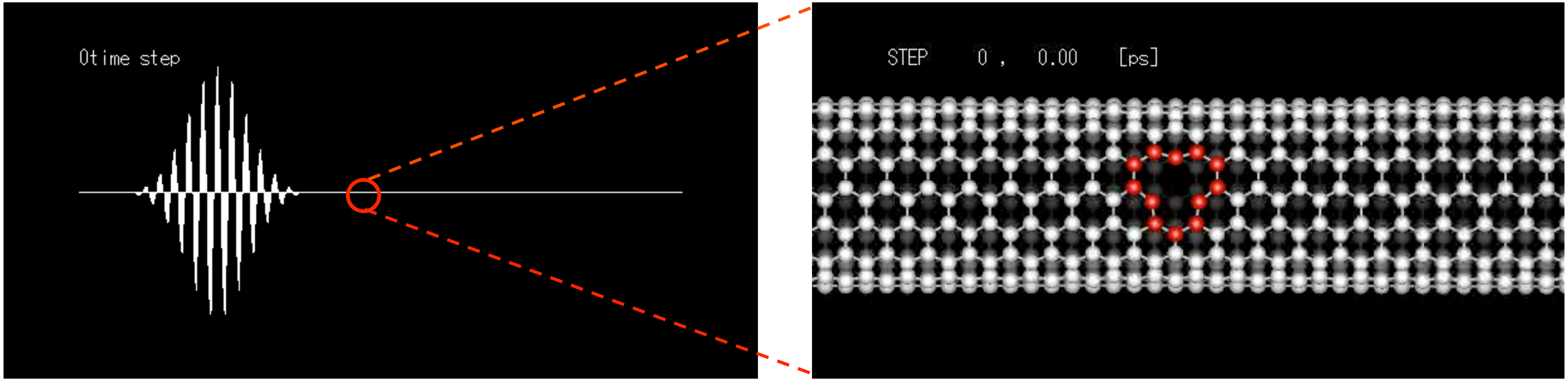


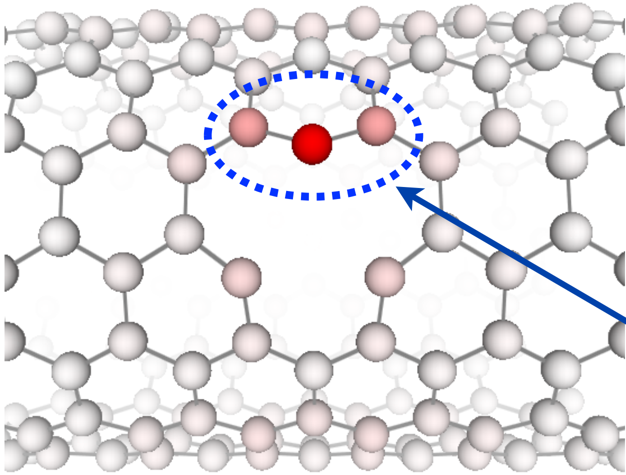
@ 11.6 meV



Kondo, Yamamoto, Watanabe: JJAP, **45**, L963 (2006)

Atomic Vibration around Vacancy



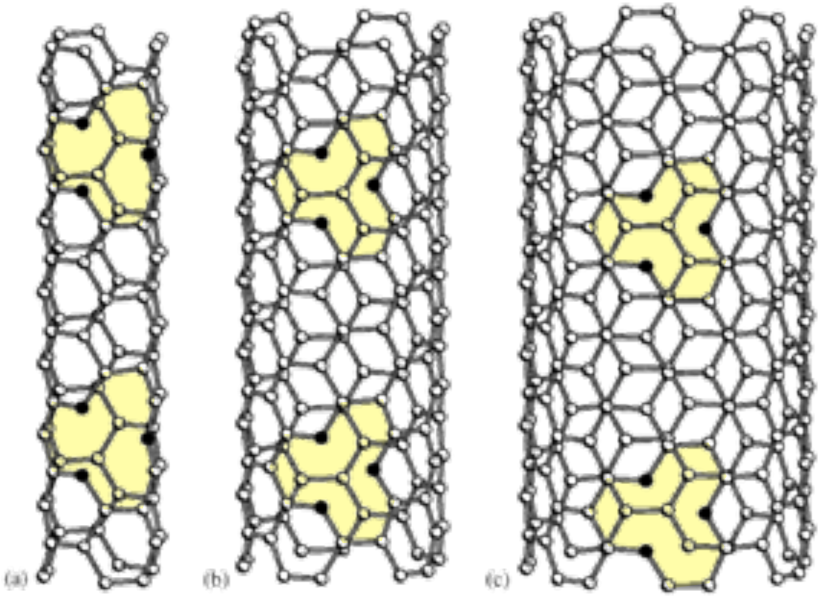


Localized phonon state @ 11.6meV

Thermal conductance after Annealing

■ Energy Gain due to Structural Change (DFT calculations)

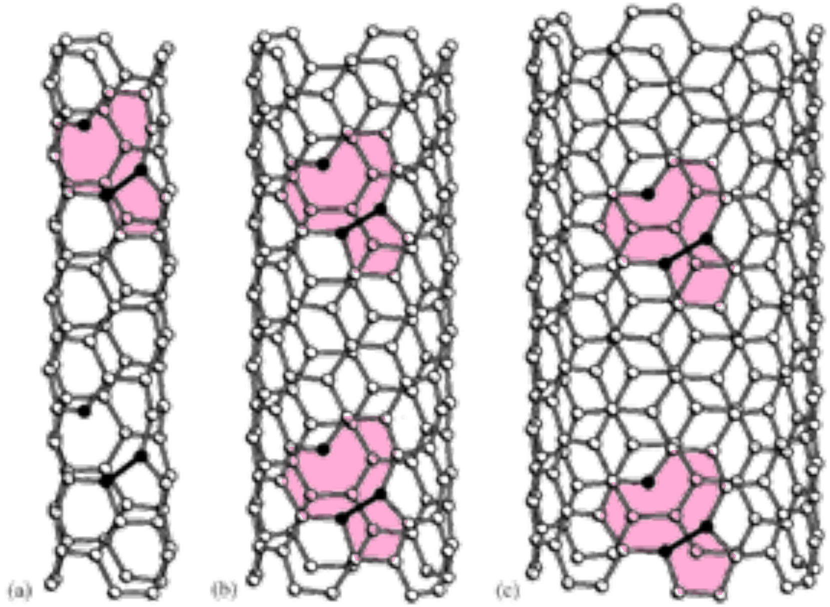
Metastable State
(Monatomic Vacancy)



(3,3) (5,5) (7,7)

Annealing

Stable State
(5−1db defect)



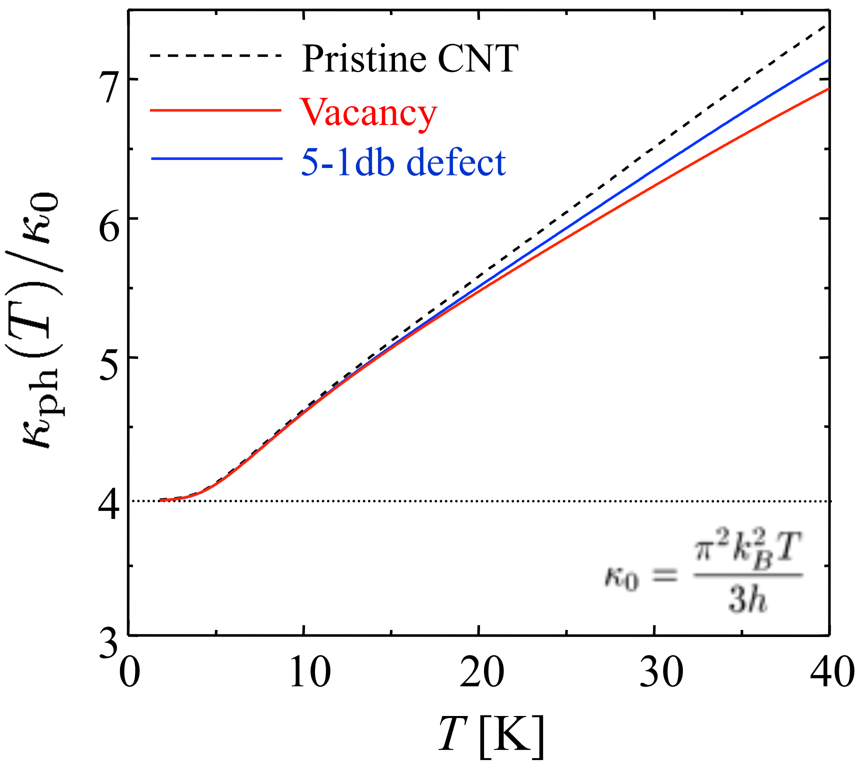
(3,3) (5,5) (7,7)

−1.76 eV −1.53 eV −1.23 eV

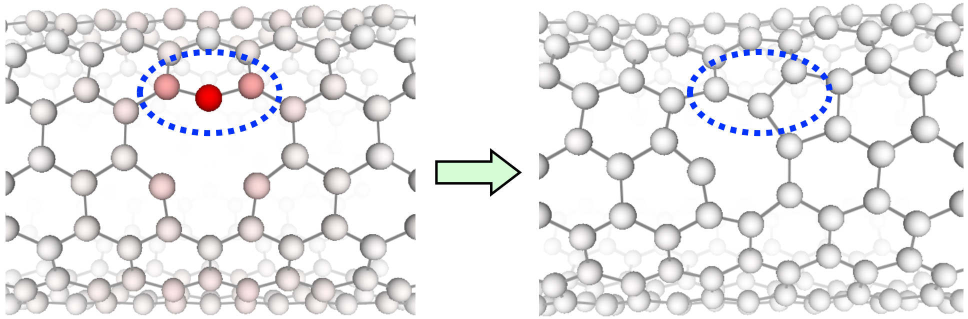
Energy gain more than 1 eV

Miyamoto *et al.*, Physica B **323**, 78 (2002)

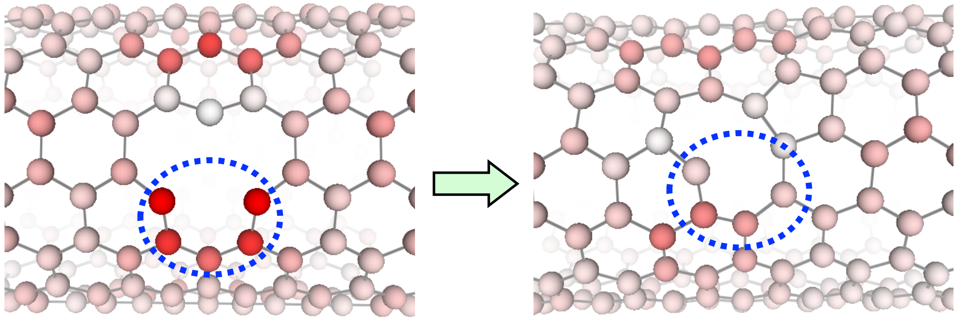
Disappearance of Localized Phonons



$\hbar\omega$=11.6 meV



$\hbar\omega$=18.5 meV

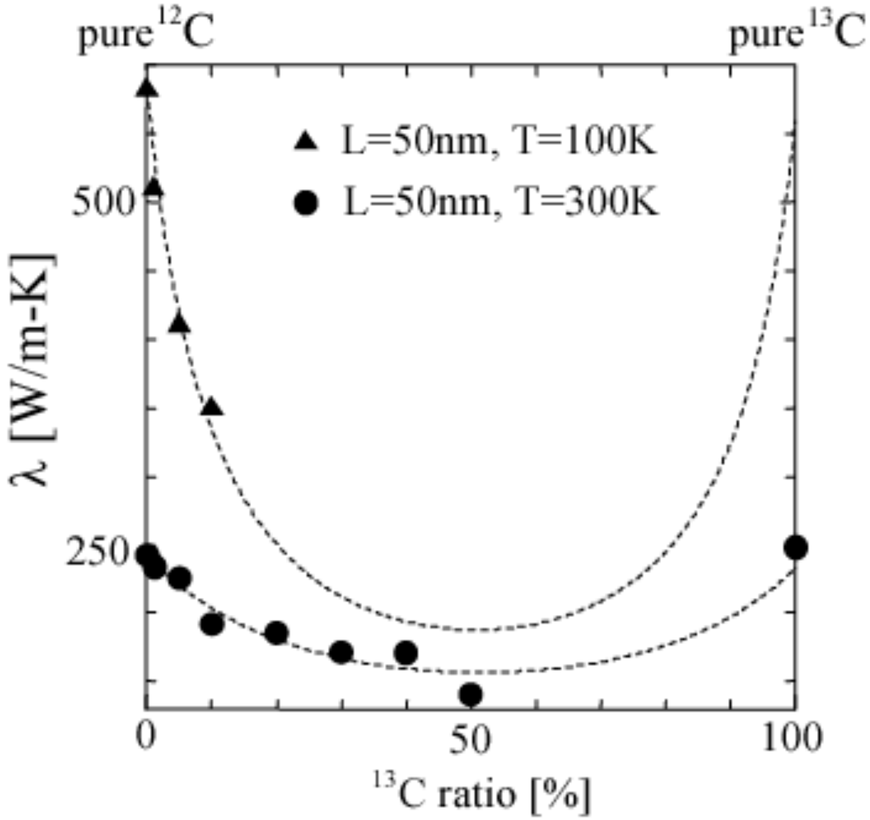


Yamamoto, Watanabe: Phys. Rev. Lett. **96**, 255503 (2006)

Influence Isotope Impurities

MD simulation results

^{13}C



Maruyama et al., J. Therm. Sci. Tech. 1, 138 (2006)

^{14}C

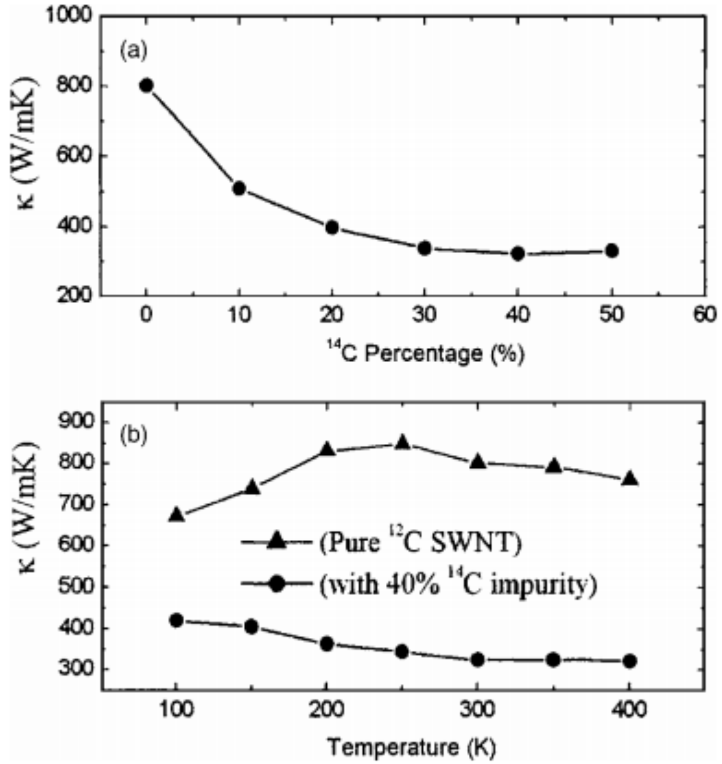
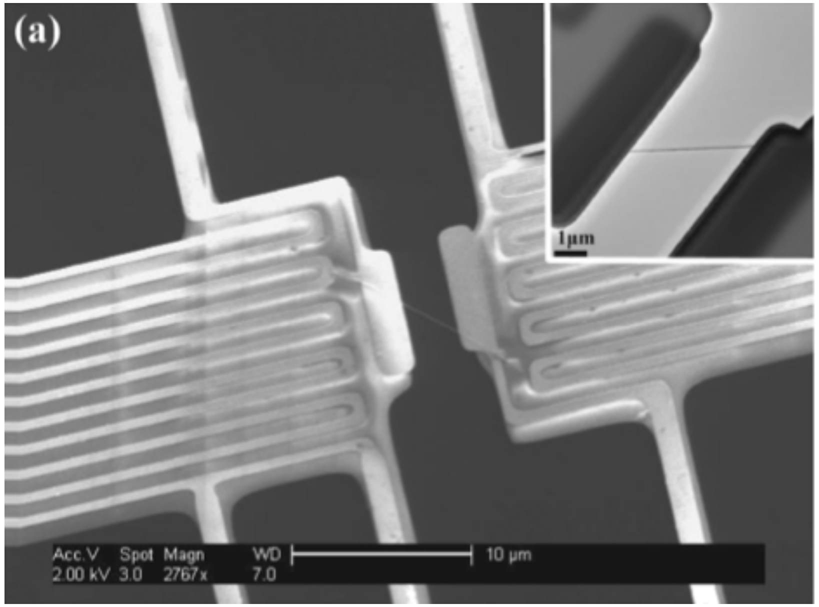


FIG. 2. (a) Thermal conductivity κ vs ^{14}C impurity percentage for a (5,5) SWNT at 300 K. (b) Thermal conductivity κ vs temperature for a (5,5) pure ^{12}C nanotube (solid ▲) and a (5,5) SWNT with 40% ^{14}C impurity (●). The curves are drawn to guide the eyes.

Zhang and Li, J. Chem. Phys. 123, 114714 (2005)

Experiments: BN nanotubes



Chang et al., PRL 97, 085901 (2006)

(Zettl group, UC Berkeley)

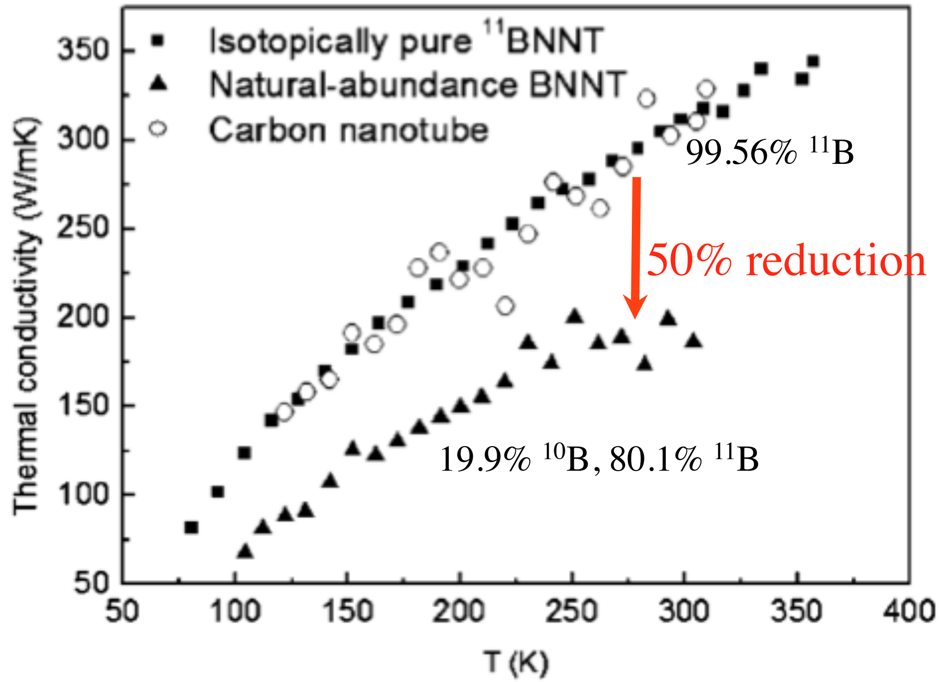
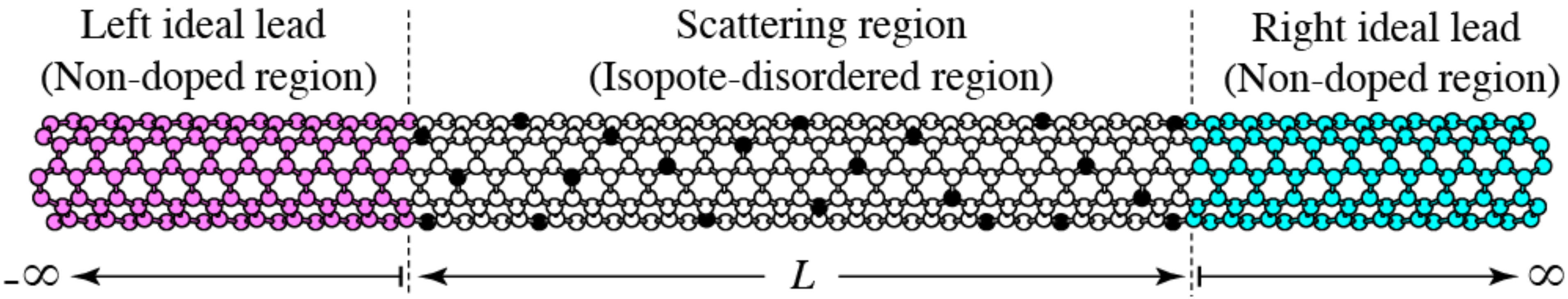


FIG. 2. The $\kappa(T)$ of a carbon nanotube (open circles), a boron nitride nanotube (BNNT, solid triangles), and an isotopically pure boron nitride nanotube (solid squares) with similar outer diameters.

Our NEGF Simulations



To clarify the dependence of

- chirality of SWNTs,
- density of isotopes,
- mass difference between ^{13}C and ^{14}C,

we discuss the phonon transport in

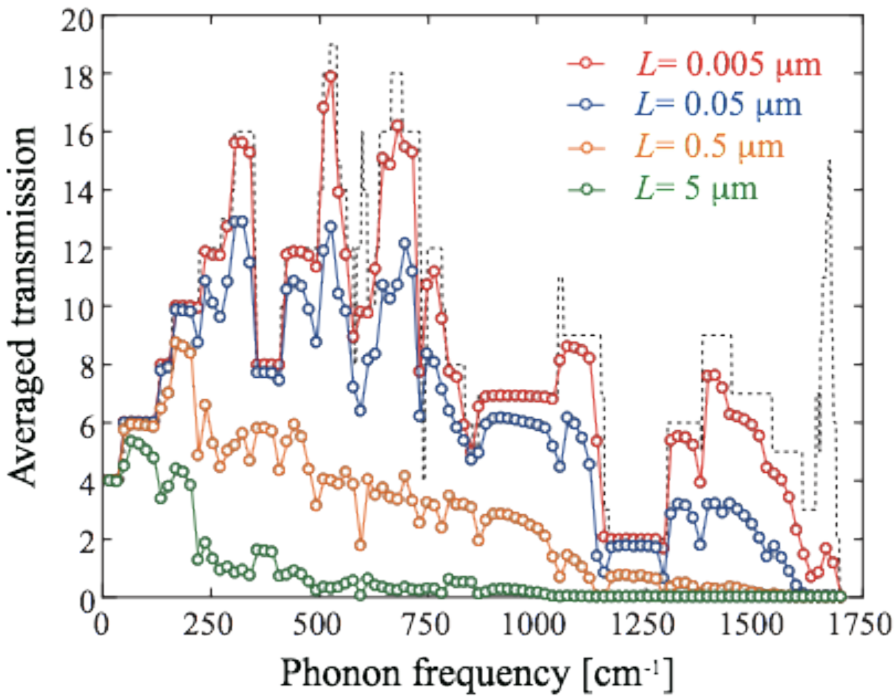
- (5,5) Metallic SWNT with 15.0% of ^{13}C isotopes
- (8,0) Semi-conducting SWNT with 9.4% of ^{14}C isotopes

Yamamoto, Sasaoka, Watanabe, Phys. Rev. Lett. **106**, 215503 (2011)

Transmission Functions

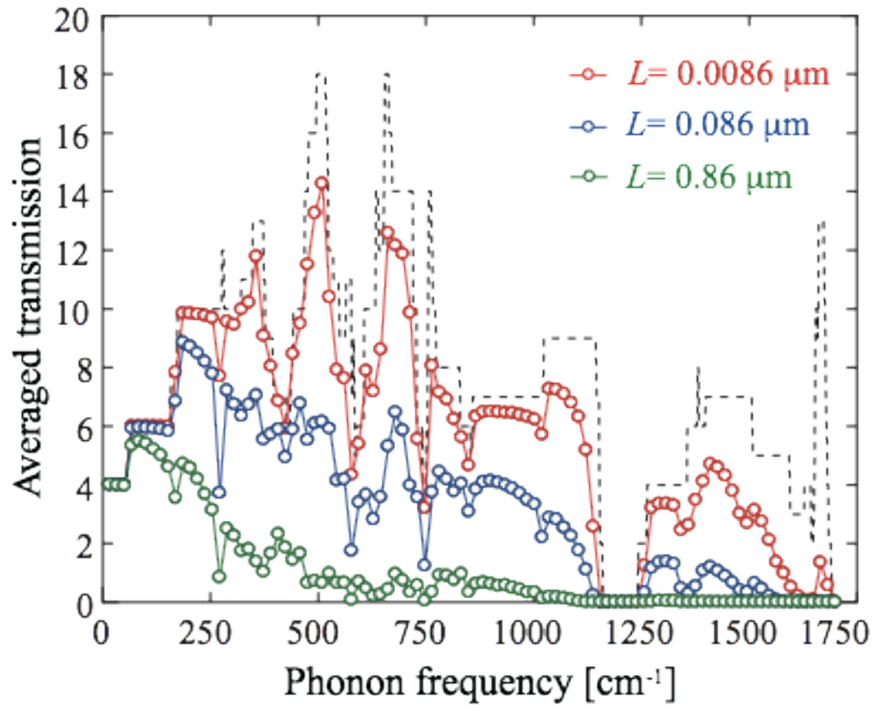
(5,5)SWNT with 15% of ^{13}C isotopes

※ Averaged over 200 random configurations



(8,0)SWNT with 9.4% of ^{14}C isotopes

※ Averaged over 200 random configurations



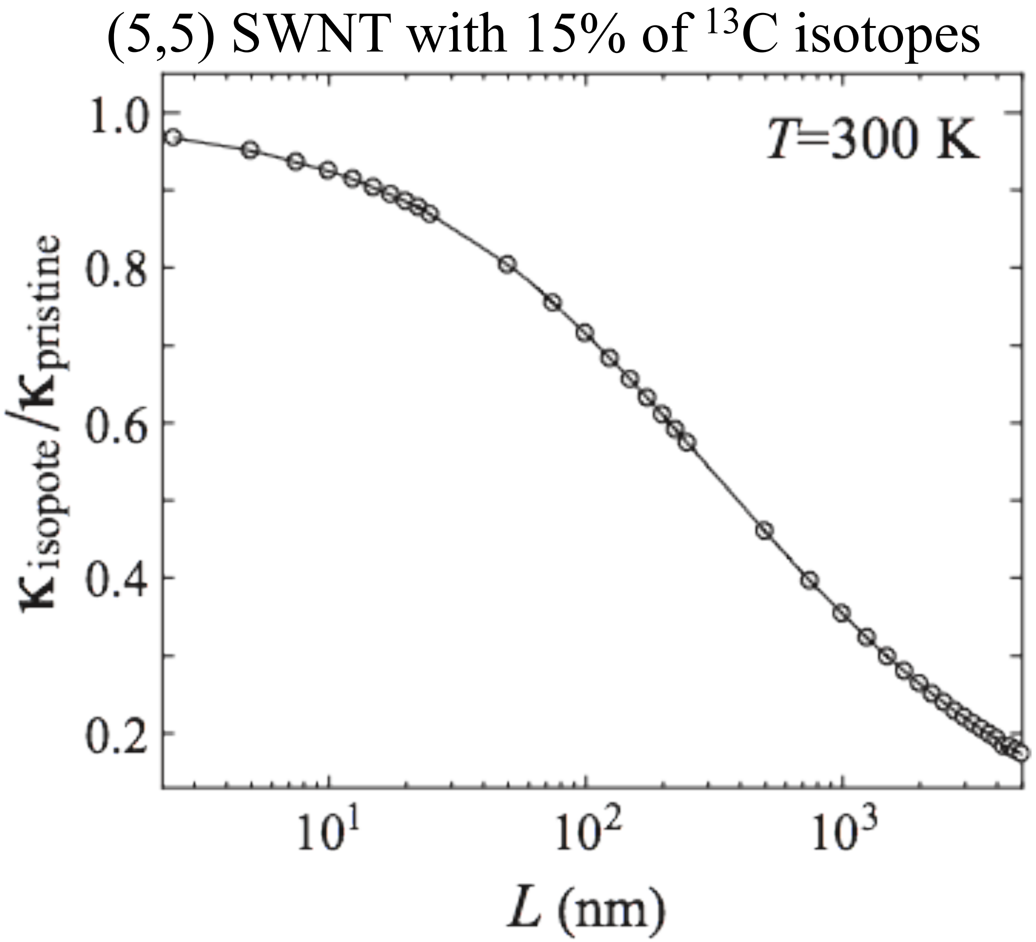
Low-ω: The transmission is not reduced by isotopes.

--> Quantized thermal conductance can be observed at low T.

Higher-ω: The transmission is strongly reduced.

--> Thermal conductance decreases at moderate T.

Thermal Conductance Reduction



$$\kappa_{\text{pristine}} = 2.8 \text{ (nW/K)}$$

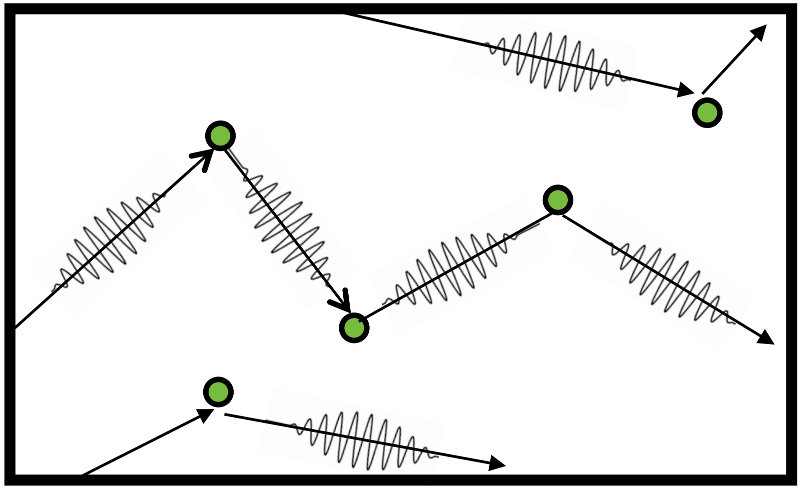
For a micrometer-SWNT, the thermal conductance goes down to ∼20%.

Transmission Reduction Mechanisms

Diffusive Scattering

(Single-phonon scattering)

$$l_{\mathrm{MFP}} \ll L \ll \xi$$



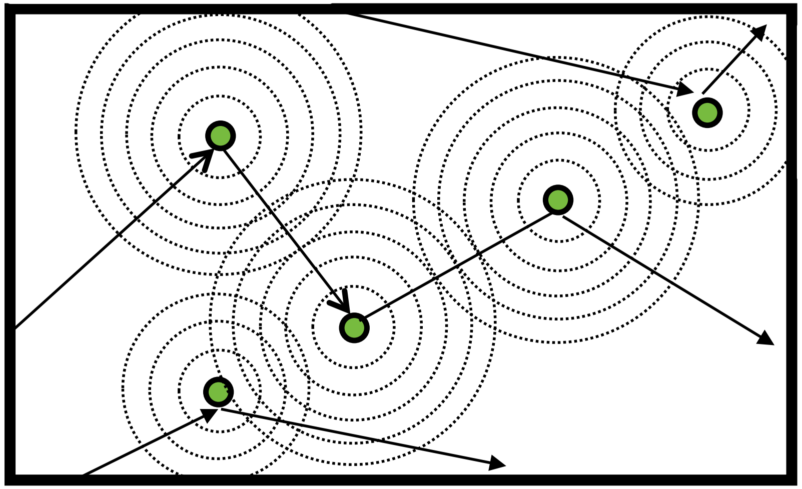
$$\langle \zeta(\omega) \rangle = \frac{M}{1 + L/l_{MFP}(\omega)}$$

Power-law decay

Localization

(Interferential effects)

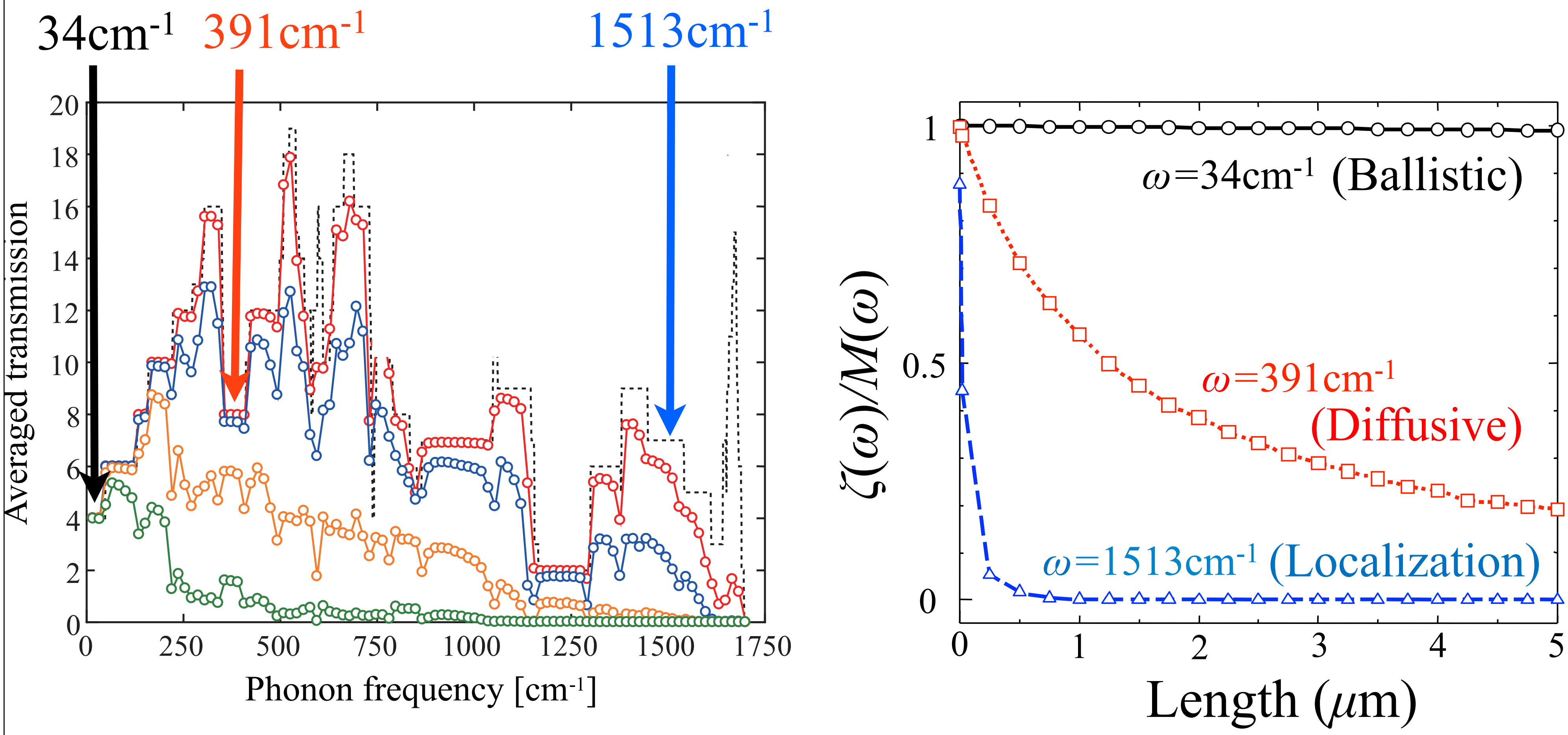
$$\xi \ll L$$



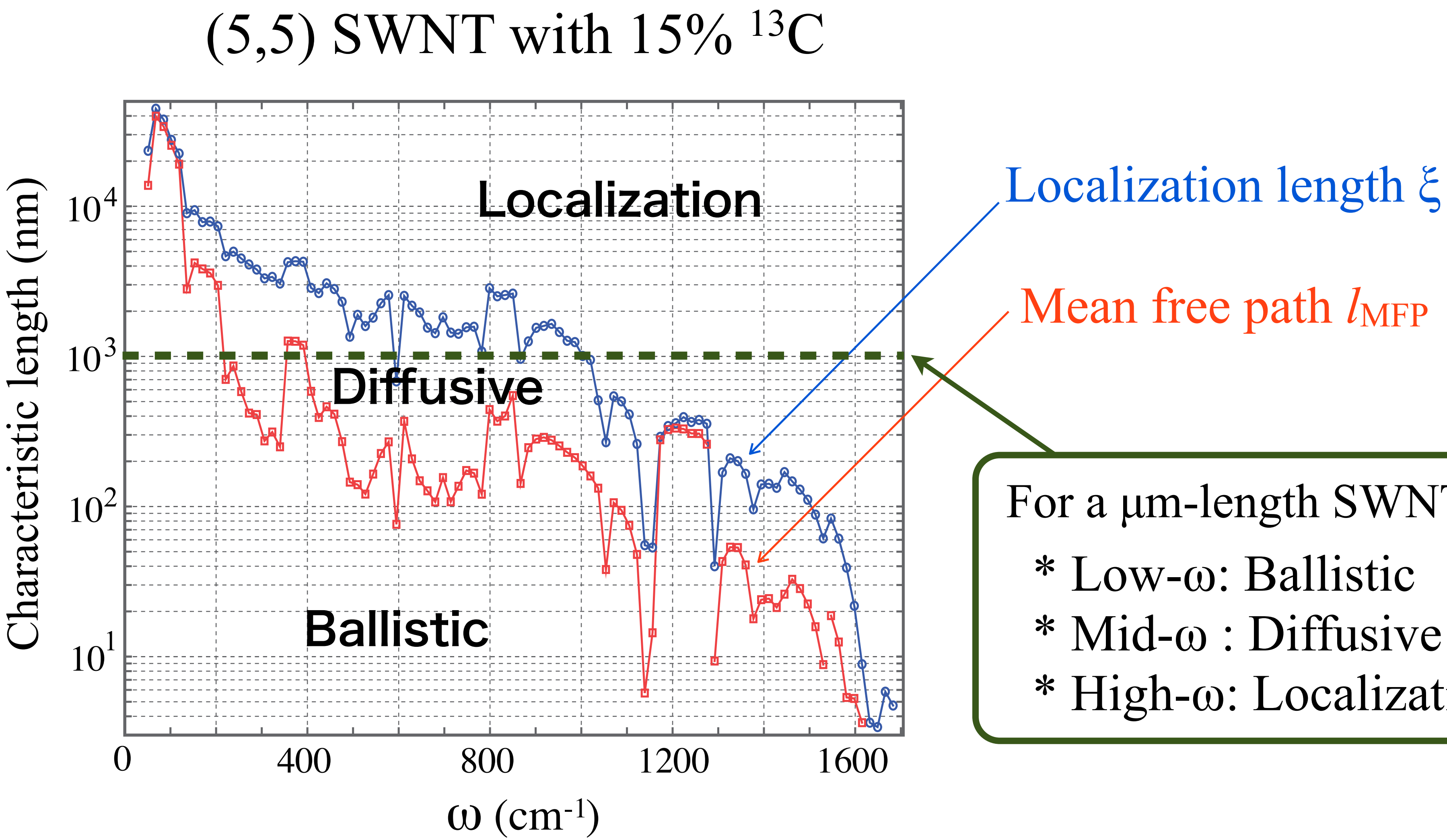
$$\langle \ln \zeta(\omega) \rangle = -L/\xi(\omega)$$

Exponential decay

Length Dependence of Transmission Decay



Mean Free Path & Localization Length

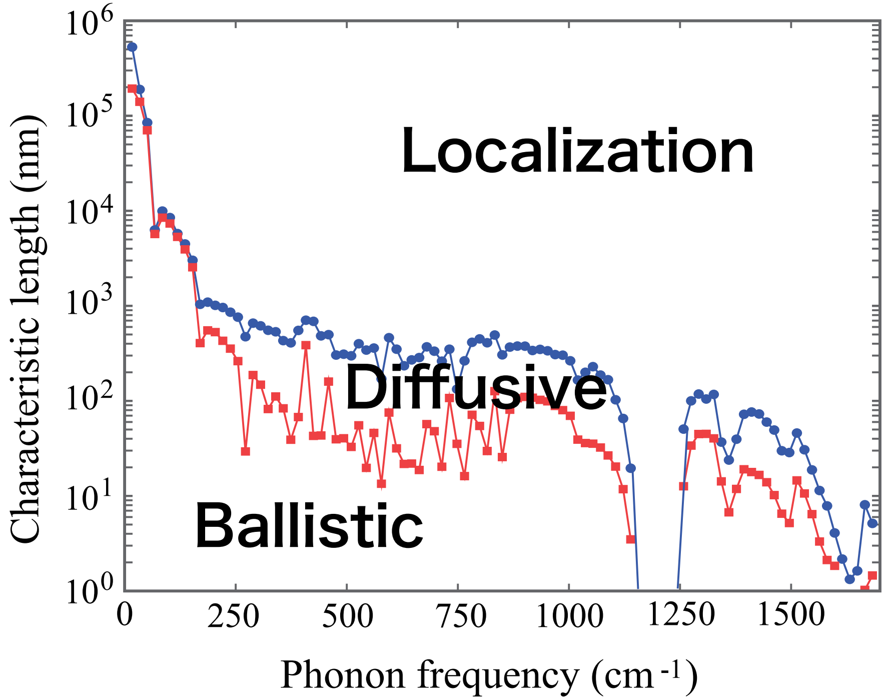


For a μm-length SWNT,

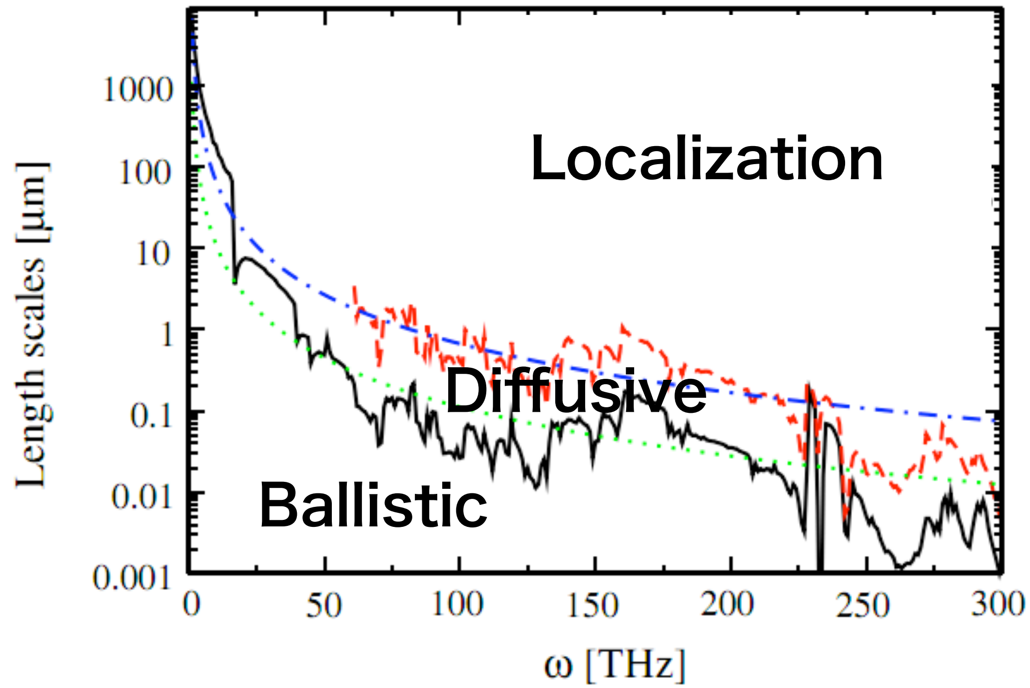
* Low-ω: Ballistic
* Mid-ω : Diffusive
* High-ω: Localization

Characteristic Lengths for Other Chiralities

(8,0) SWNT with 9.4% ^{14}C isotopes



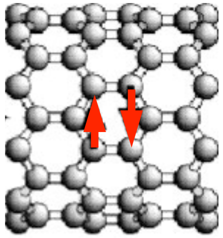
(7,0) SWNT with 10.7% ^{14}C isotopes



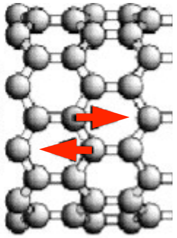
Savić, *et al.*, PRL. **101**, 165502 (2008)

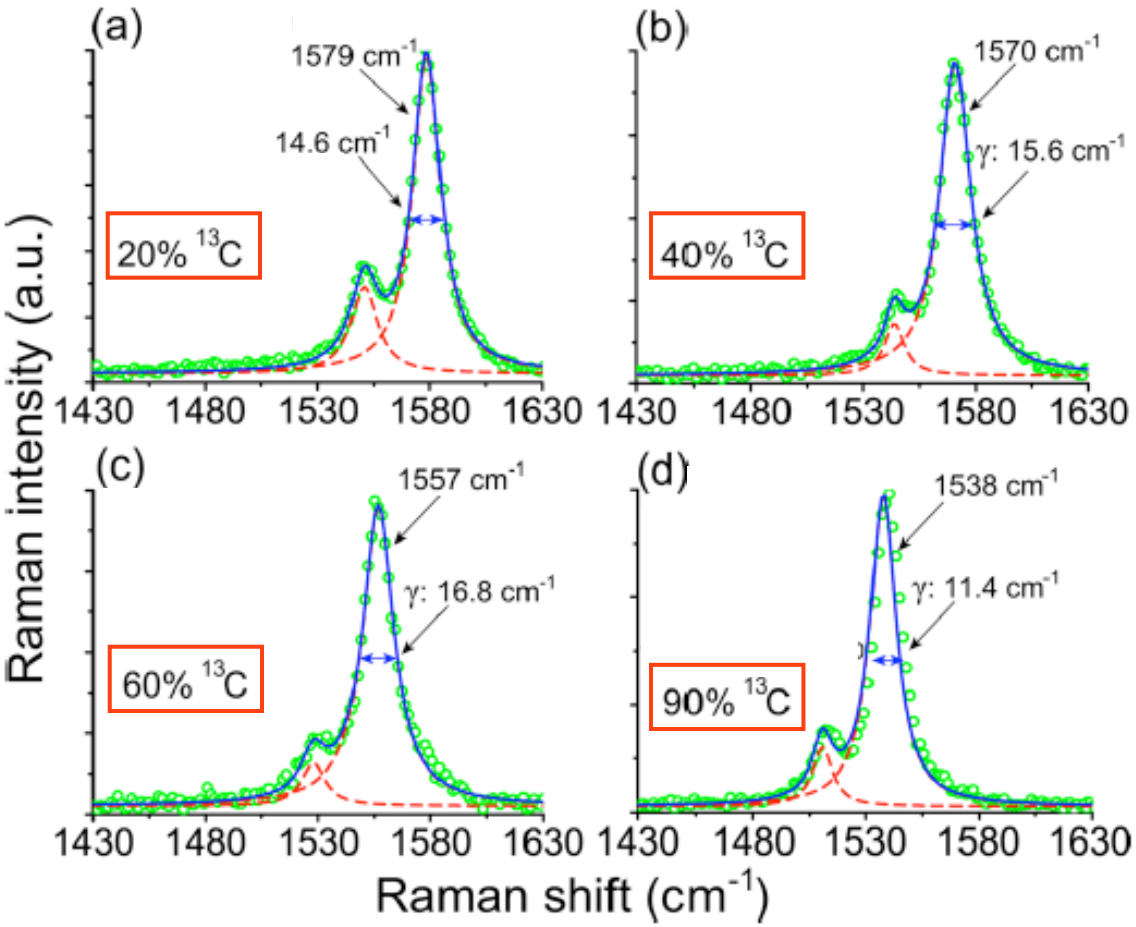
Experimental Evidence of Phonon Anderson's Localization

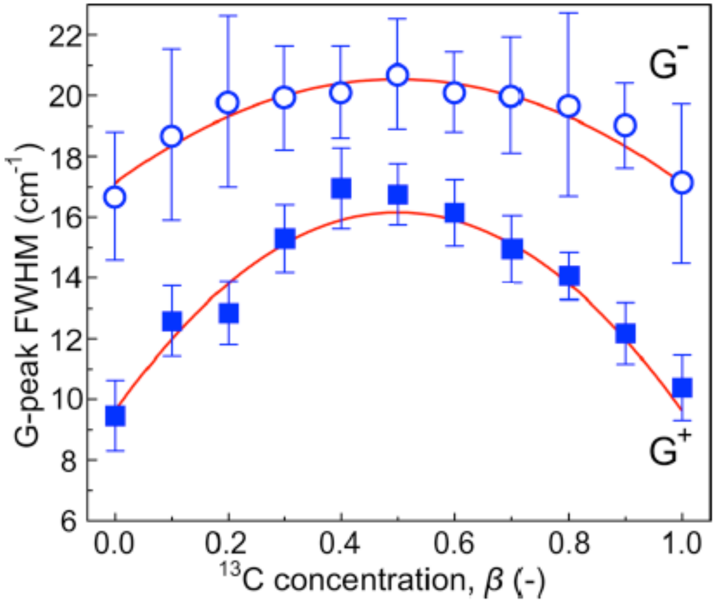
G⁻ mode



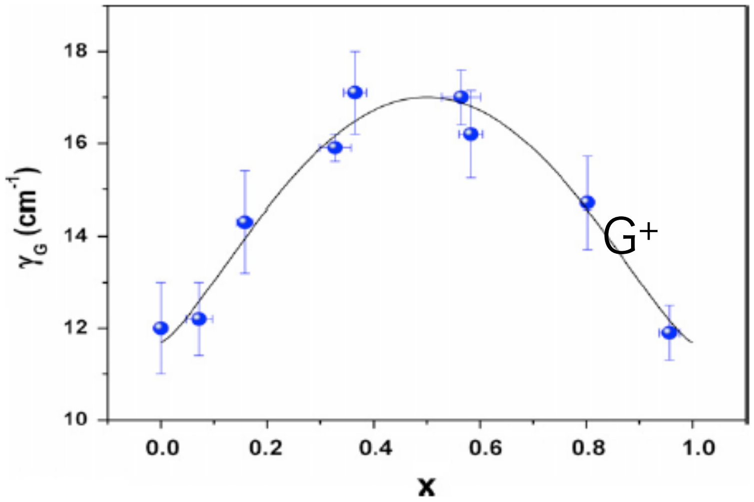
G⁺ mode







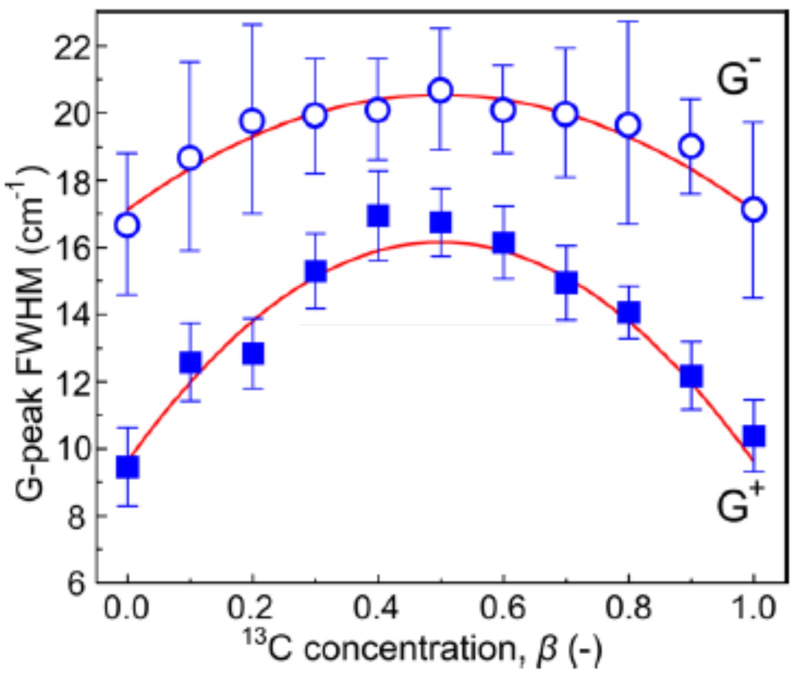
Zhao, *et al*., APL **99**, 093104 (2011)



Casta, *et al*., Carbon 49, 4719 (2011)

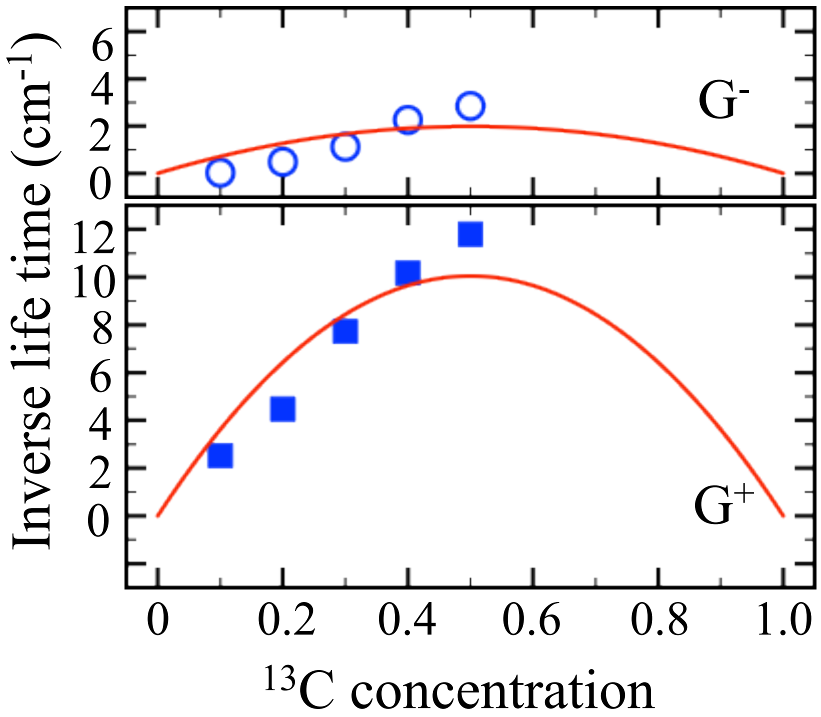
Comparison between Exp. and Calc.

Experiment



Zhao, *et al*., APL **99**, 093104 (2011)

Our Calc.

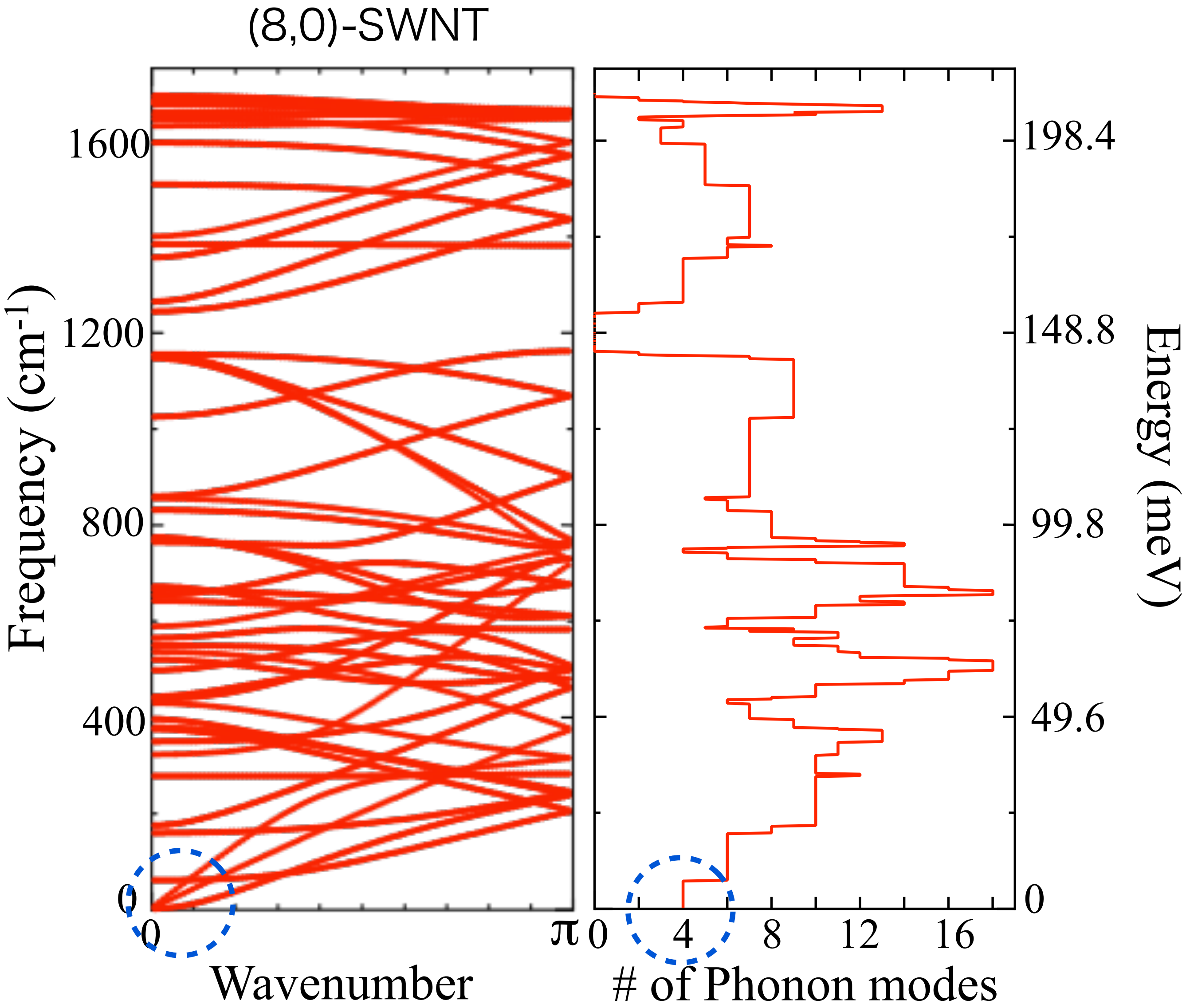


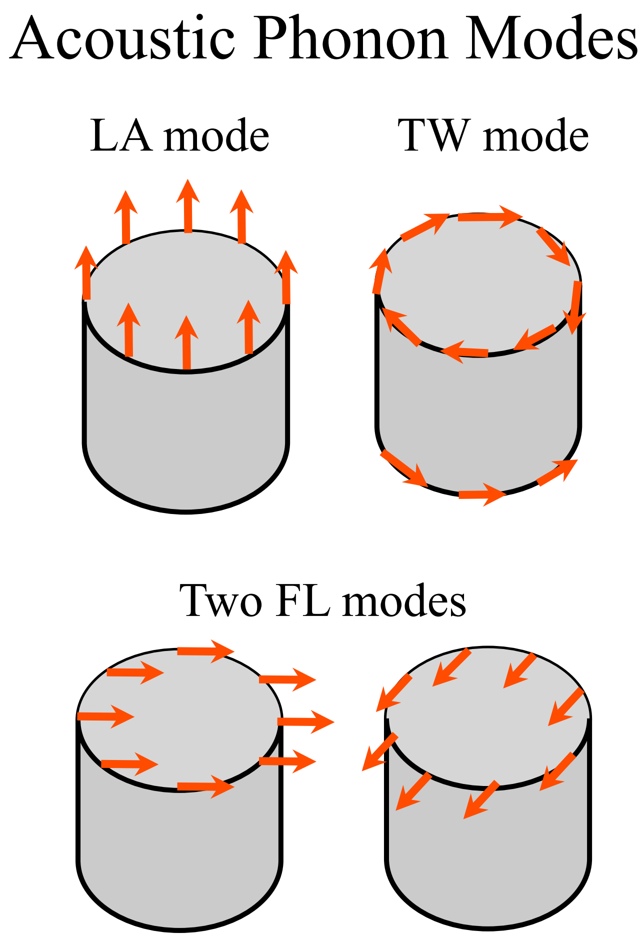
Summary

- Introduction
- Boltzmann Theory of Thermal Transport
- Landau Theory of Thermal Transport
- Thermal Transport in Defective Carbon Nanotubes
    - Vacancy defect scattering
    - Isotope effects

Phonon Dispersion Relations

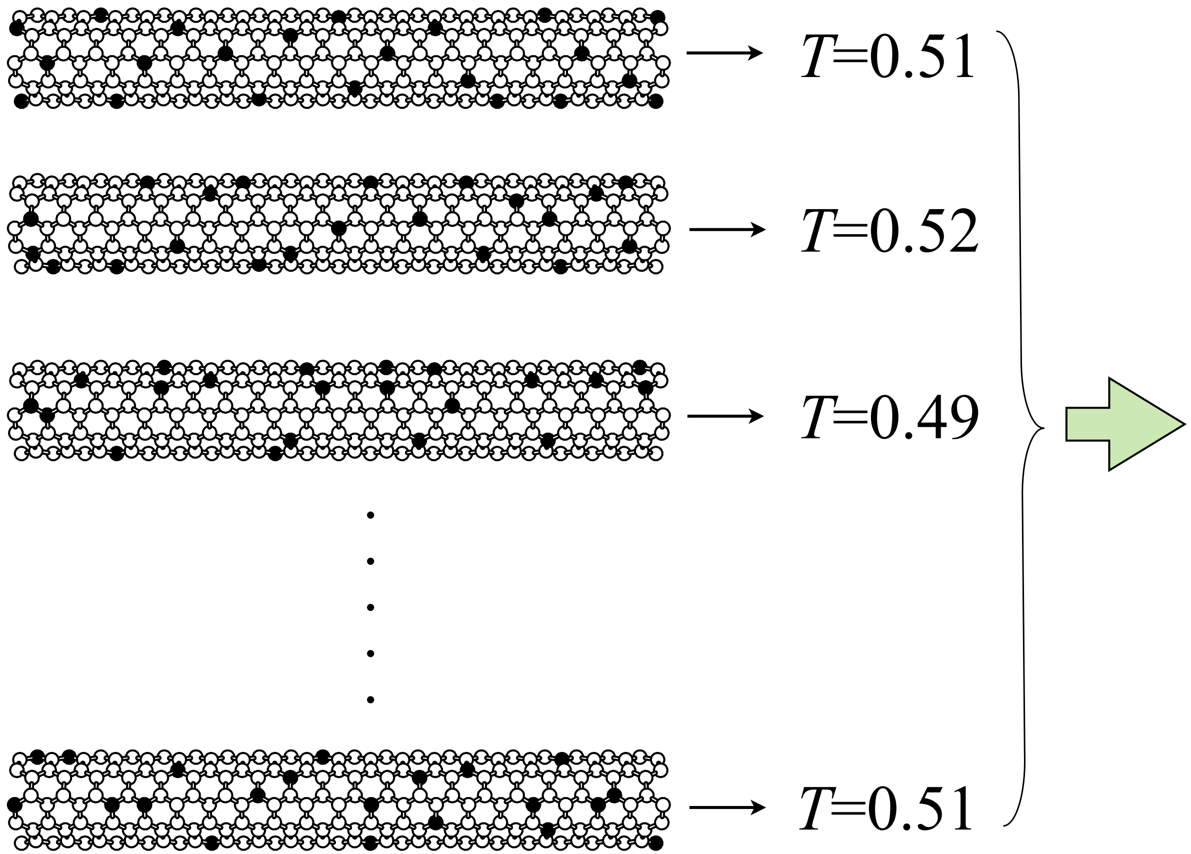
Force field: Brenner bond-order potential [D.W. Brenner, PRB 42, 9458 (1990)]



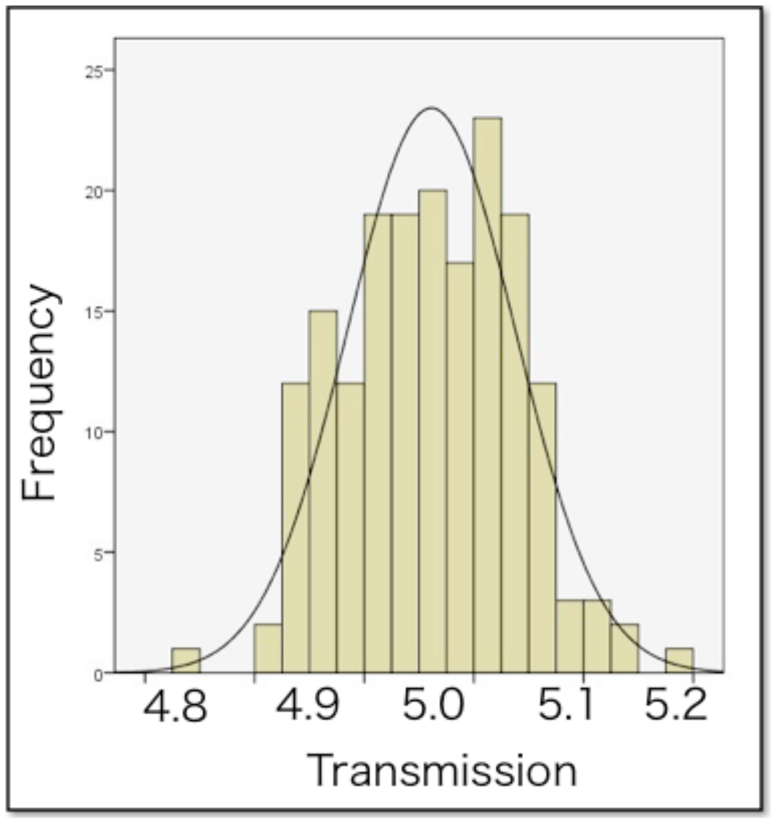


Transmission Fluctuation & Histogram

Various ^{13}C configurations   Transmissions



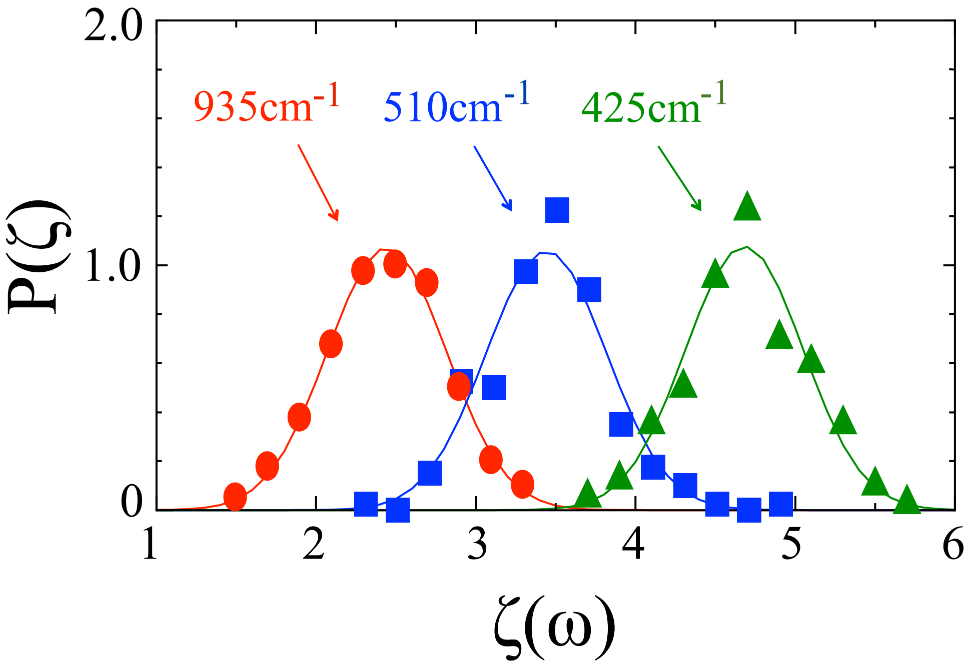
Transmission Histogram



Transmission Histogram

System: (5,5)SWNT with 15% ^{13}C and L=625nm

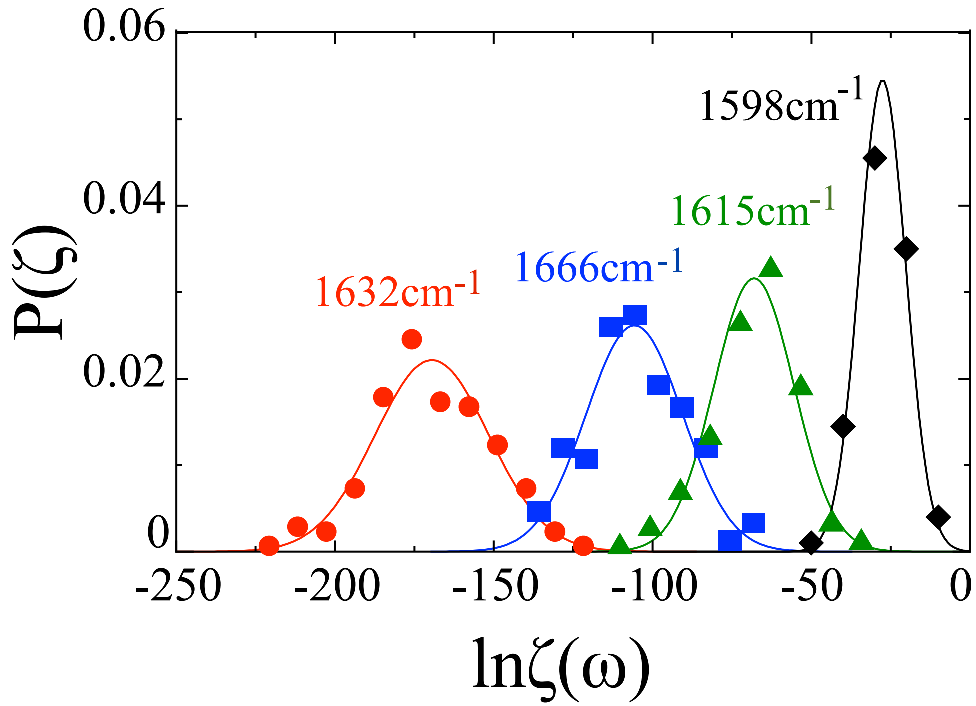
Diffusive Regime



Gaussian distribution with same standard deviation

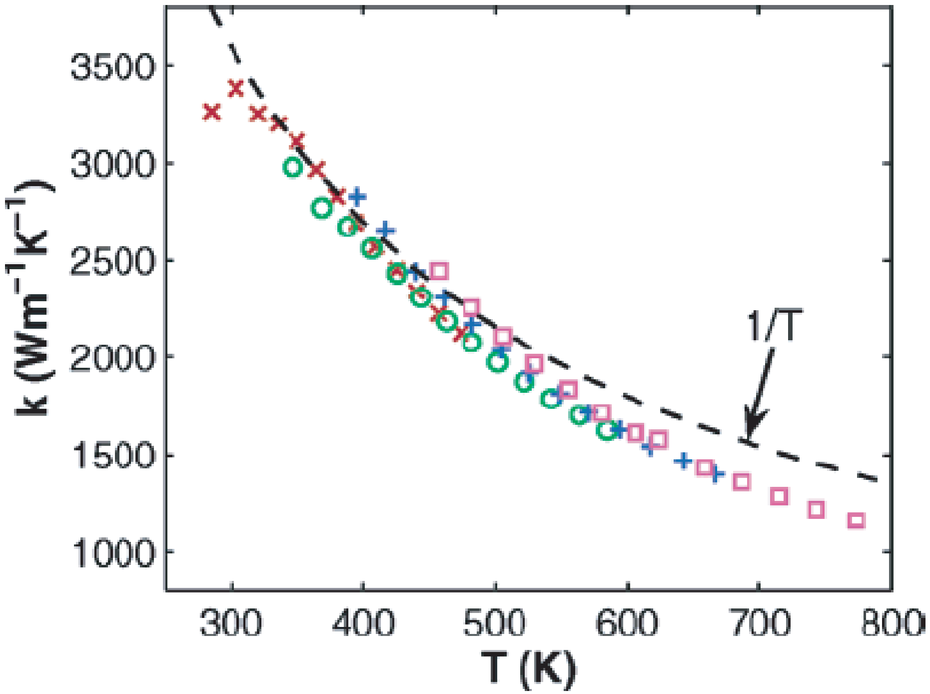
$$\Delta\zeta(\omega) \approx \mathbf{0.36}$$

Localization Regime



* Lognormal distribution
* Std. Dev. of P(ζ) decreases with increasing ζ.

High-T Thermal Conductivity of Carbon Nanotubes

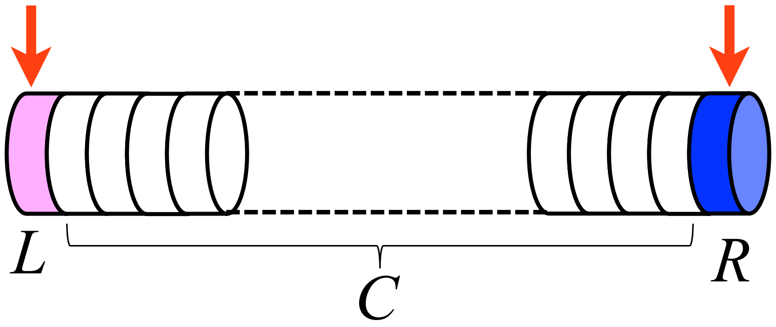


E. Pop, *et al*., Nano Lett. **6**, 96 (2006).

The thermal conductivity of an isolated suspended SWNT with a length L=2.6 μm and diameter d=1.7 nm in T = 300 to 800 K.

The dashed curve indicates the $1/T$ behavior expected from the 3-phonon Umklapp scattering.

Merit of NEGF Method for Large-Scale Simulation



$$\mathbf{G} = \begin{pmatrix} \mathbf{G}_{LL} & \mathbf{G}_{LC} & \mathbf{G}_{LR} \\ \mathbf{G}_{CL} & \mathbf{G}_{CC} & \mathbf{G}_{CR} \\ \mathbf{G}_{RL} & \mathbf{G}_{RC} & \mathbf{G}_{RR} \end{pmatrix} \quad \mathbf{\Gamma}_L = \begin{pmatrix} \mathbf{\Gamma}_{LL} & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

$$\mathbf{G}^\dagger = \begin{pmatrix} \mathbf{G}^\dagger_{LL} & \mathbf{G}^\dagger_{CL} & \mathbf{G}^\dagger_{RL} \\ \mathbf{G}^\dagger_{LC} & \mathbf{G}^\dagger_{CC} & \mathbf{G}^\dagger_{RC} \\ \mathbf{G}^\dagger_{LR} & \mathbf{G}^\dagger_{CR} & \mathbf{G}_{RR}{}^\dagger \end{pmatrix} \quad \mathbf{\Gamma}_R = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \mathbf{\Gamma}_{RR} \end{pmatrix}$$

$$\zeta(\omega) = \mathrm{Tr}[\mathbf{\Gamma}_L(\omega)\mathbf{G}(\omega)\mathbf{\Gamma}_R(\omega)\mathbf{G}^\dagger(\omega)]$$

$$= \mathrm{Tr}\begin{pmatrix} \mathbf{\Gamma}_{LL}\mathbf{G}_{LR}\mathbf{\Gamma}_{RR}\mathbf{G}^\dagger_{LR} & \mathbf{\Gamma}_{LL}\mathbf{G}_{LR}\mathbf{\Gamma}_{RR}\mathbf{G}^\dagger_{CR} & \mathbf{\Gamma}_{LL}\mathbf{G}_{LR}\mathbf{\Gamma}_{RR}\mathbf{G}^\dagger_{RR} \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

$$= \mathrm{Tr}[\mathbf{\Gamma}_{LL}(\omega)\mathbf{G}_{LR}(\omega)\mathbf{\Gamma}_{RR}(\omega)\mathbf{G}^\dagger_{LR}(\omega)]$$

The transmission function is described by small matrices!!