

日本熱物性学会「マイクロ・ナノスケールの熱物性とシステムデザイン」第13回研究会
キャンパス・イノベーションセンター4階（東京，田町）
2009年12月11日（金）

カーボンナノチューブ 熱伝導シミュレーションの最近の進展

山本 貴博

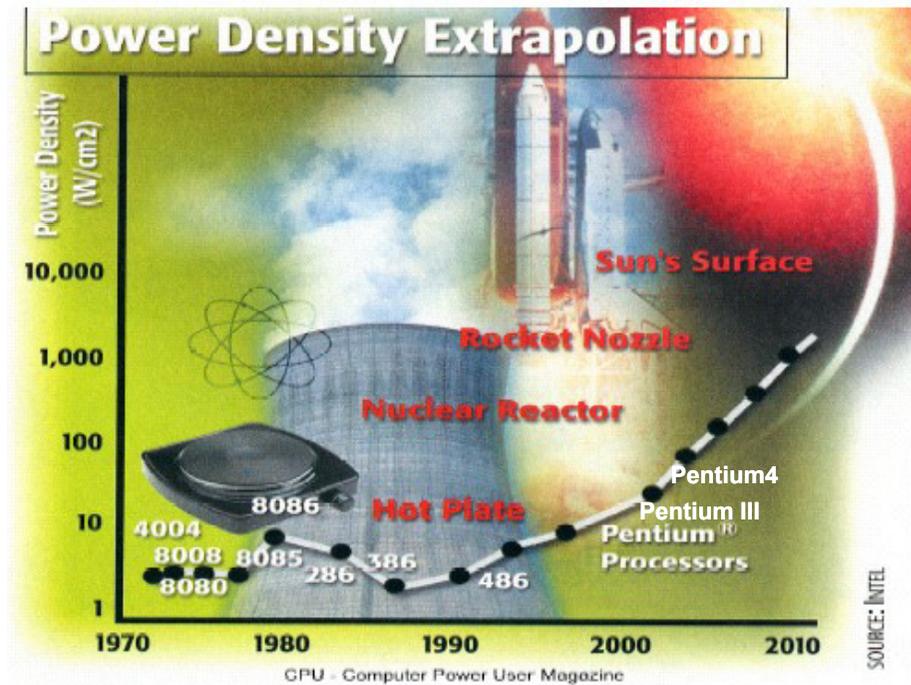
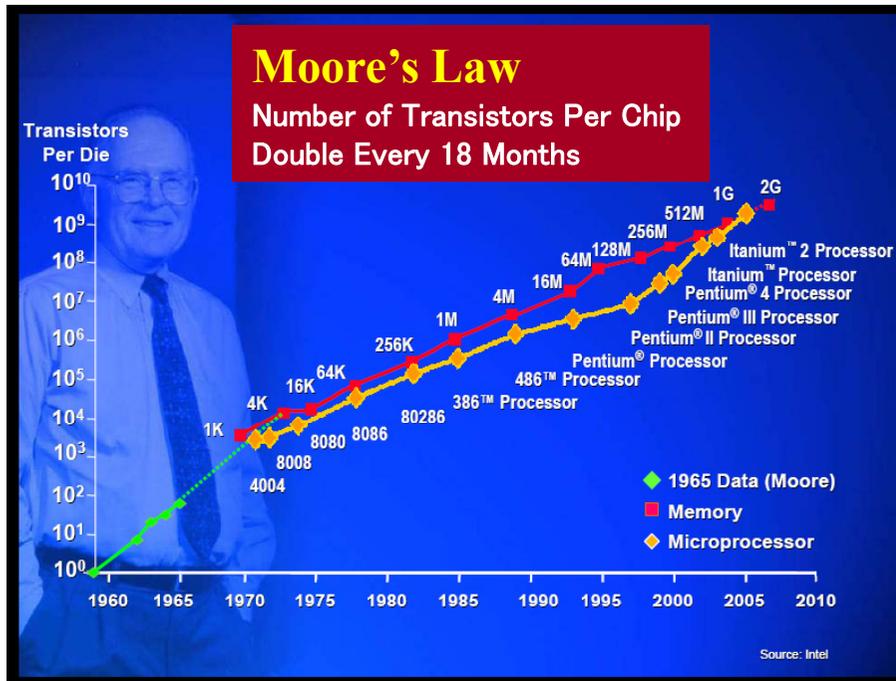
東京大学 大学院工学系研究科 マテリアル工学専攻



半導体デバイスの微細化と発熱問題



Intel CPU



P.Gelsinger (Intel CTO): ISSCC 2001

カーボンナノチューブの高い熱伝導率

Berber, Kwon and Tománek, *Phys. Rev. Lett.* **84**, 4613 (2000).

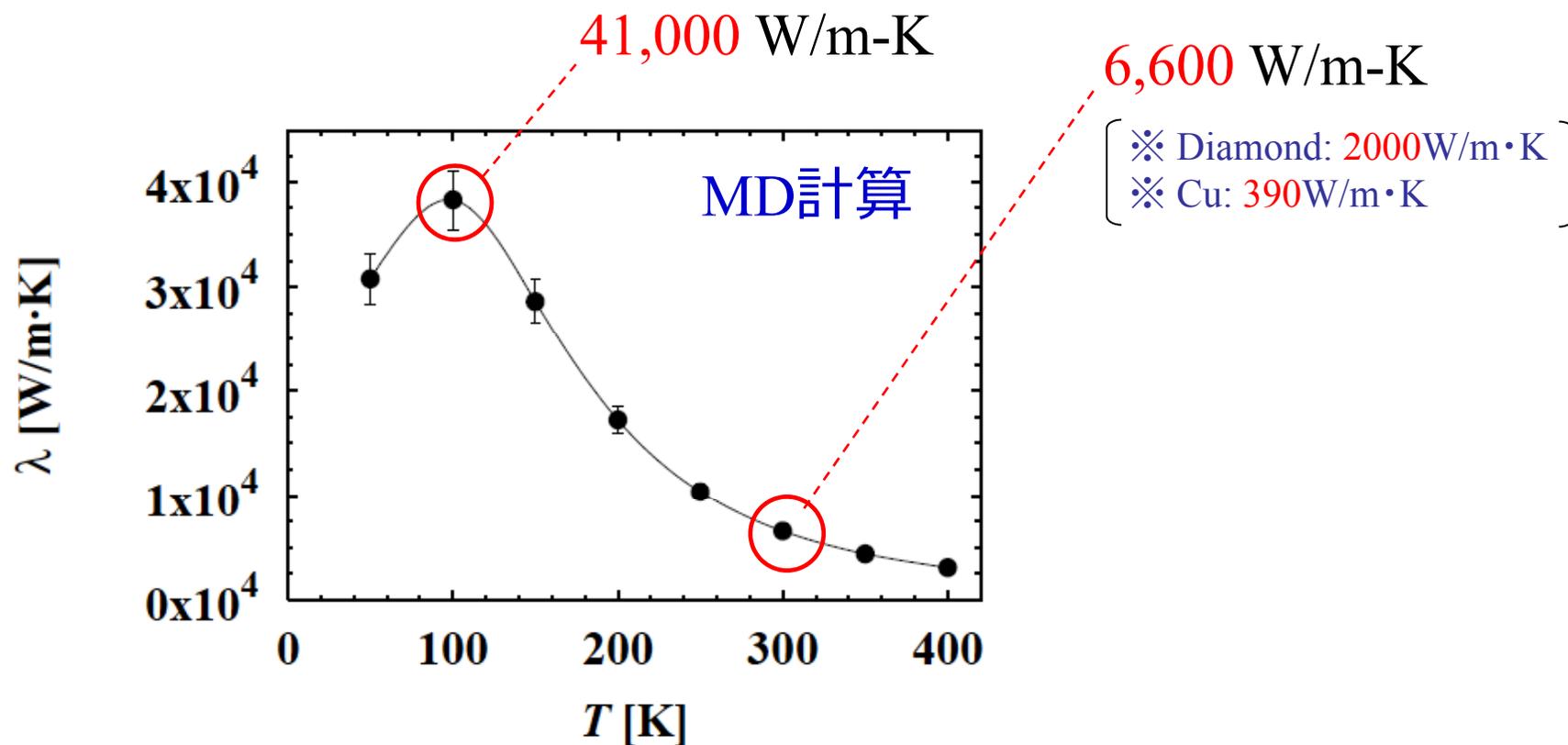


FIG. 2. Temperature dependence of the thermal conductivity λ for a (10, 10) carbon nanotube for temperatures below 400 K.

放熱材料としてのナノチューブ



熱物性値

- 高い熱伝導率: $\sim 2000 \text{ W/m}\cdot\text{K}$ (300K)
- 優れた熱的安定性: $T_{\text{melt}} > 4000\text{K}$
- 機械的に柔軟かつ強靱:
ヤング率 0.9TPa, 比強度は最大150GPa

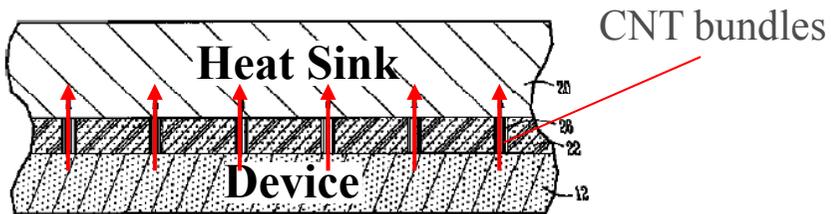
細くて強い

同じ重さの鉄の
数百倍の強度がある

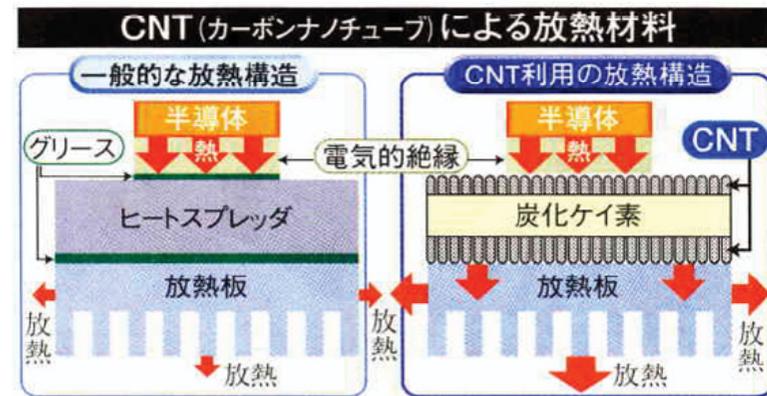
カーボン
ナノチューブ線
0.3mm

1トン

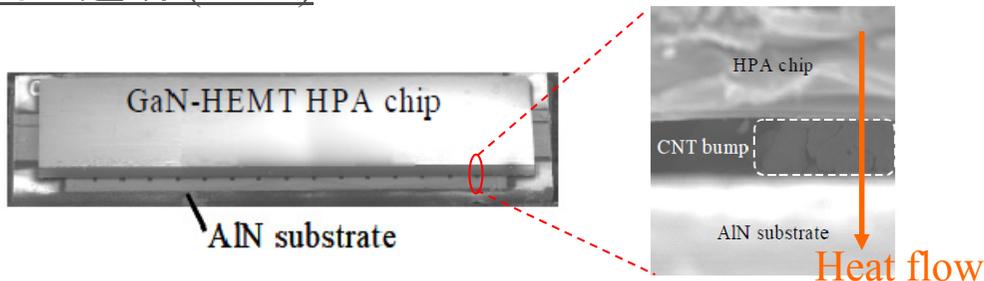
インテル (2003)



名大エコ研・楠グループ(2008)

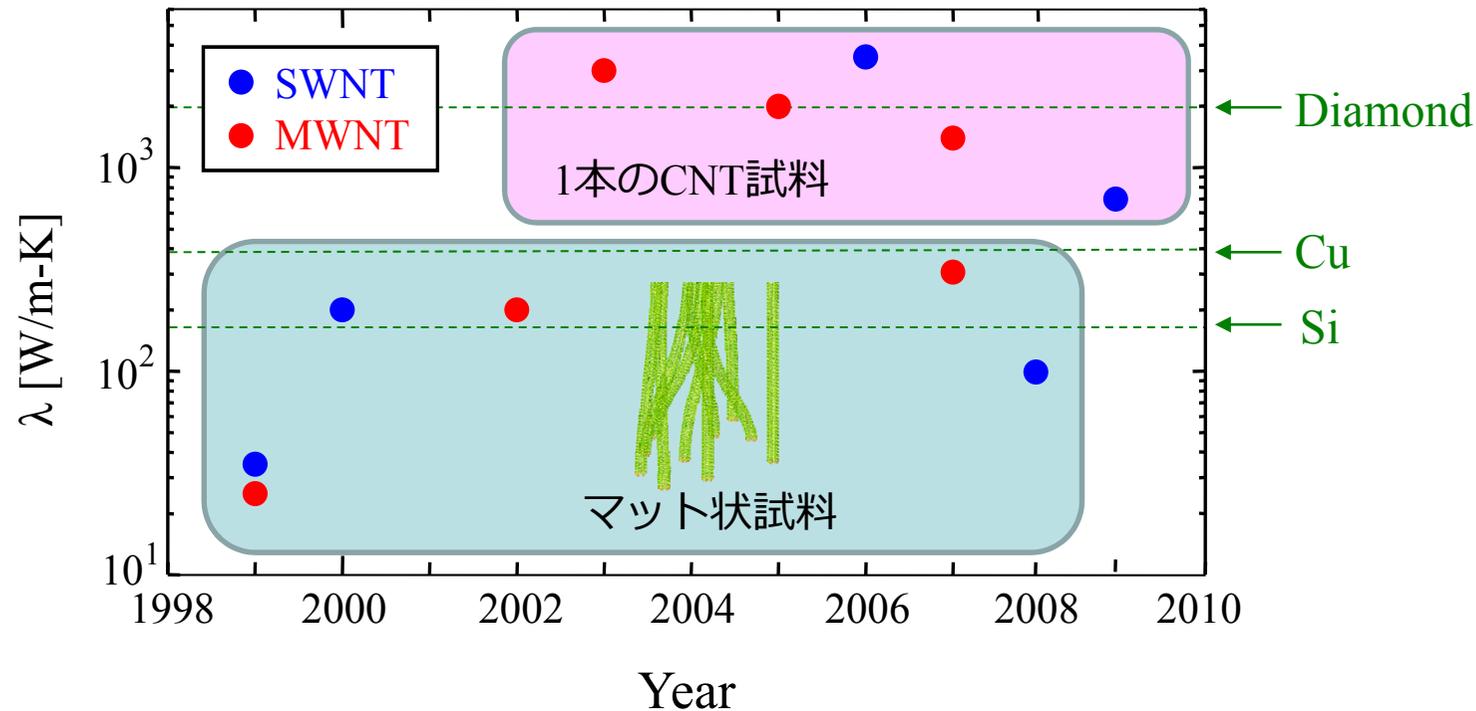


富士通研 (2005)



放熱効率15倍向上

CNT熱伝導率の測定値



考えられ得るいくつかの理由

- 1) 測定方法の違い: 3 ω 法, レーザーフラッシュ法など
- 2) 試料の違い: 単層, 多層, 長さ, 直径など
- 3) 純度: 欠陥, 不純物, 構造変形など

本日の話題



1 CNTにおける熱流の担い手：電子 vs フォノン

2 CNT熱伝導の形状（長さと直径）依存性

3 湾曲変形によるCNT熱伝導への影響

4 欠陥や不純物によるCNT熱伝導への影響

ナノチューブ中の熱流の担い手は？



CNT中の熱流の担い手

- 半導体: フォノン
- 金属: フォノン + ~~電子~~

■ 自由電子に対するヴィーデマン・フランツの法則

$$\frac{\lambda_{el}}{\sigma_{el}T} = \frac{\pi^2}{3} \left(\frac{k_B}{e} \right)^2 = 2.45 \times 10^{-8} (V/K)^2$$

■ CNTに対するローレンツ比の測定値

$$\frac{\lambda_{tot}}{\sigma_{el}T} \sim 10^{-6} (V/K)^2 \quad T=30K \sim 350K$$

Hone, *et al.*, PRB **59**, R2514 ('99)

→ フォノン熱伝導

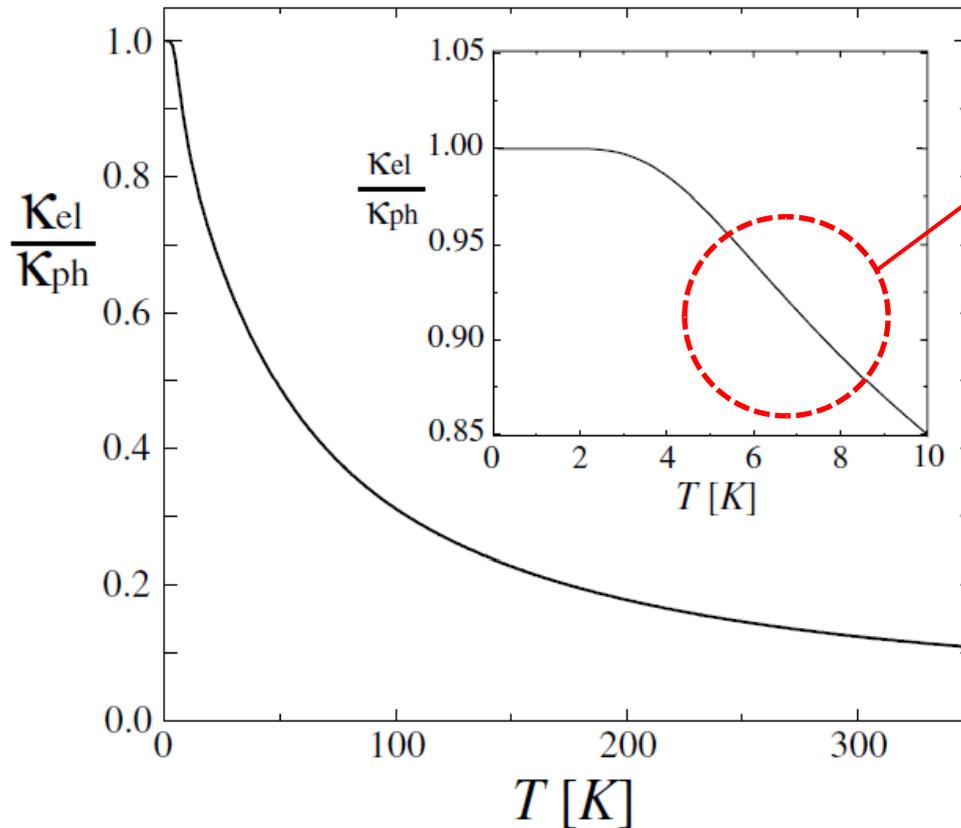
$$\frac{\lambda_{ph}}{\lambda_{el}} = \frac{\lambda_{tot}}{\lambda_{el}} - 1 \approx 10^2$$

$\lambda_{tot} = \lambda_{el} + \lambda_{ph}$

熱伝導度への寄与：フォノン vs 伝導電子



Yamamoto, Watanabe, Watanabe: PRL 96, 255503 (2004)



光学的フォノン励起

■ サブバンド励起エネルギー

電子： $\Delta E_{el} \sim eV$

フォノン： $\Delta E_{ph} \sim meV$

(10, 10) 金属カーボンナノチューブの
電子熱伝導度とフォノン熱伝導度の比

本日の話題



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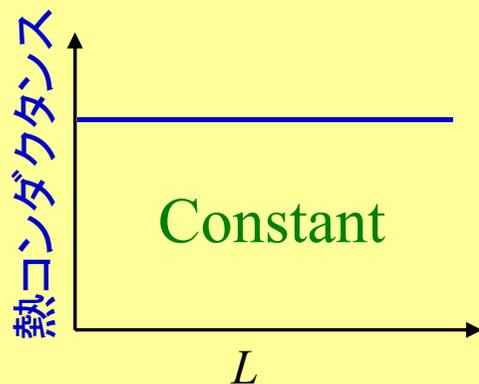
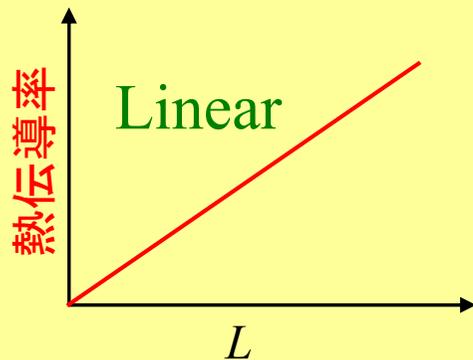
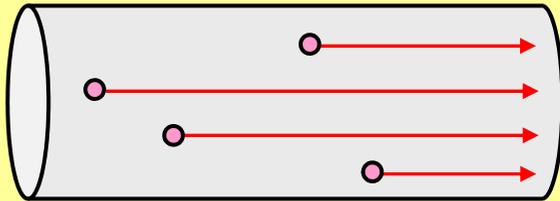
4 欠陥や不純物によるCNT熱伝導への影響

熱伝導率と熱コンダクタンスの長さ依存性



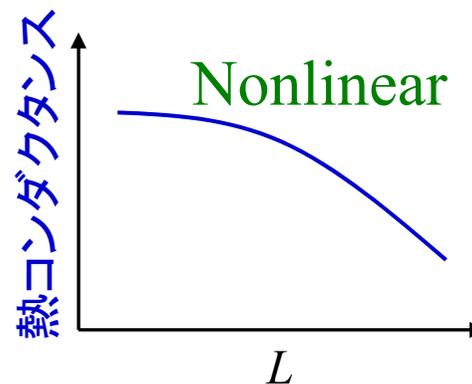
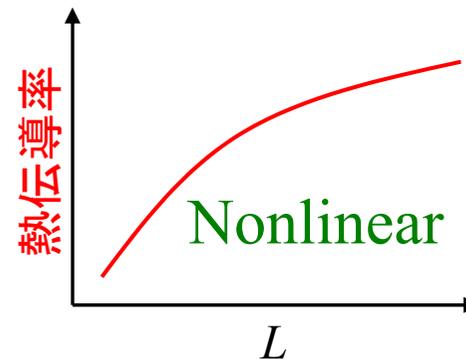
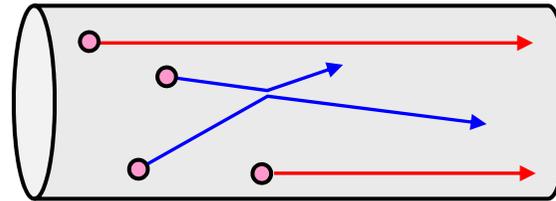
バリスティック領域

$$L \ll \Lambda$$



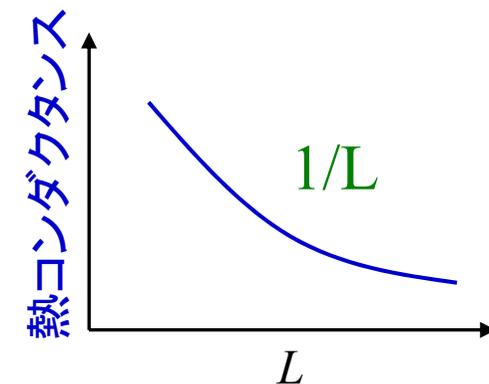
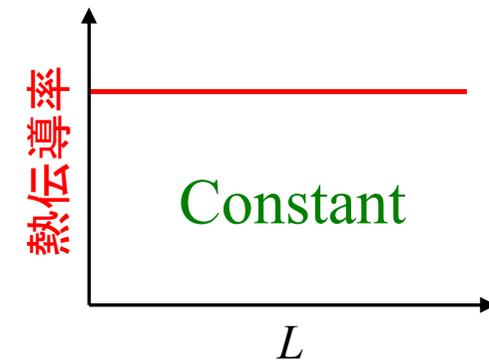
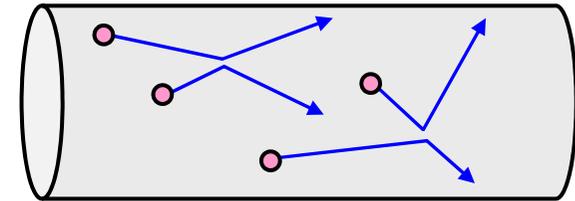
準バリスティック領域

$$L \approx \Lambda$$



拡散領域

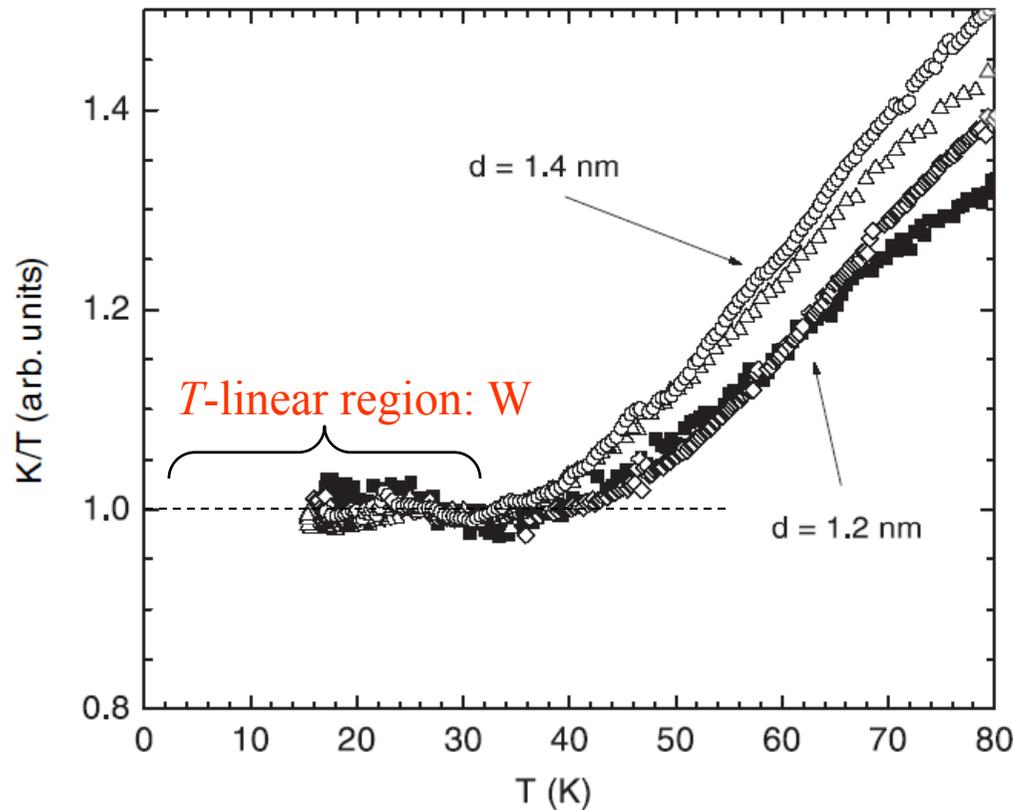
$$L \gg \Lambda$$



低温におけるナノチューブ熱伝導実験



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



■ Temperature dependence

$$\kappa_{\text{ph}}(T) \propto T$$

Quantum & 1D effects

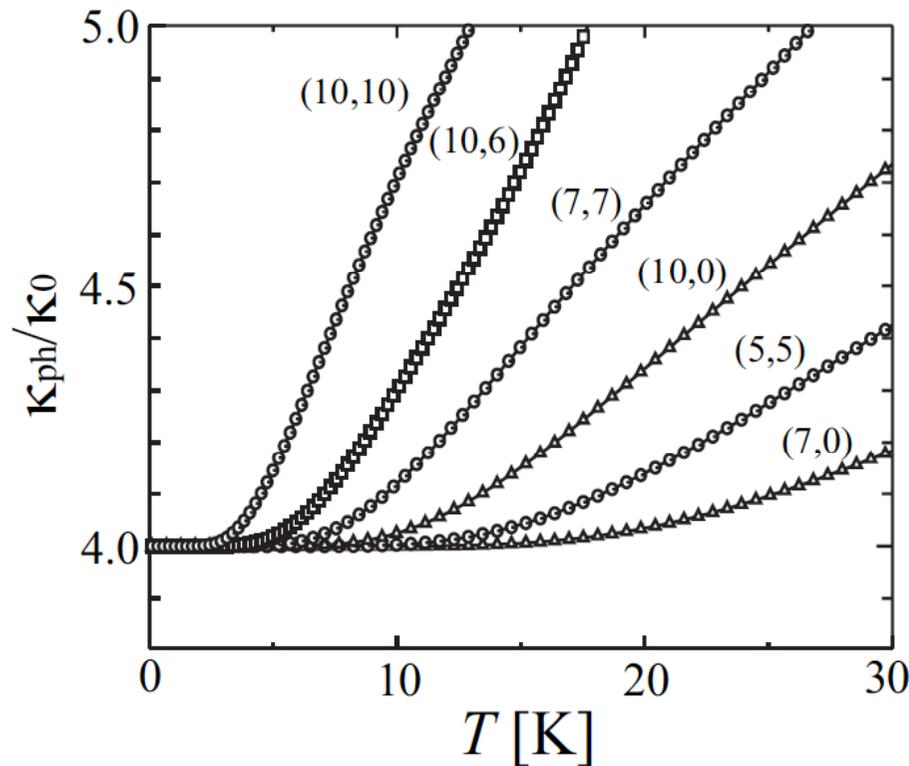
■ Plateau width

$$W_{1.4\text{nm}} < W_{1.2\text{nm}}$$

Fig.: Thermal conductance of single-walled CNTs with diameter $d=1.2\text{nm}$ and $d=1.4\text{nm}$.

低温での熱伝導 (バリスティック領域)

Yamamoto, Watanabe, Watanabe: PRL 96, 255503 (2004)



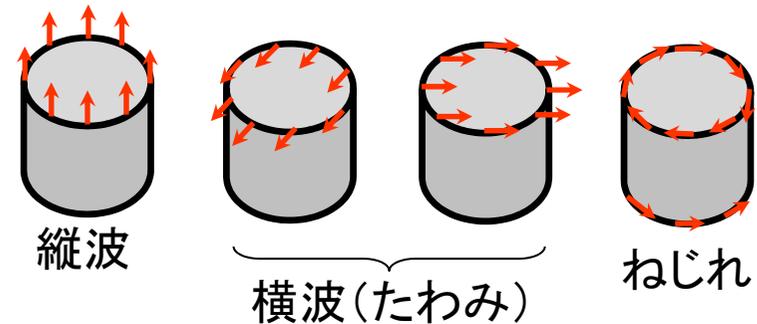
Quantized Thermal Conductance

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

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

At Extremely Low T

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



Quantization Plateau Width

直径が**細い** → 量子化プラトーが**広い**

(光学的フォノン励起ギャップ $\propto 1/d$)

熱コンダクタンス量子の実験的検証



PRL 95, 226101 (2005)

PHYSICAL REVIEW LETTERS

week ending
25 NOVEMBER 2005

Ballistic Phonon Thermal Transport in Multiwalled Carbon Nanotubes

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(Received 6 July 2005; published 21 November 2005)

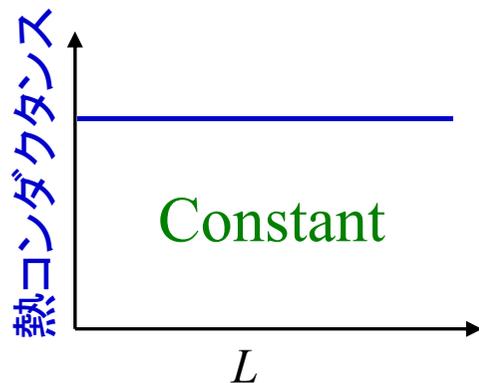
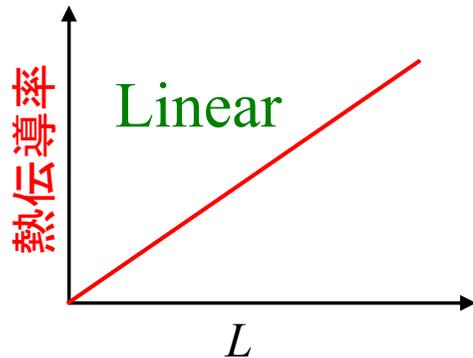
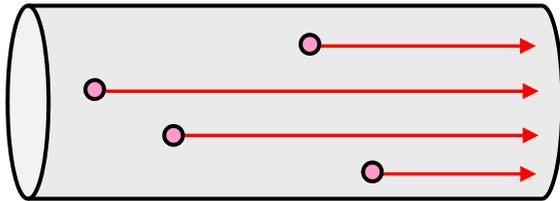
We report electrical transport experiments, using the phenomenon of electrical breakdown to perform thermometry, that probe the thermal properties of individual multiwalled carbon nanotubes. Our results show that nanotubes can readily conduct heat by ballistic phonon propagation. We determine the thermal conductance quantum, the ultimate limit to thermal conductance for a single phonon channel, and find good agreement with theoretical calculations. Moreover, our results suggest a breakdown mechanism of thermally activated C-C bond breaking coupled with the electrical stress of carrying $\sim 10^{12}$ A/m². We also demonstrate a current-driven self-heating technique to improve the conductance of nanotube devices dramatically.

熱伝導率と熱コンダクタンスの長さ依存性



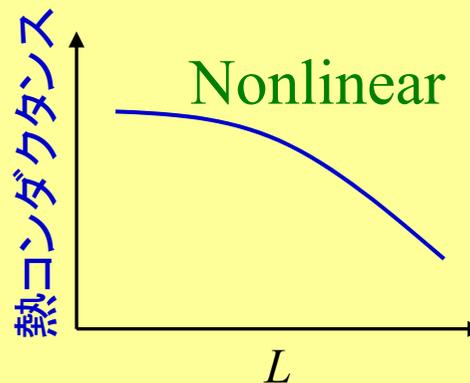
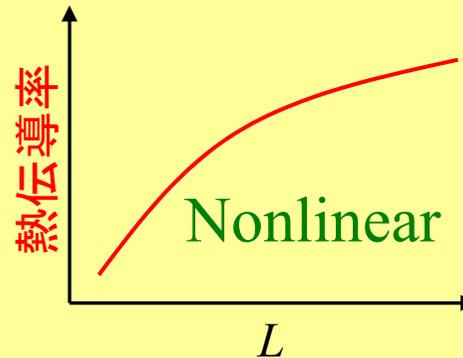
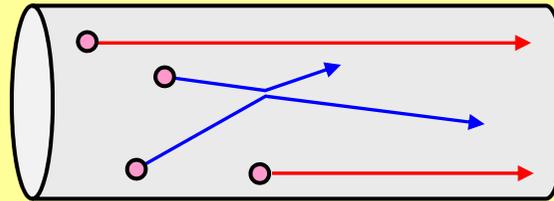
バリスティック領域

$$L \ll \Lambda$$



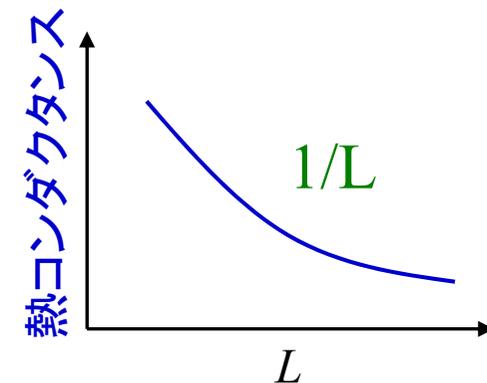
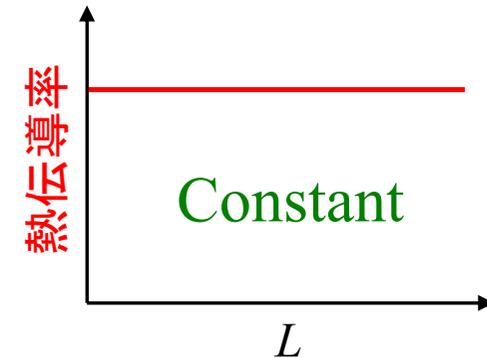
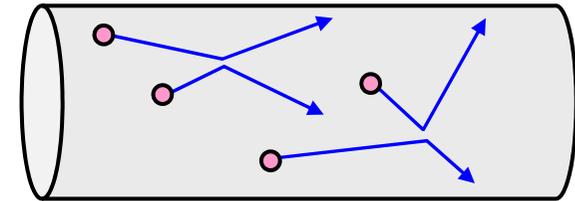
準バリスティック領域

$$L \approx \Lambda$$

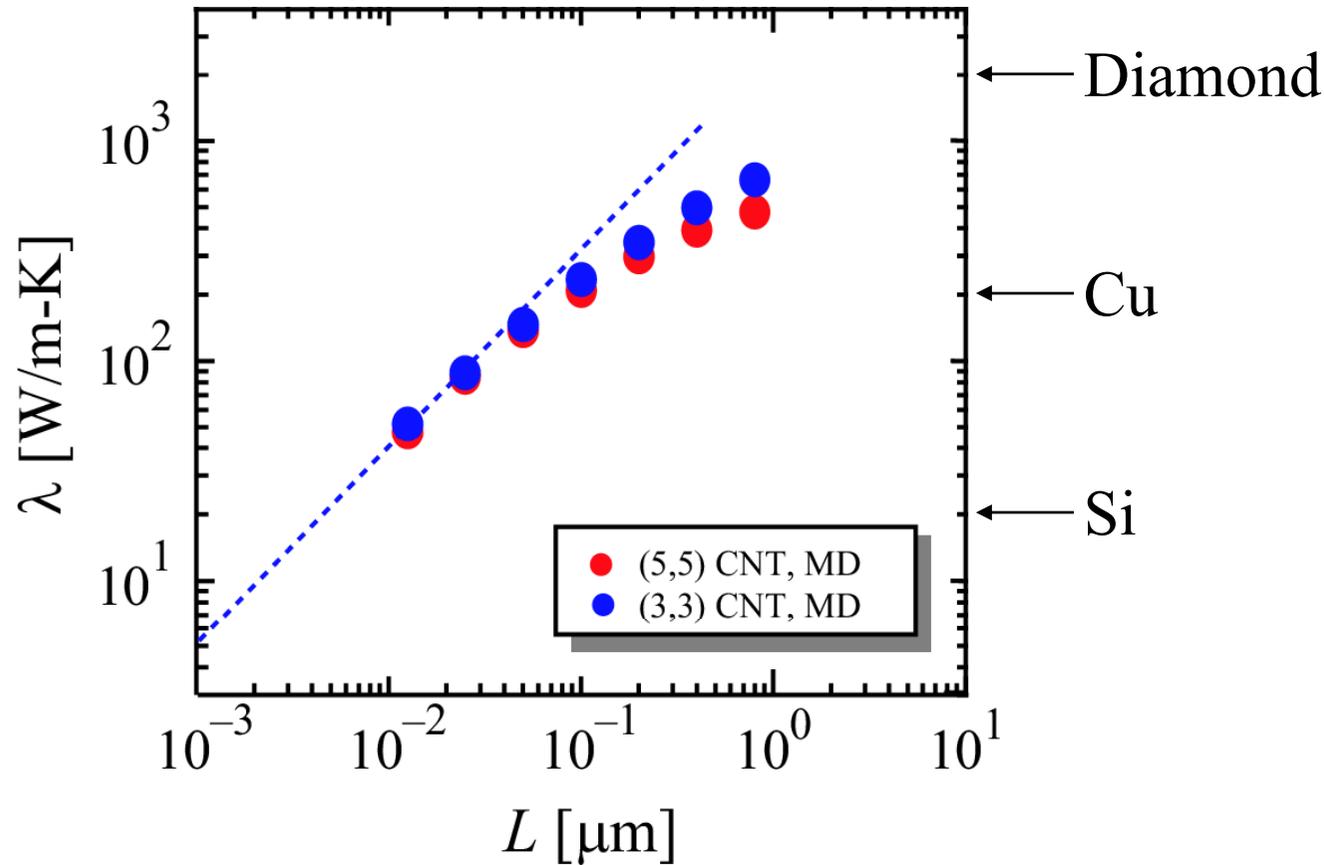


拡散領域

$$L \gg \Lambda$$



室温での熱伝導 (準バリスティック領域)



$d=0.69$ nm for (5,5)CNT
 $d=0.41$ nm for (3,3)CNT

S. Maruyama: Physica B **323** (2002) 193.

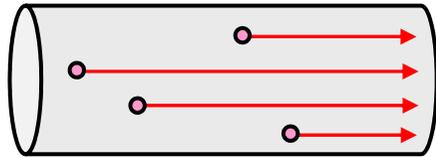
S. Maruyama: Nanoscale Microscale Thermophys. Eng. **7** (2003) 41.

J. Shiomi & S. Maruyama: Jpn. J. Appl. Phys. **47** (2008) 2005.



準バリスティック熱伝導の理論

Ballistic Regime

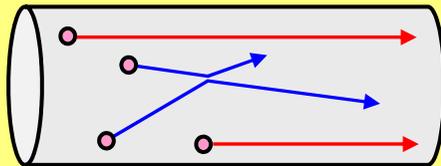


Landauer formula

$$\kappa(T) = \sum_{\nu} \int_{\omega_{\nu}^{\min}}^{\omega_{\nu}^{\max}} \frac{d\omega}{2\pi} \hbar\omega \left[\frac{\partial f_B(\omega, T)}{\partial T} \right] \times 1$$

Ballistic limit : $L \ll \Lambda_{\nu}(\omega)$

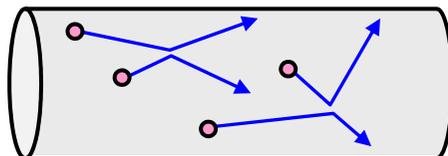
Quasi-Ballistic Regime



$$\kappa(T) = \sum_{\nu} \int_{\omega_{\nu}^{\min}}^{\omega_{\nu}^{\max}} \frac{d\omega}{2\pi} \hbar\omega \left[\frac{\partial f_B(\omega, T)}{\partial T} \right] \frac{\Lambda_{\nu}(\omega)}{L + \Lambda_{\nu}(\omega)}$$

Diffusive limit : $L \gg \Lambda_{\nu}(\omega)$

Diffusive Regime



Boltzmann-Peierls formula

$$\kappa(T) = \sum_{\nu} \int_{\omega_{\nu}^{\min}}^{\omega_{\nu}^{\max}} \frac{d\omega}{2\pi} \hbar\omega \left[\frac{\partial f_B(\omega, T)}{\partial T} \right] \frac{\Lambda_{\nu}(\omega)}{L}$$



カーボンナノチューブへの応用

$$\kappa_{\text{CNT}} = \sum_{\nu} \int_{\omega_{\nu}^{\min}}^{\omega_{\nu}^{\max}} \frac{d\omega}{2\pi} \hbar\omega \left[\frac{\partial f_B(\omega, T)}{\partial T} \right] \frac{\Lambda_{\nu}(\omega)}{L + \Lambda_{\nu}(\omega)}$$

♠ Classical limit

Bose-Einstein distribution → Maxwell distribution

$$f_B(\omega, T) = \frac{1}{\exp(\hbar\omega/k_B T) - 1} \approx \frac{k_B T}{\hbar\omega}$$

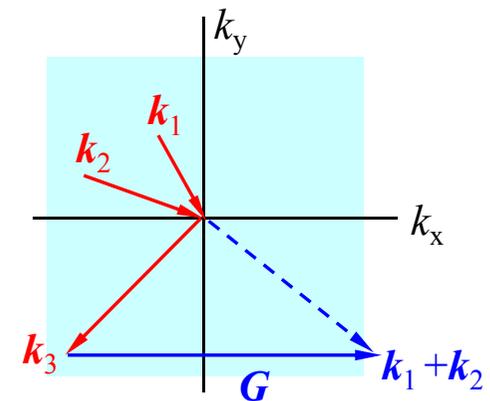
♠ Empirical expression of MFP

Mean free path $\Lambda_{\nu}(\omega) = \frac{cA}{T\omega^2}$ for Umklapp scattering

Here, $A \approx 2.5 \times 10^{23} \text{ mK/s}^2$ for graphene, c is a curvature parameter

3-phonon U process

$$\mathbf{k}_1 + \mathbf{k}_2 = \mathbf{k}_3 + \mathbf{G}$$



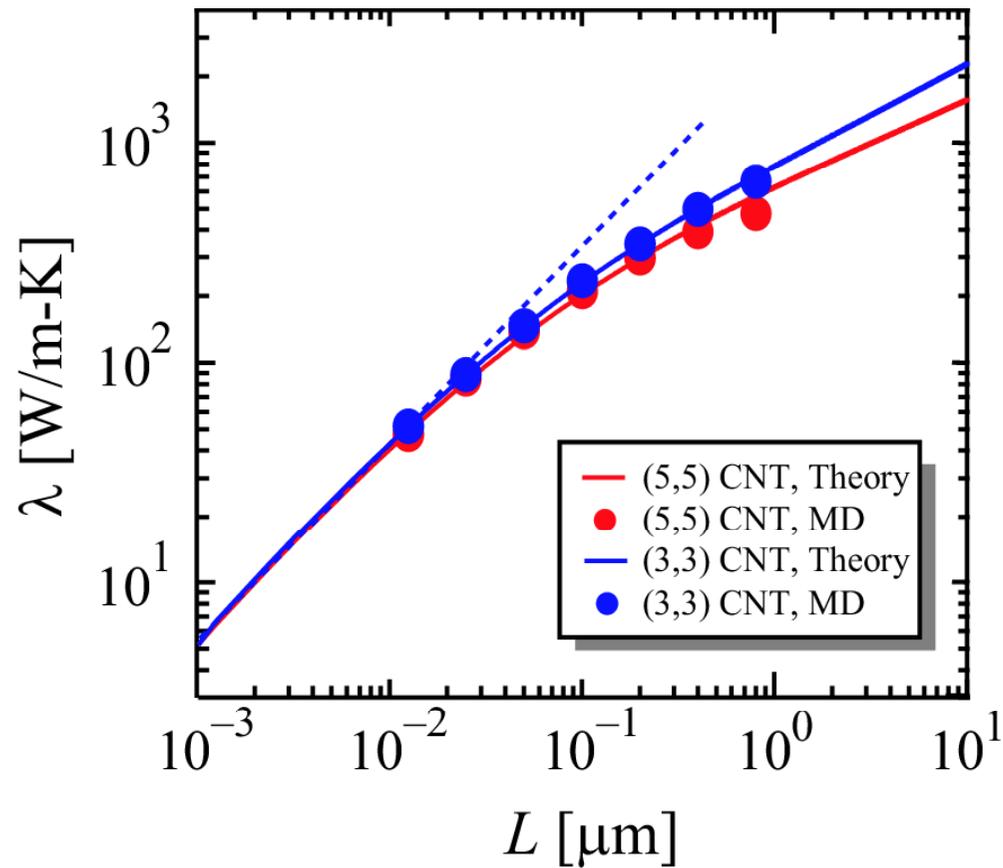
$$\kappa_{\text{CNT}} = \frac{k_B}{2\pi} \Omega(L) \sum_{\nu} \left\{ \arctan \left(\frac{\omega_{\nu}^{\max}}{\Omega(L)} \right) - \arctan \left(\frac{\omega_{\nu}^{\min}}{\Omega(L)} \right) \right\}$$

Characteristic frequency

$$\Omega(L) \equiv \sqrt{\frac{cA}{TL}}$$

MD計算と新規理論との比較

Yamamoto, Konabe, Shiomi, Maruyama: Appl. Phys. Exp. 2, 095003 (2009)

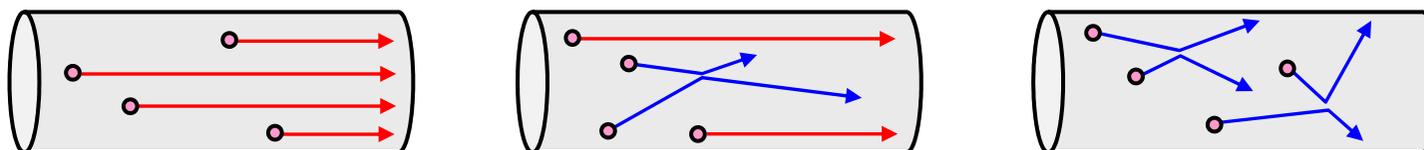
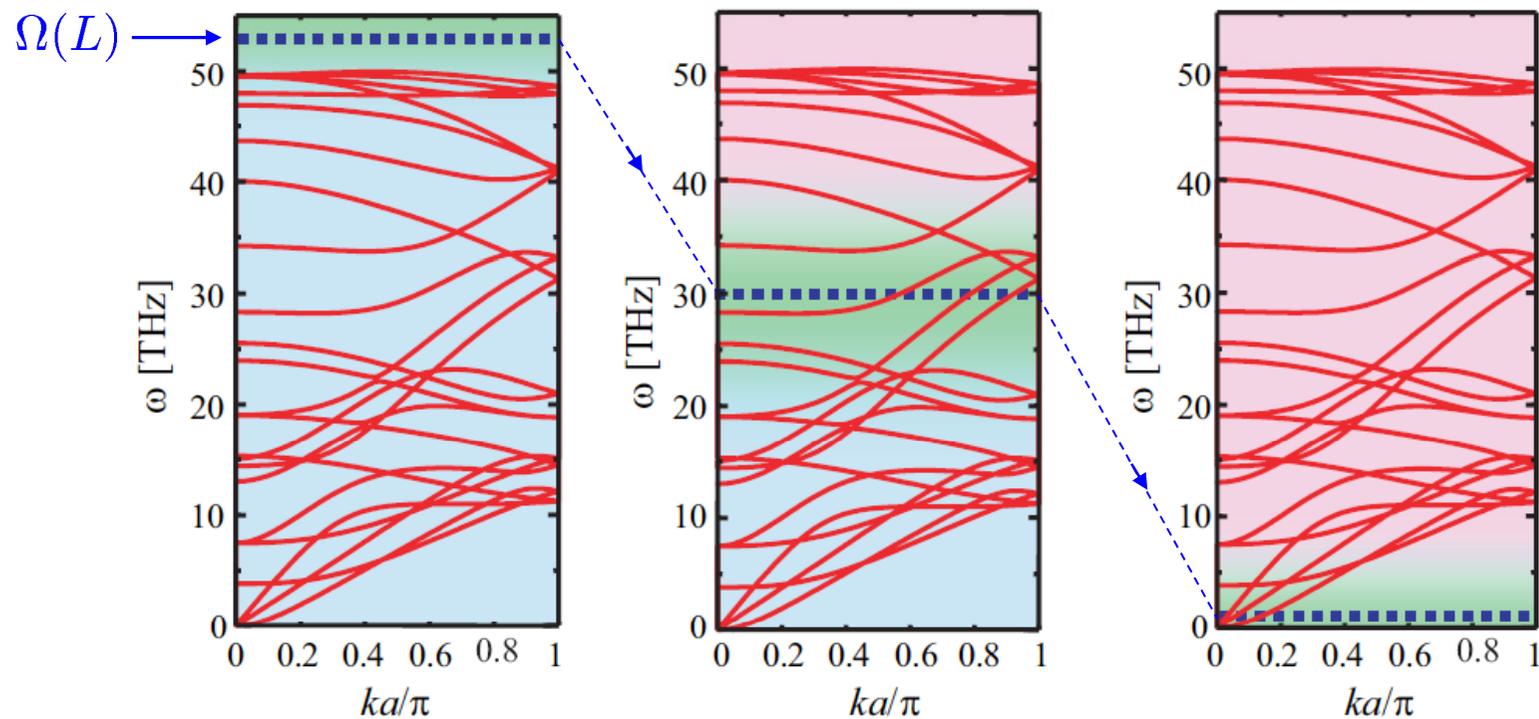


弾道フォノン伝導から拡散フォノン伝導への移行



Ballistic Regime Quasi-Ballistic Regime Diffusive Regime

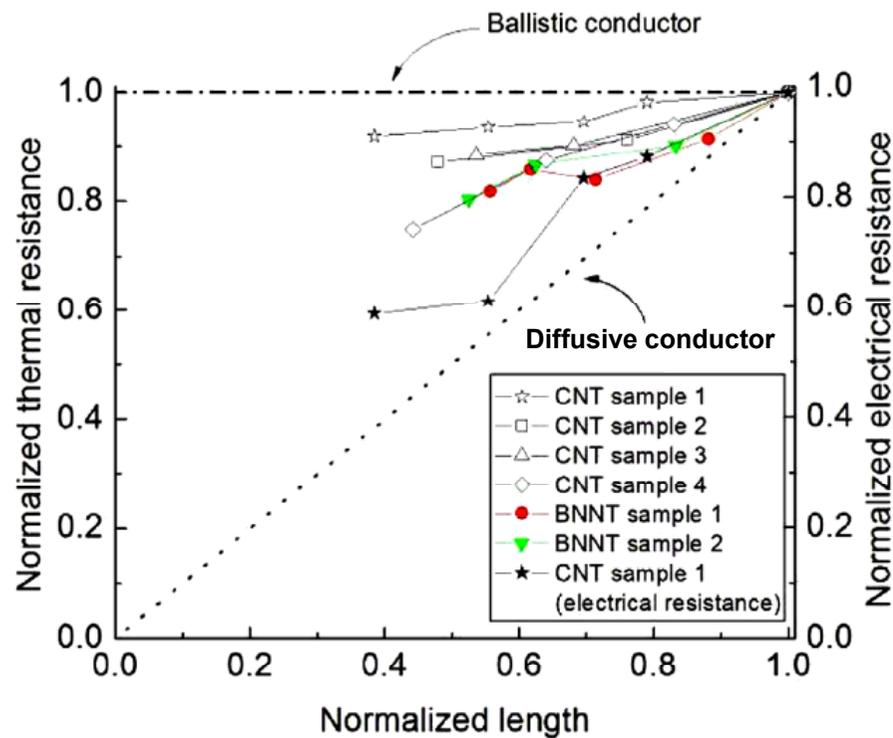
Short CNT nm μm mm Long CNT



実験：長さ依存性と直径依存性

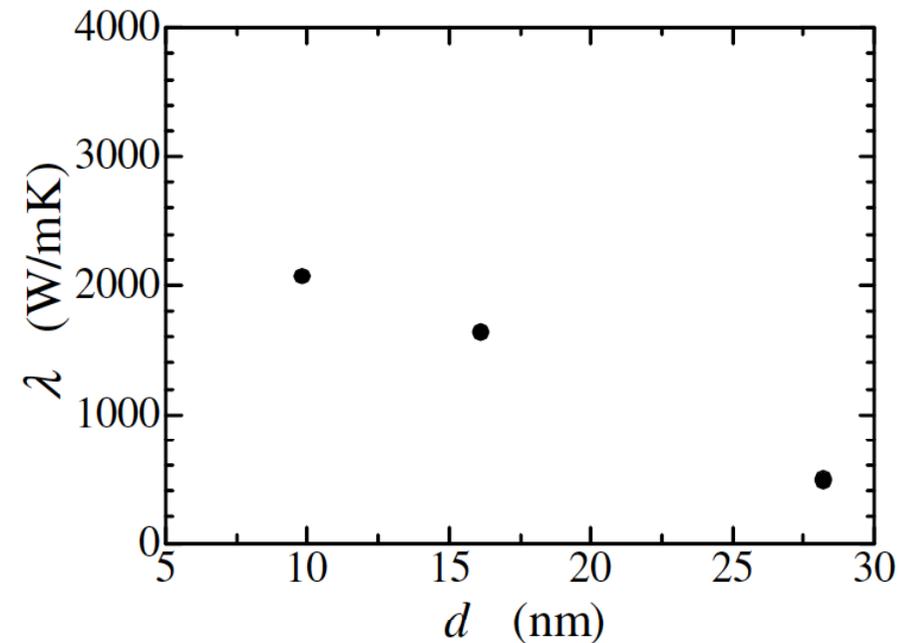


長さ依存性



Chang, et al., PRL **101**, 075903 (2008)
(UCバークレー・Majumdarグループ)

直径依存性



Fujii, et al., PRL **95**, 065502 (2005)
(九州大学・藤井グループ)

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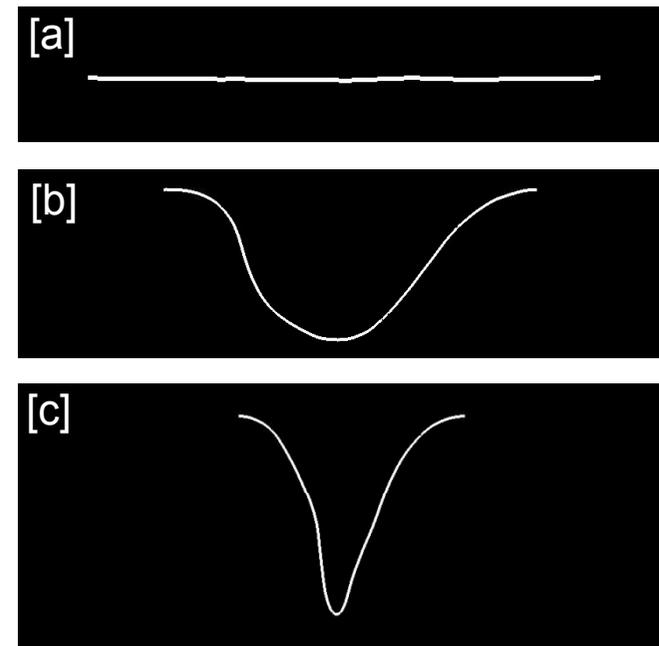
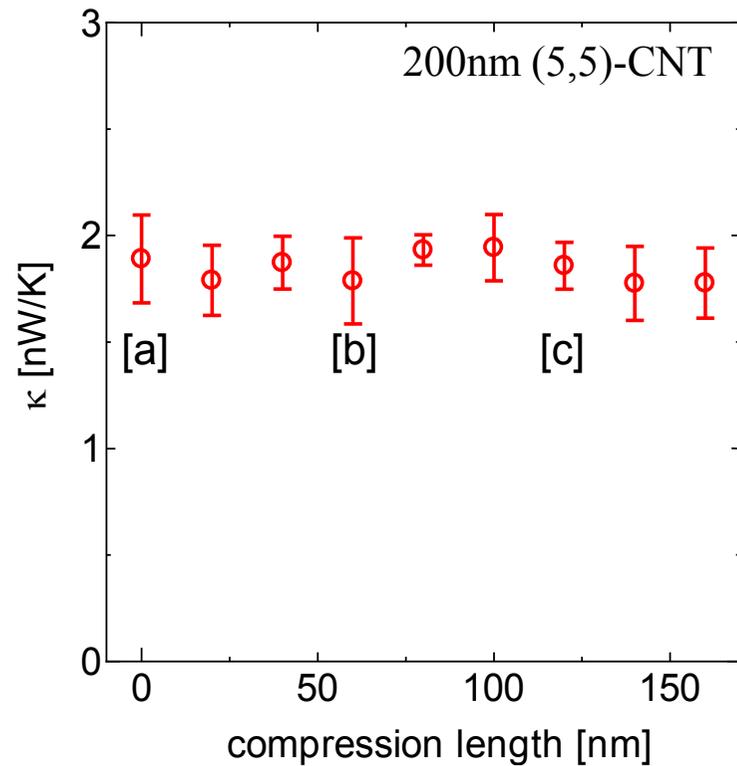
1 CNTにおける熱流の担い手：電子 vs フォノン

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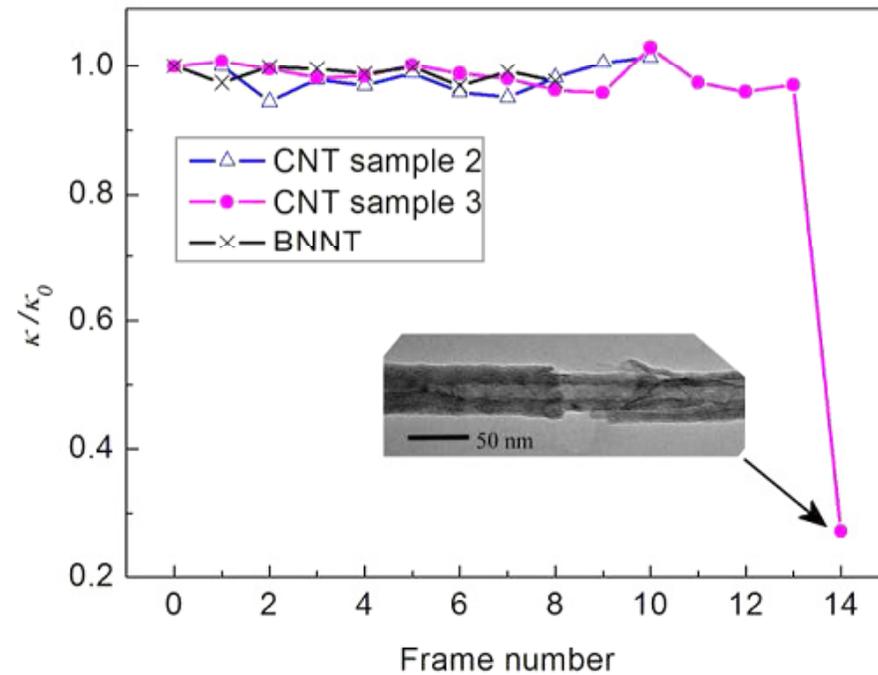
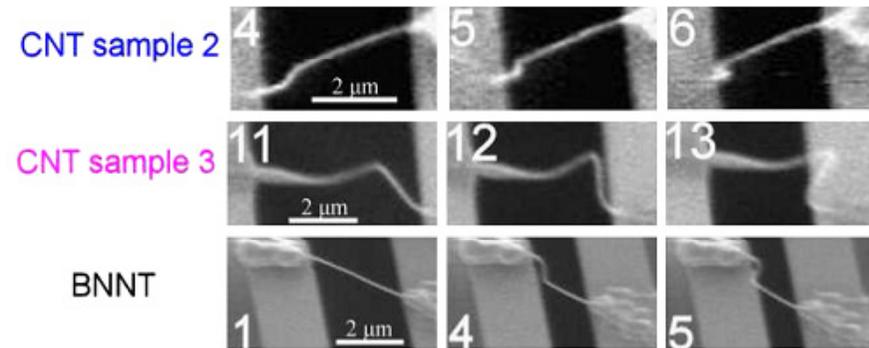
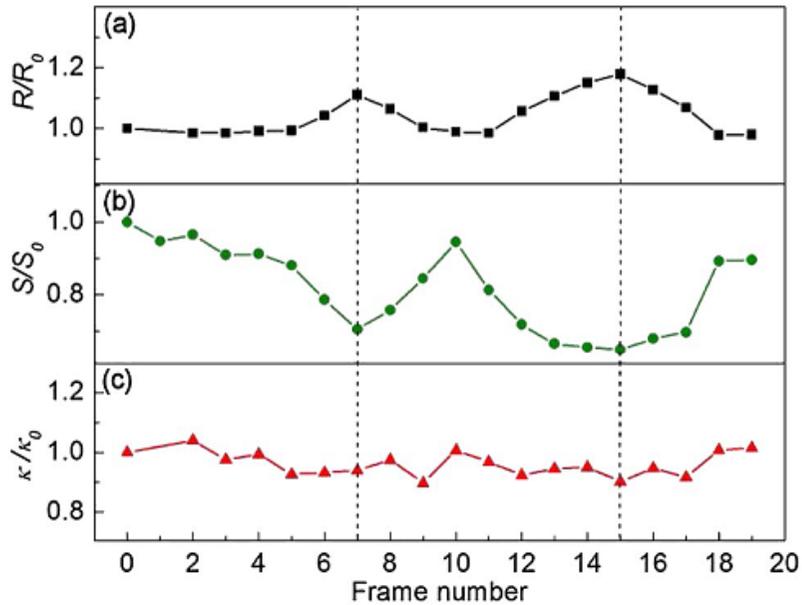
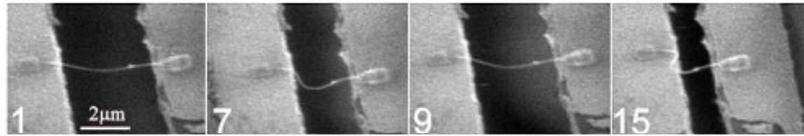
3 湾曲変形によるCNT熱伝導への影響

4 欠陥や不純物によるCNT熱伝導への影響

湾曲変形効果 (MDシミュレーション)



湾曲变形效果(实验)



外層切断による熱コンダクタンスの低下



● Pristine DWNT



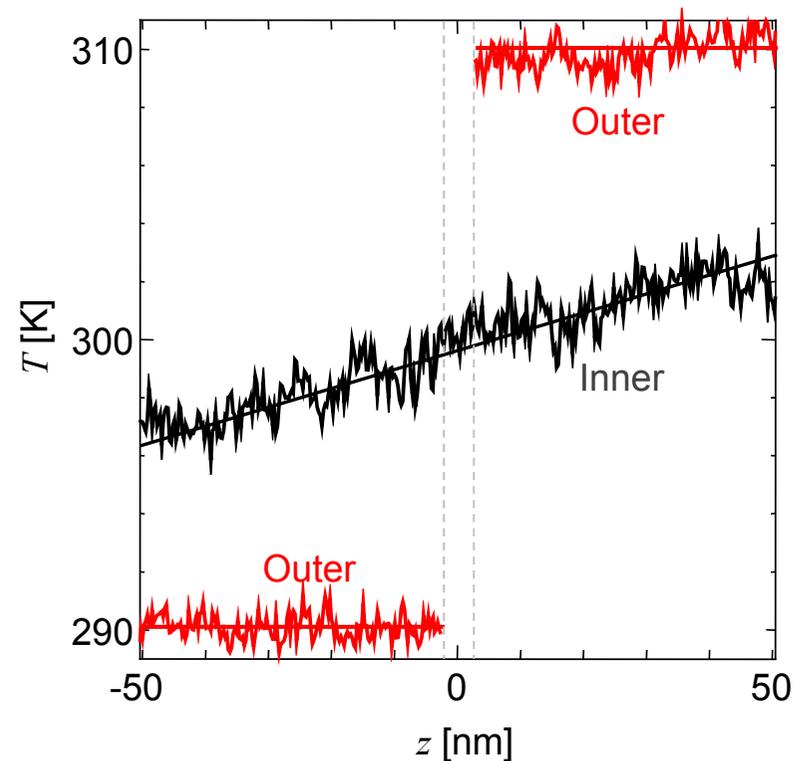
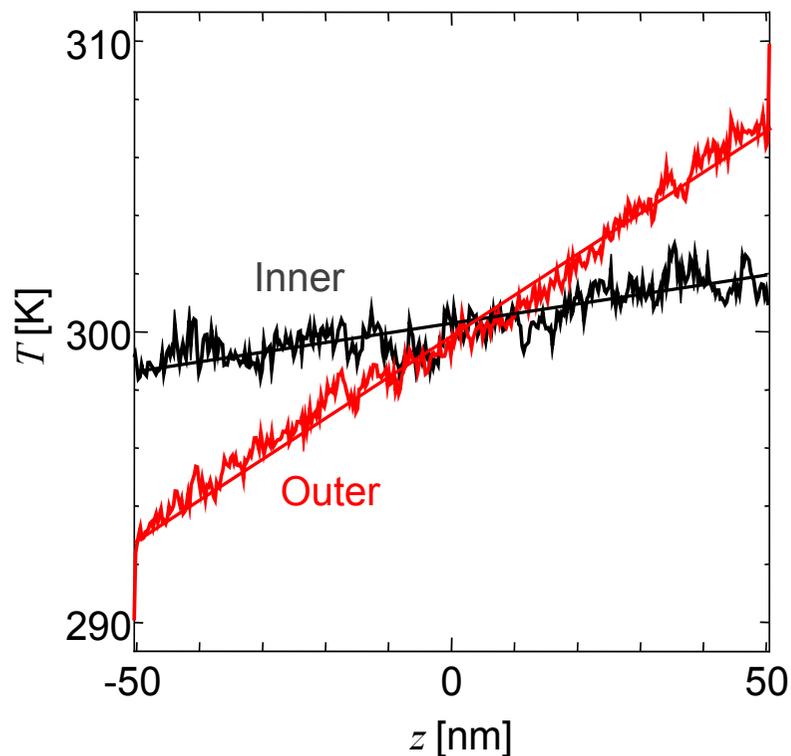
4.26 [nW/K]

Down to 20%

● Disconnected DWNT



0.86 [nW/K] ($\ll 1.87$ [nW/K])



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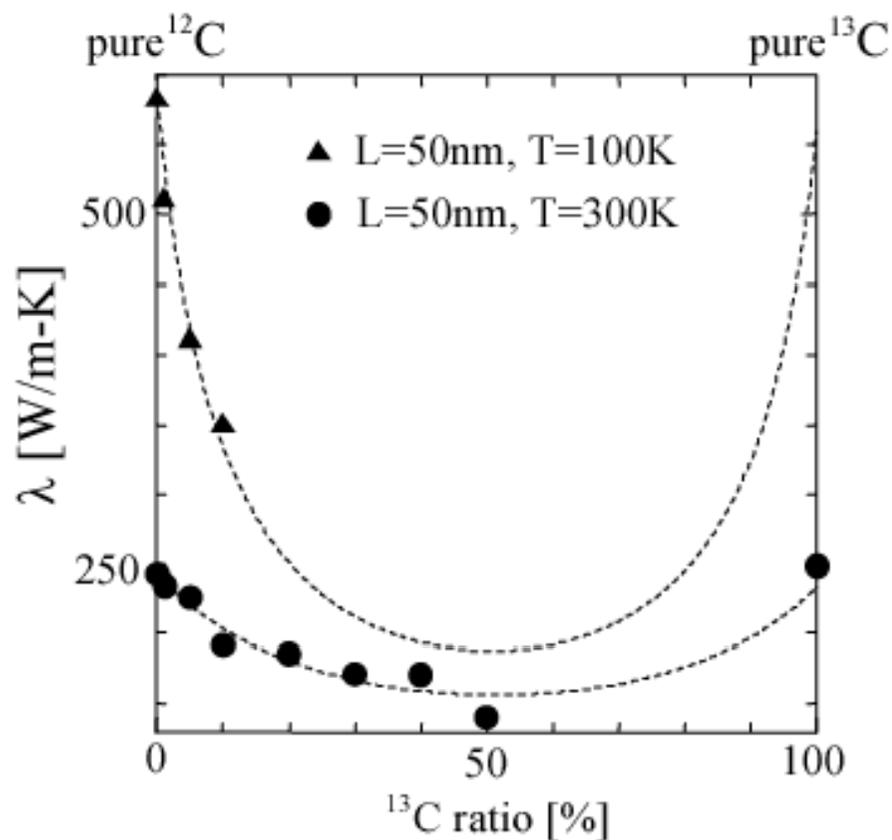
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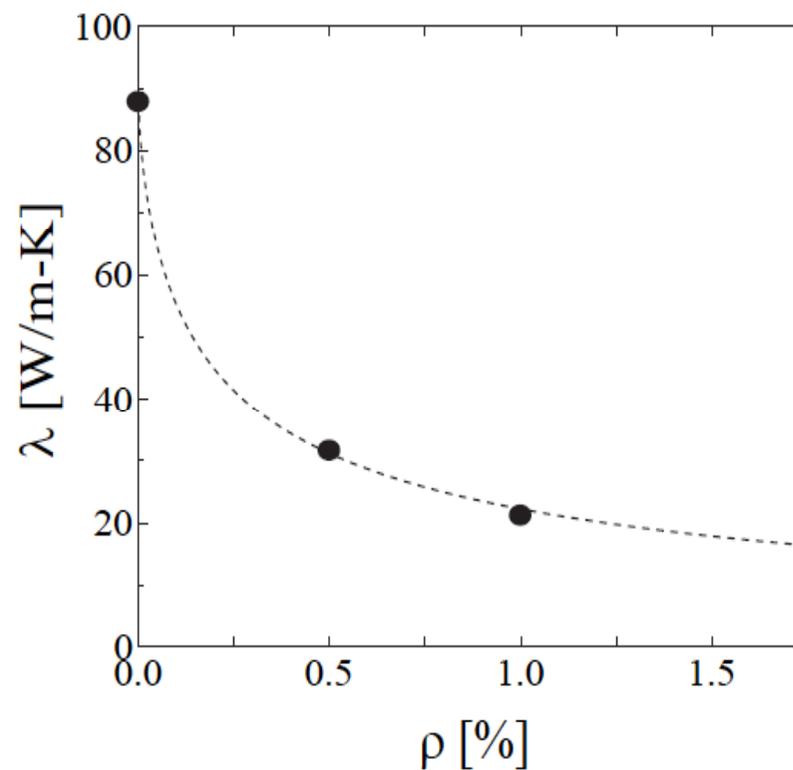
4 欠陥や不純物によるCNT熱伝導への影響

熱伝導率への不純物・欠陥効果 (MD計算)



熱伝導率の ^{13}C 同位体濃度依存性

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

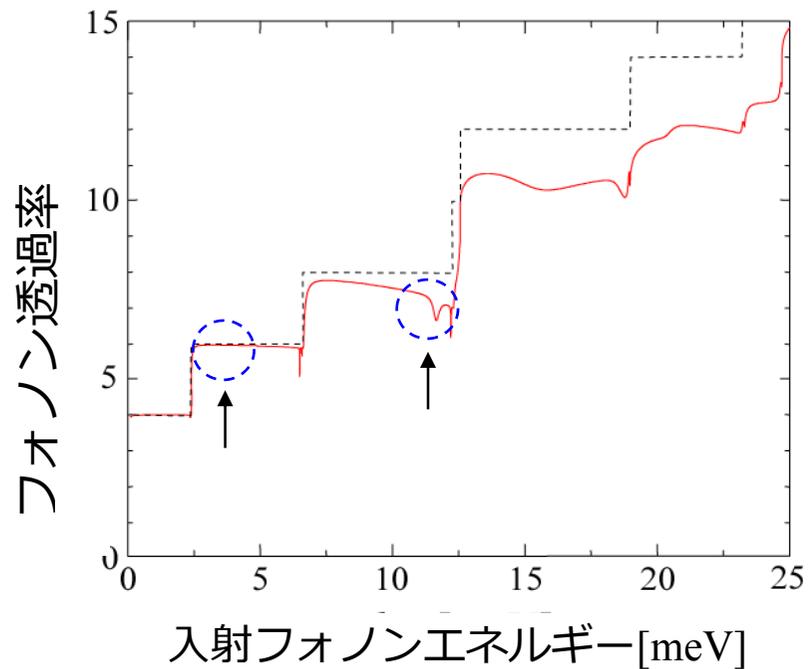
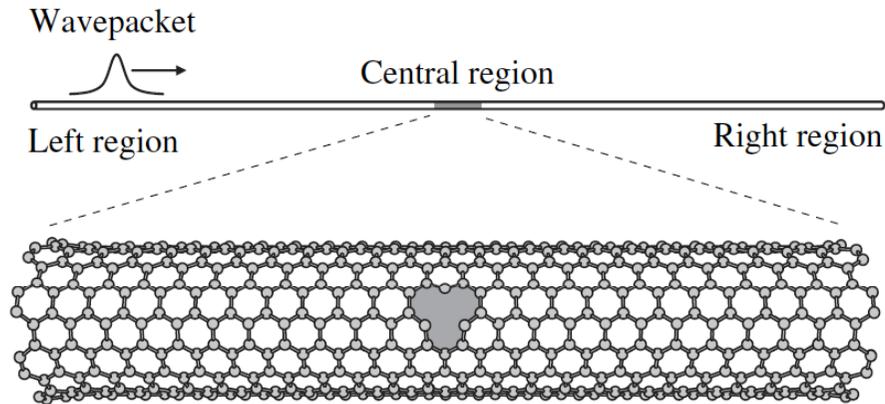


熱伝導率の原子空孔欠陥濃度依存性

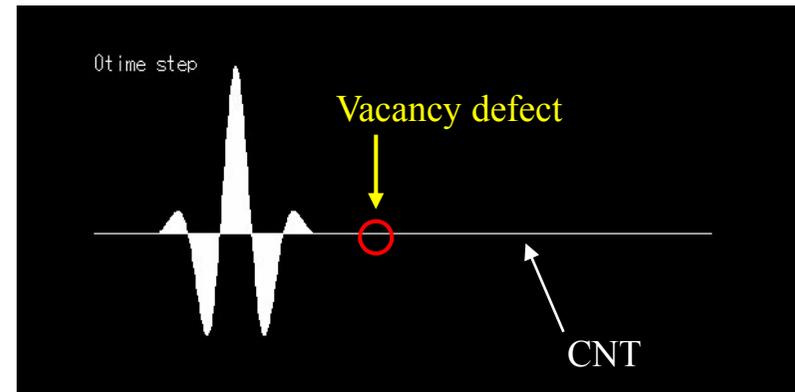
Kondo, Yamamoto, Watanabe,
e-JSSN 4, 239 (2006)

フォノン散乱シミュレーション

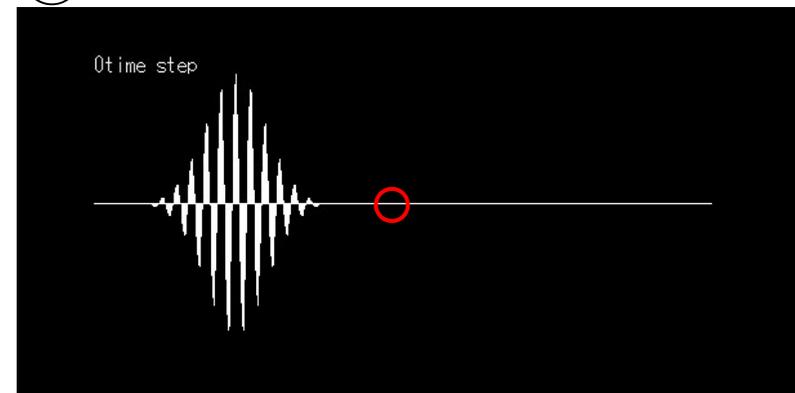
Kondo, Yamamoto, Watanabe: JJAP, 45, L963 (2006)



@ 3.0 meV



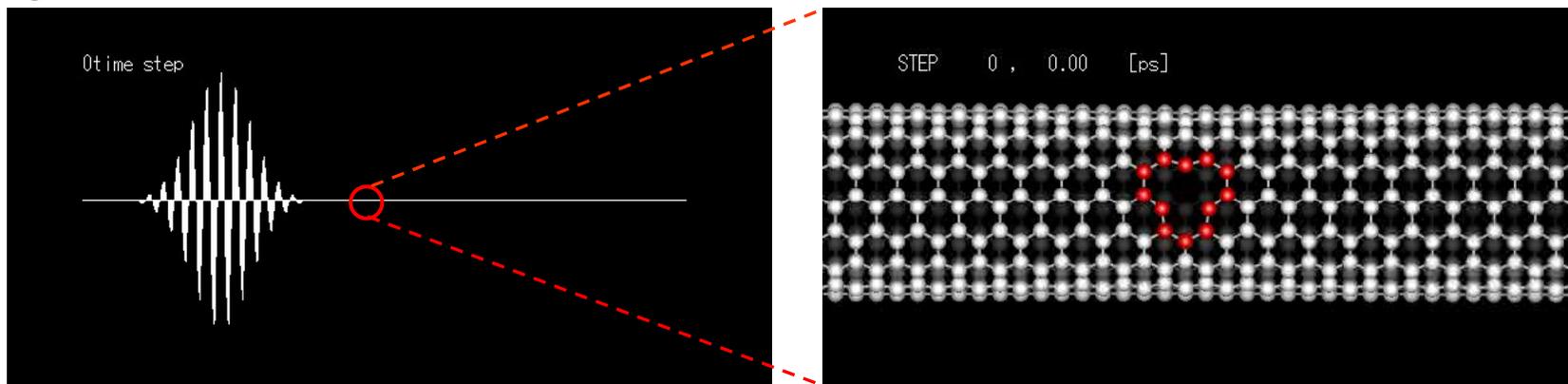
@ 11.6 meV



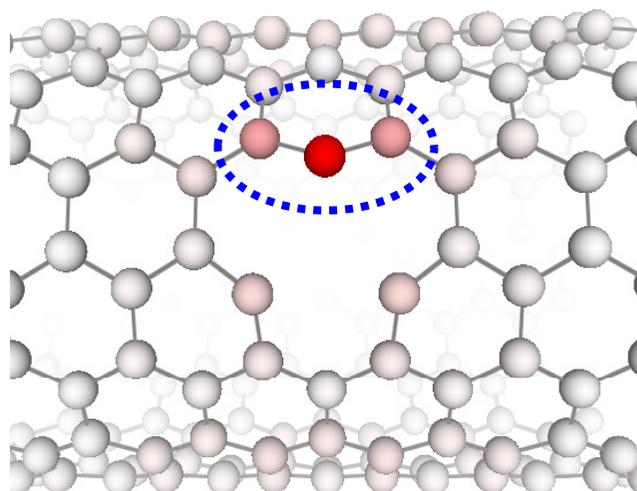
局在フォノンによる共鳴散乱



@ 11.6meV



$$\hbar\omega = 11.6 \text{ meV}$$



アニーリングによる構造変形

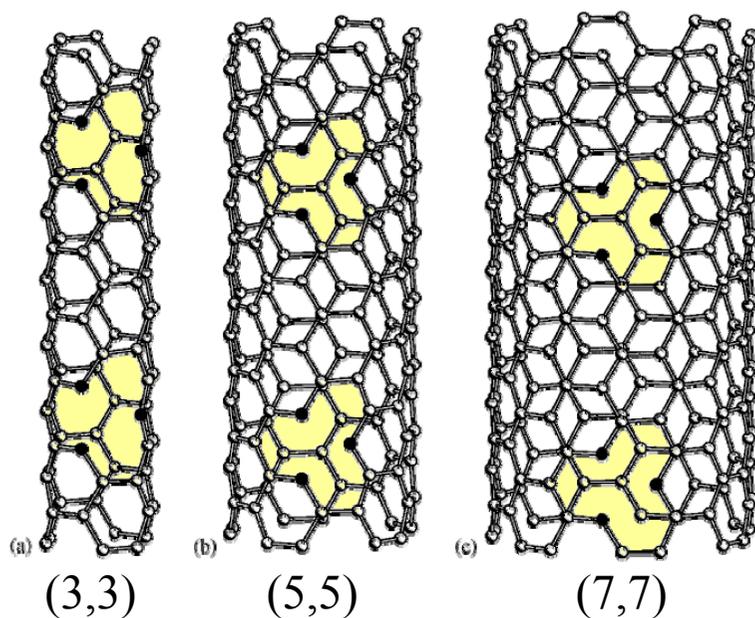
Miyamoto *et al.*, Physica B 323, 78 (2002)



■ Energy Gain due to Structural Change (DFT calculations)

Metastable State

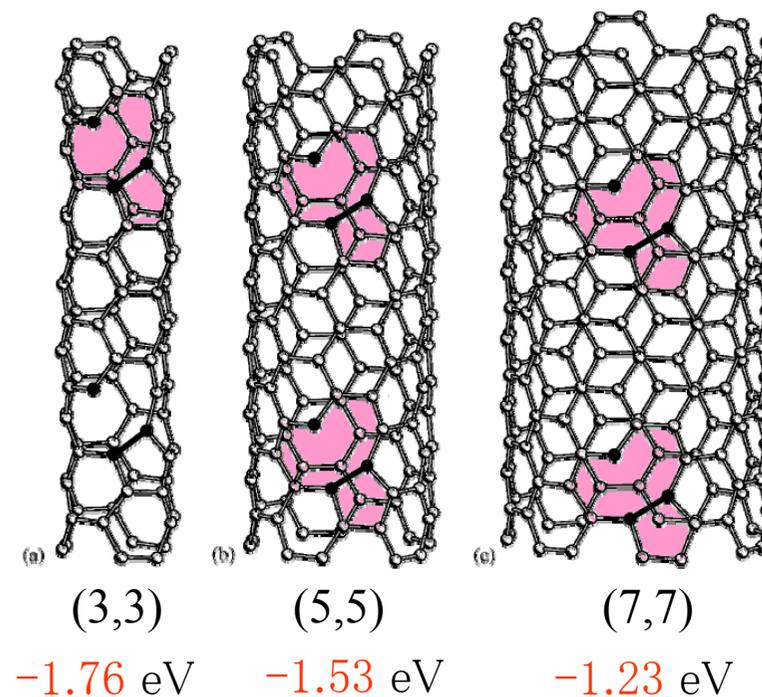
(Monatomic Vacancy)



Annealing
→

Stable State

(5-1db defect)



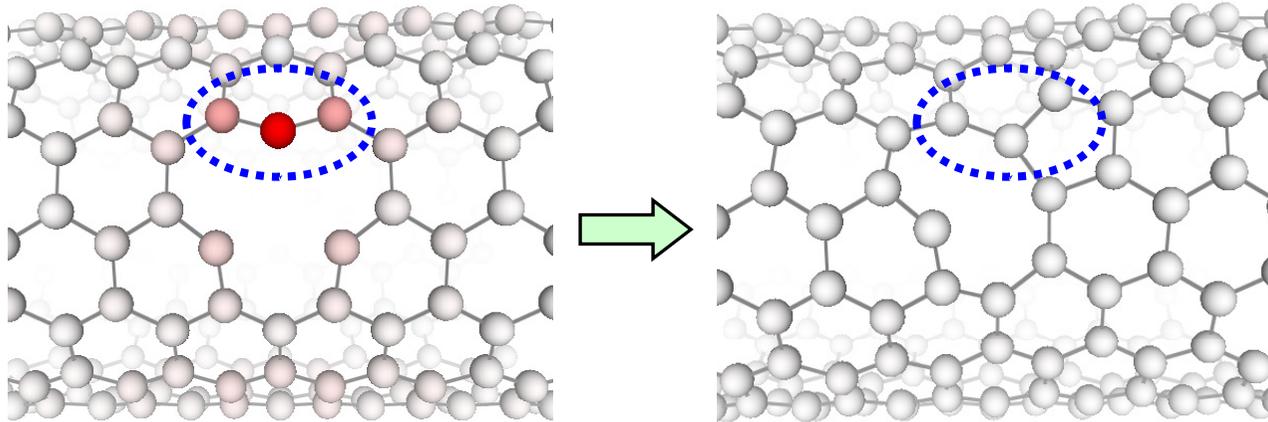
Energy gain more than 1 eV

アニーリングによる局在フォノンの消失

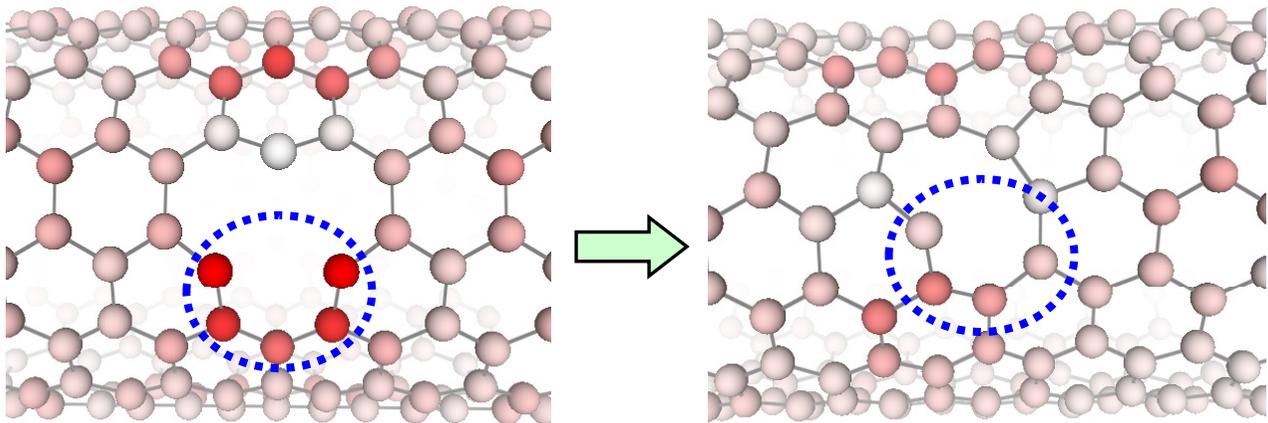


Yamamoto, Watanabe: Phys. Rev. Lett. 96, 255503 (2006)

$\hbar\omega=11.6$ meV



$\hbar\omega=18.5$ meV





カーボンナノチューブの熱伝導シミュレーション

1. 熱流の担い手

金属・半導体ナノチューブいずれもフォノンが支配的

2. 長さと半径依存性

細くて長いナノチューブほど熱伝導率が高い

3. 湾曲変形効果

折り曲げてても（6員環構造が壊れない限り）熱伝導率に影響はさほどない。

4. 欠陥・不純物効果

欠陥周辺の局在フォノンが熱抵抗の原因