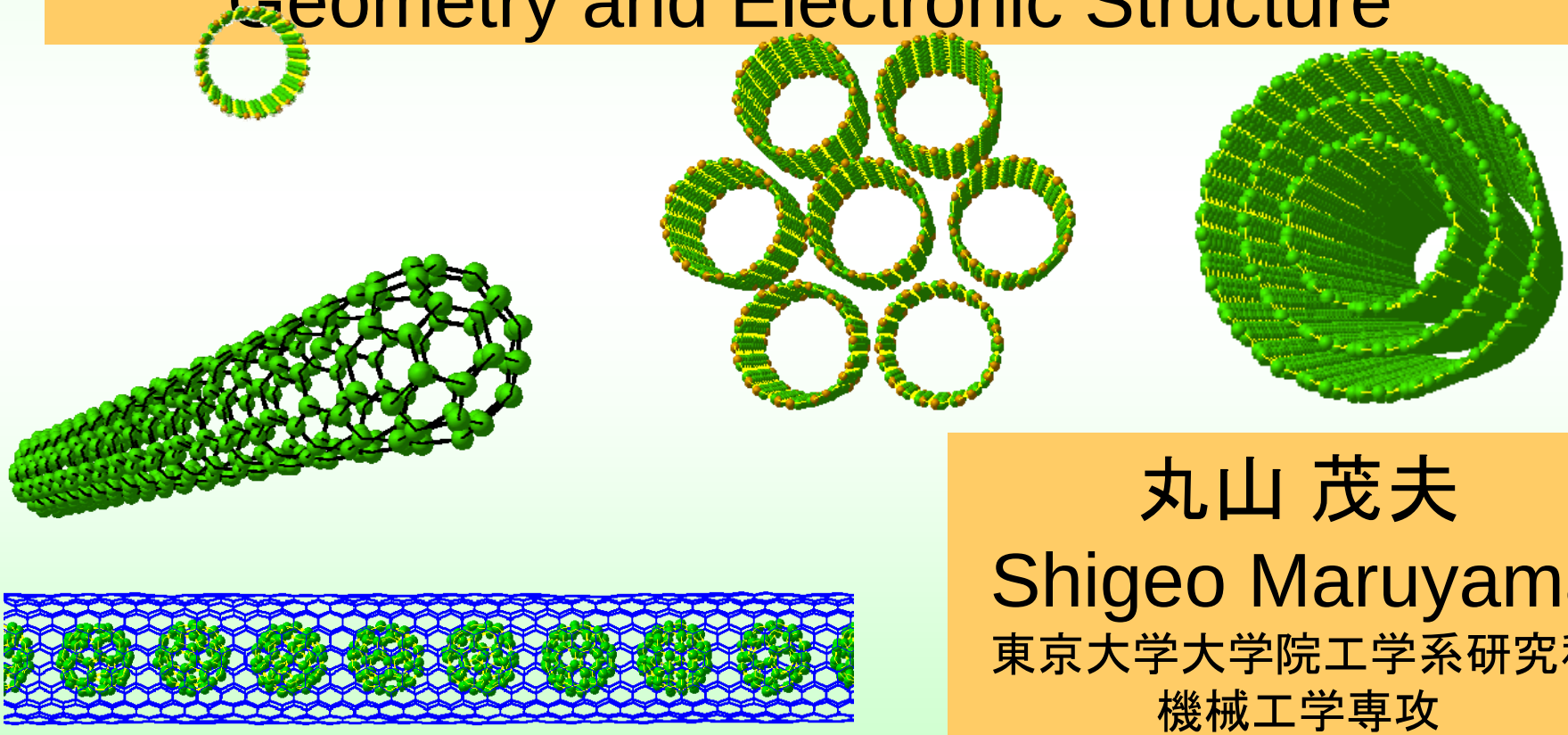
分子熱流体工学(Molecular Thermo-Fluid Engineering) 2013

単層カーボンナノチューブ
Single-Walled Carbon Nanotubes
1. 幾何学と電子構造
Geometry and Electronic Structure

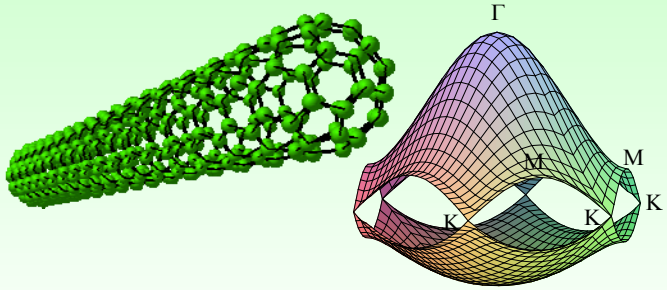


丸山 茂夫
Shigeo Maruyama
東京大学大学院工学系研究科
機械工学専攻

http://www.photon.t.u-tokyo.ac.jp

Contents

１．幾何学と電子構造
Geometry & Electronic Structure



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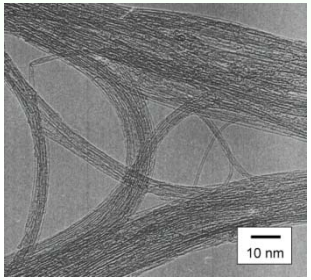

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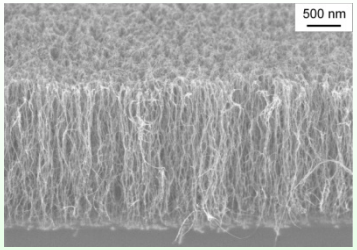

４．ナノチューブの伝熱
Heat Transfer

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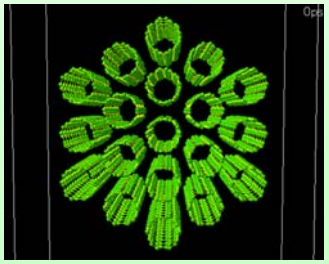
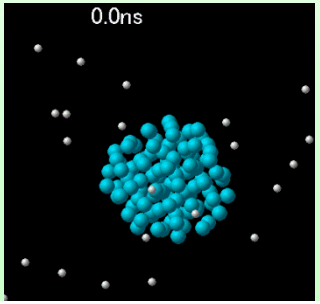
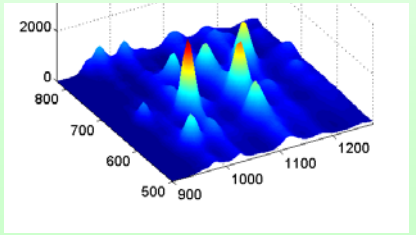
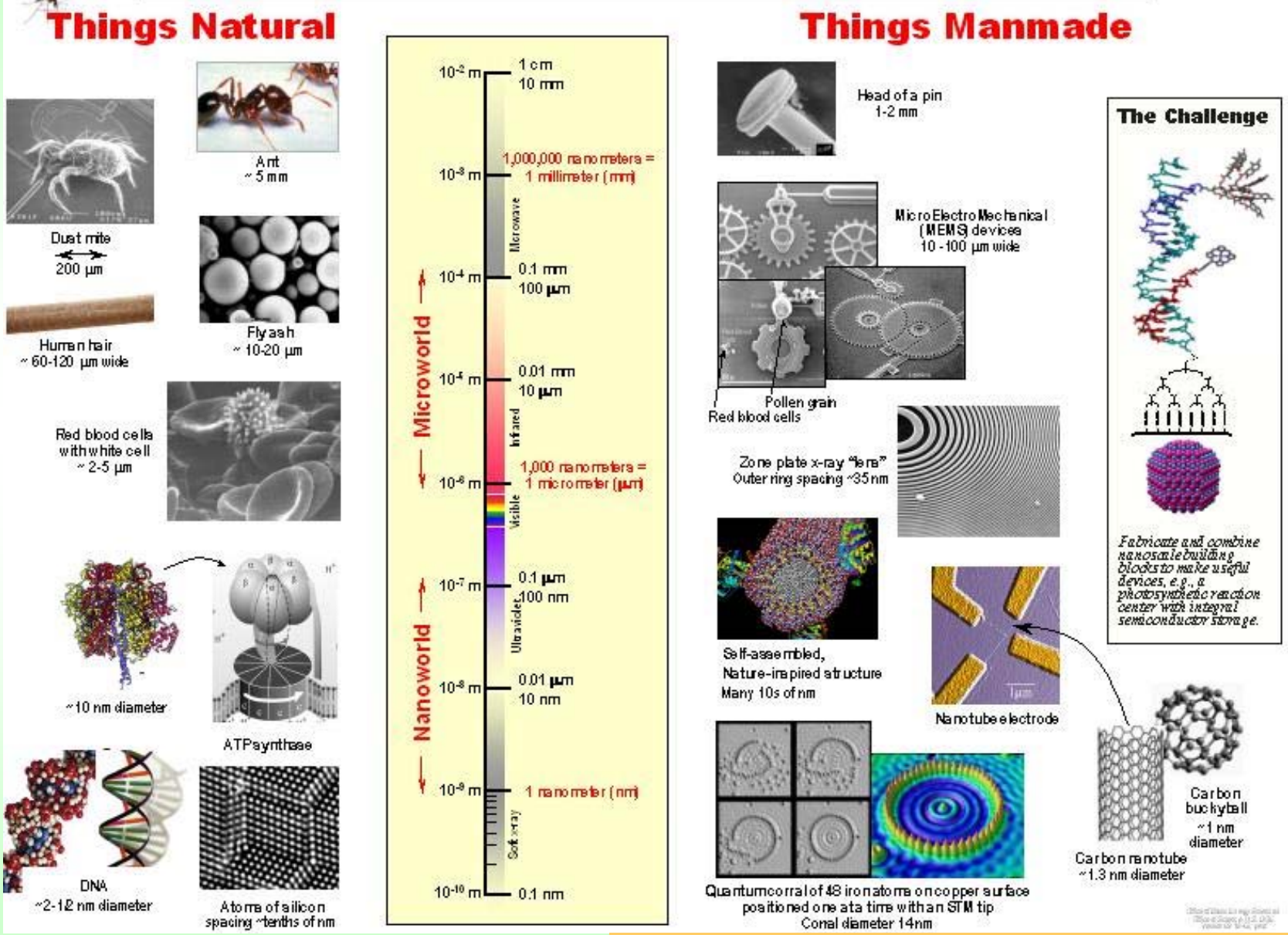


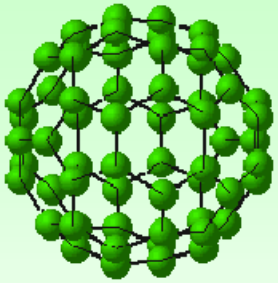




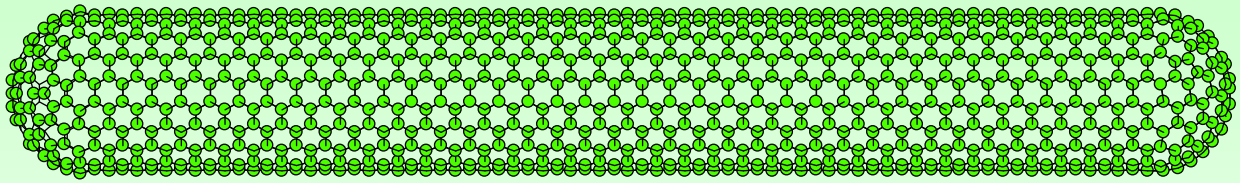
Nanometer Scale



from NNI Home Page: http://www.nano.gov

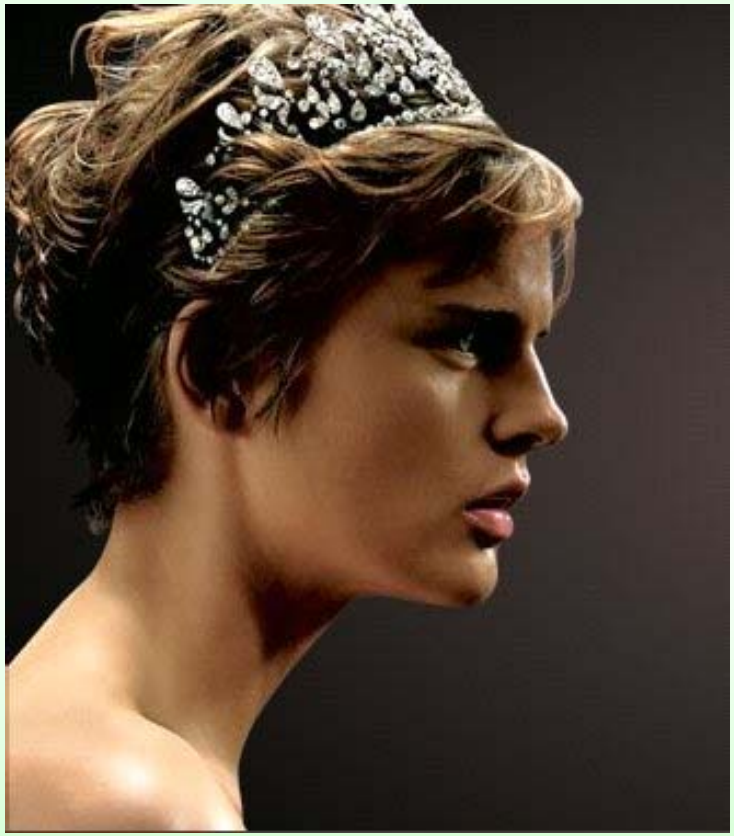


0-D: Fullerene



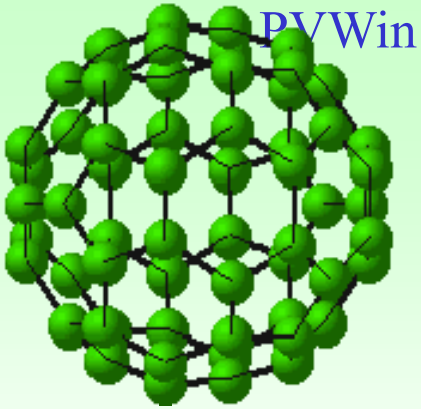
1-D: Carbon Nanotube

Graphite

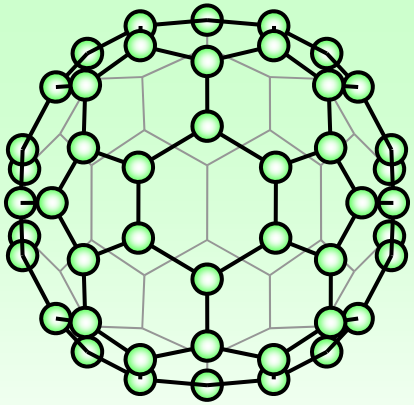


Diamond (from CHAUMET Paris HP)

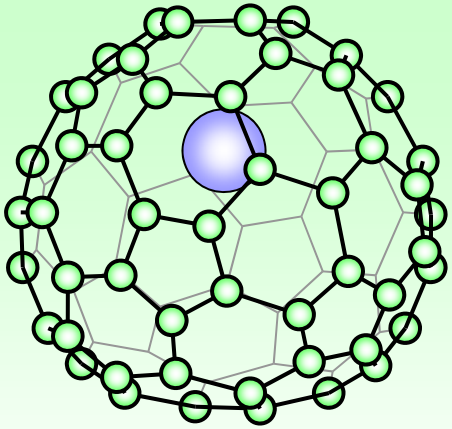
Allotropes of Carbon



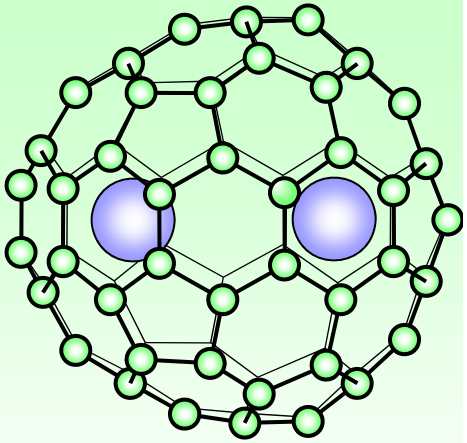
(a) C_{60}



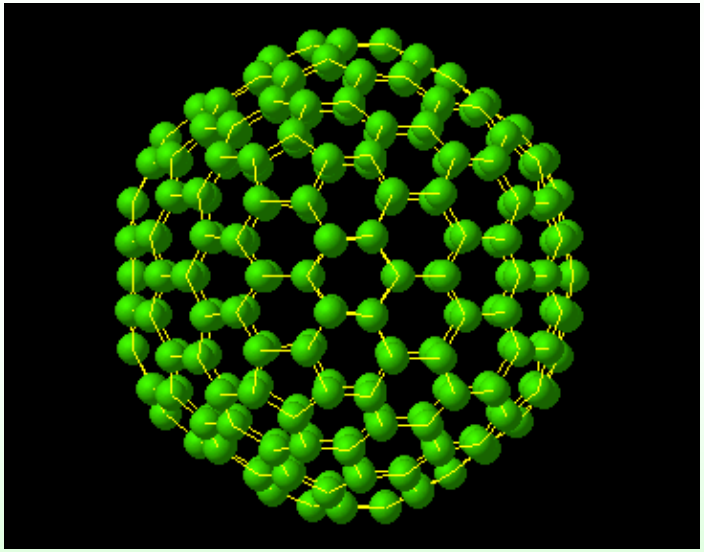
(b) C_{70}



(c) $La@C_{82}$

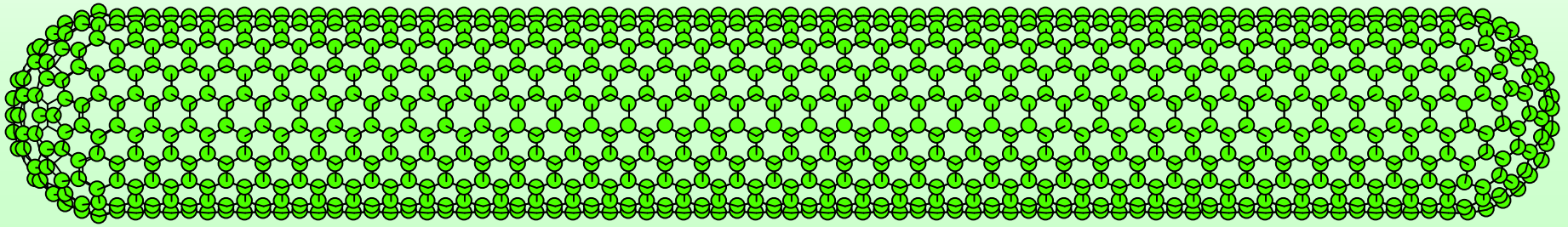


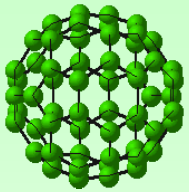
(d) $Sc_2@C_{84}$



(e) C_{240}

Fullerene Structures





ノーベル
化学賞
（1996）

C_{60}のアイデア: 大澤(1975)

フラーレンの発見: Smalley, Kroto & Curl (1985)

フラーレンの量的生成: Krätschmer & Huffman(1990)

フラーレンの超伝導の発見: Hebard(1991)

ナノチューブの生成: 飯島(1991)

金属内包フラーレンの量的生成: Smalley (1991)

単層ナノチューブの量的生成: Smalley (1996)

~~電子ドープ超伝導: Batlog (2000)~~ ？？

フラーレンの発見

BuckminsterFullerene

BuckminsterFullerene

Euler's Theorem

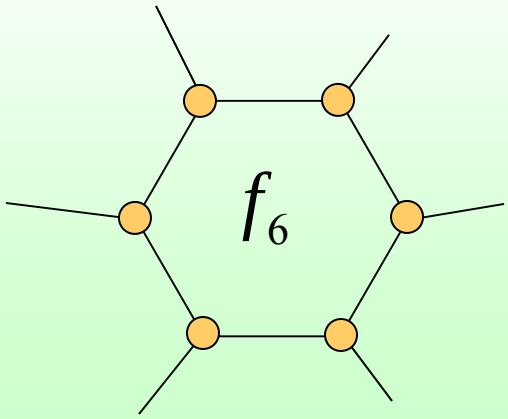
Euler's Theorem: $f + v = e + 2$

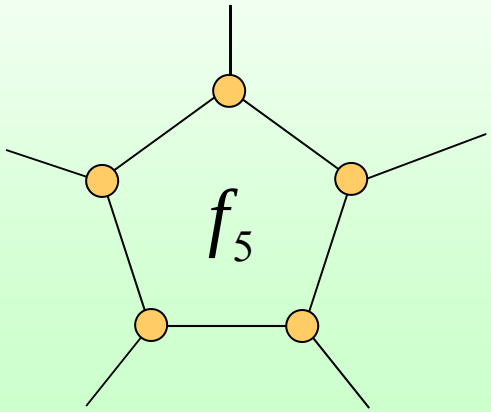
f: faces, *v*: vertices, *e*: edges

Usual Explanation of Even Numbered Positive Spectra

$$f = f_5 + f_6$$

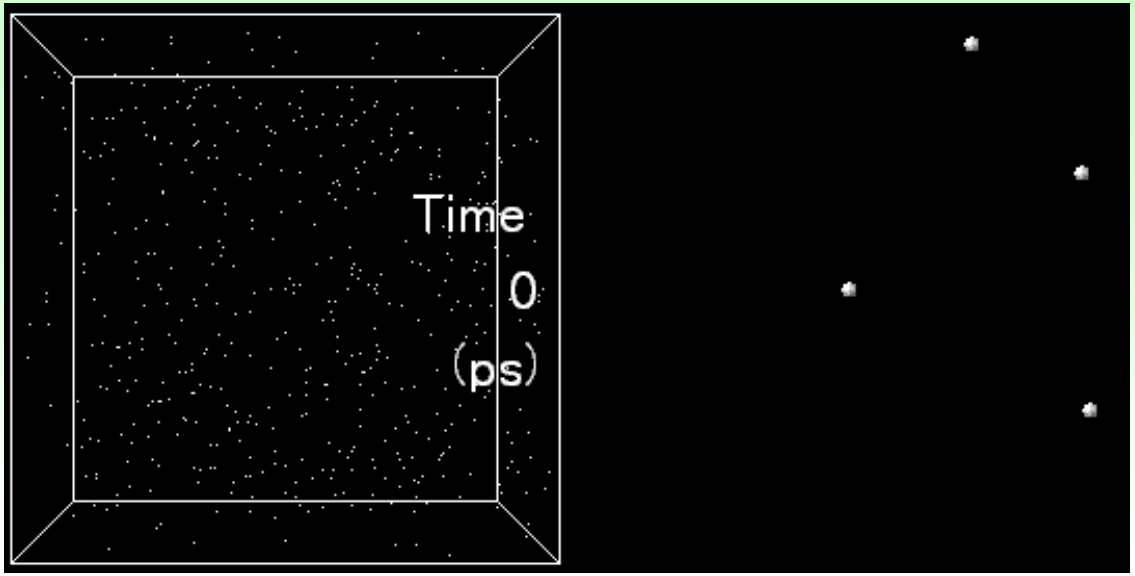
$$\begin{cases} 2e = 5f_5 + 6f_6 \\ 3v = 5f_5 + 6f_6 \end{cases} \Rightarrow \begin{cases} f_5 = 12 \\ v = 20 + 2f_6 \end{cases}$$

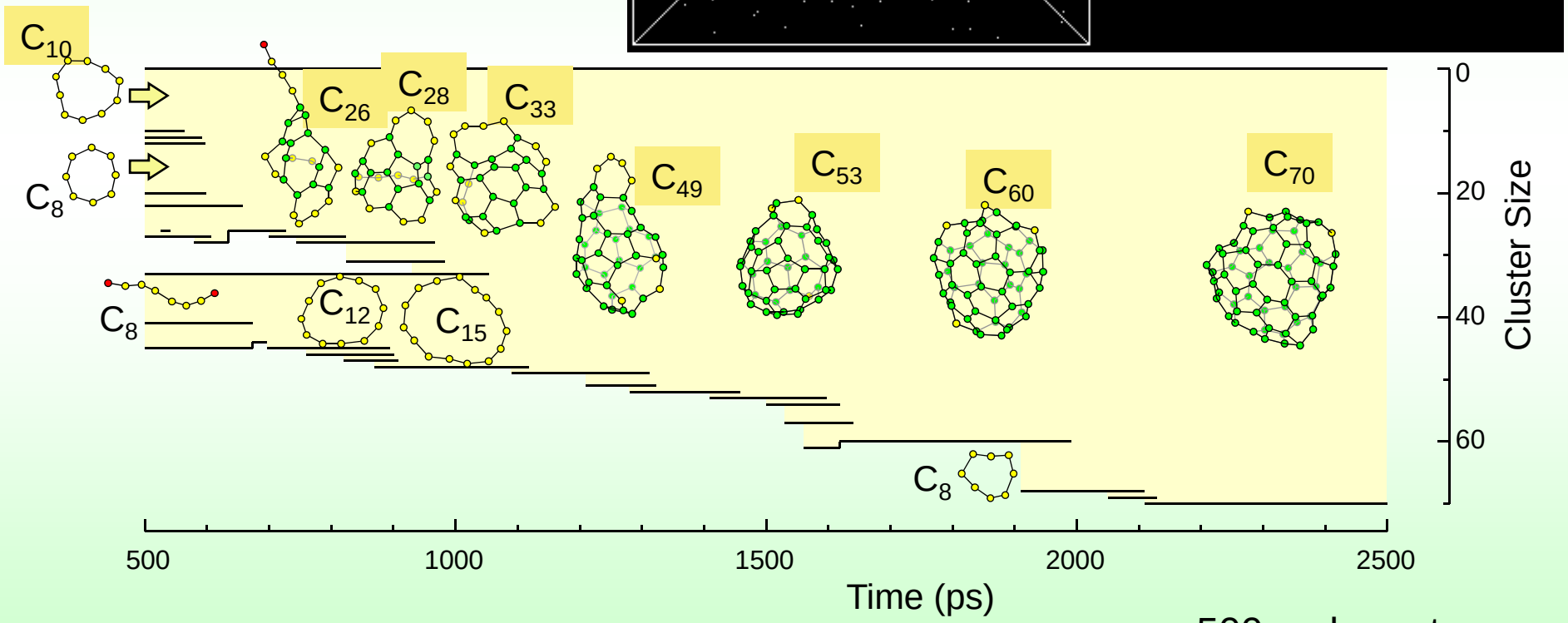




PVWin

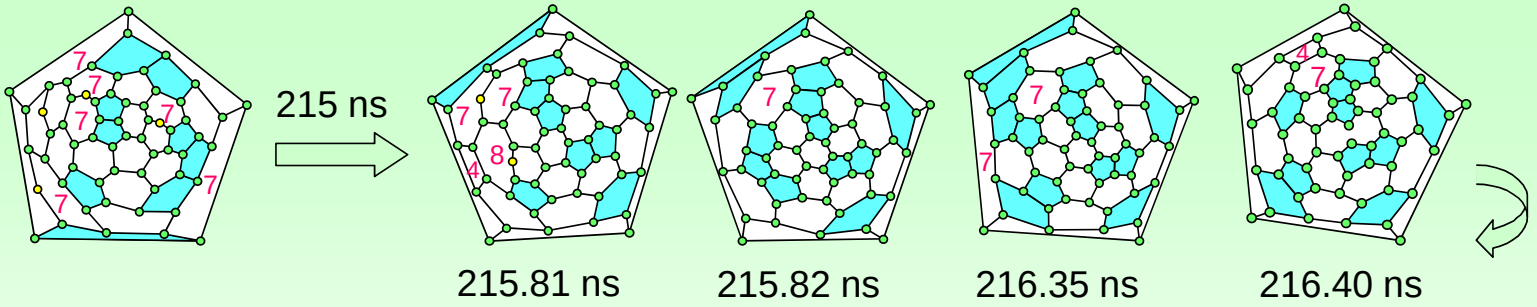
Growth Process of Fullerene

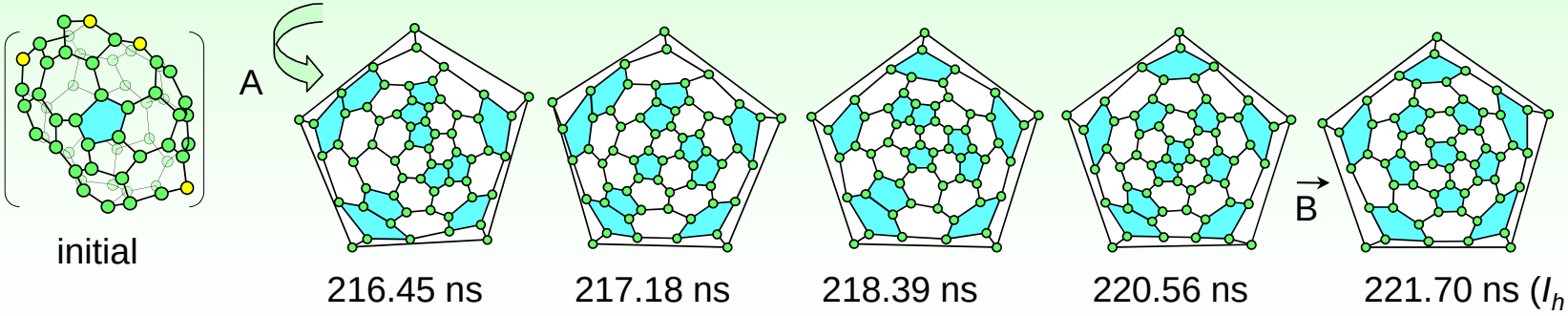


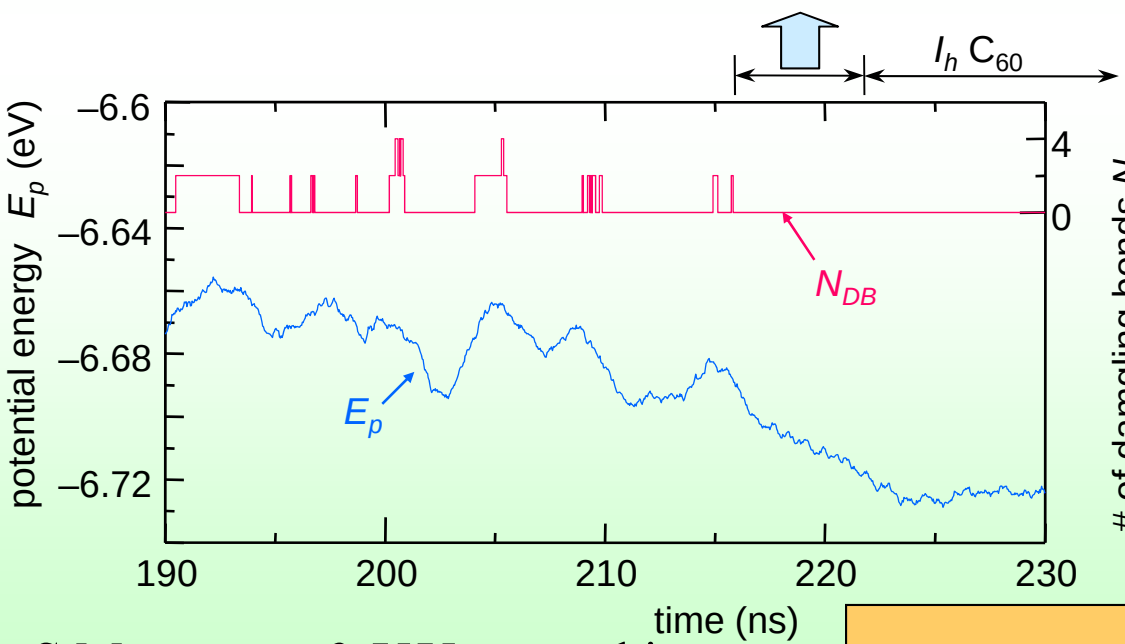


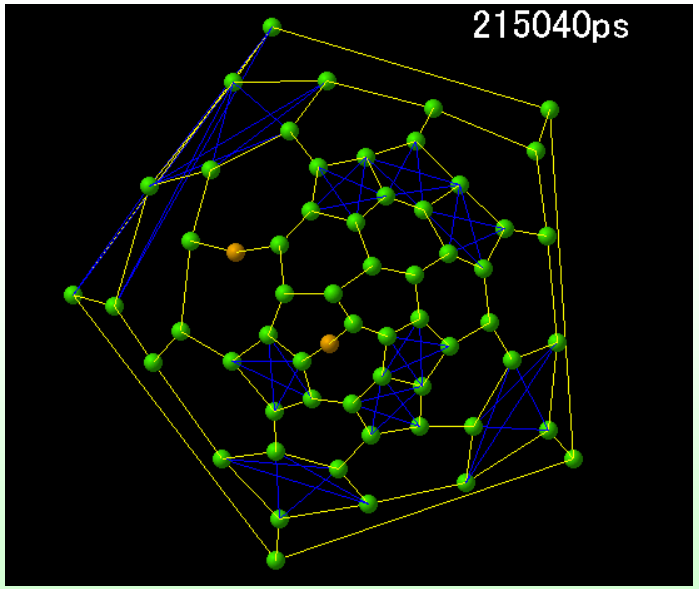
Y.Yamaguchi & S.Maruyama,
Chem. Phys. Lett., **286**, 336 (1998).

500 carbon atoms
342 Å cubic box
T_c = 3000 K



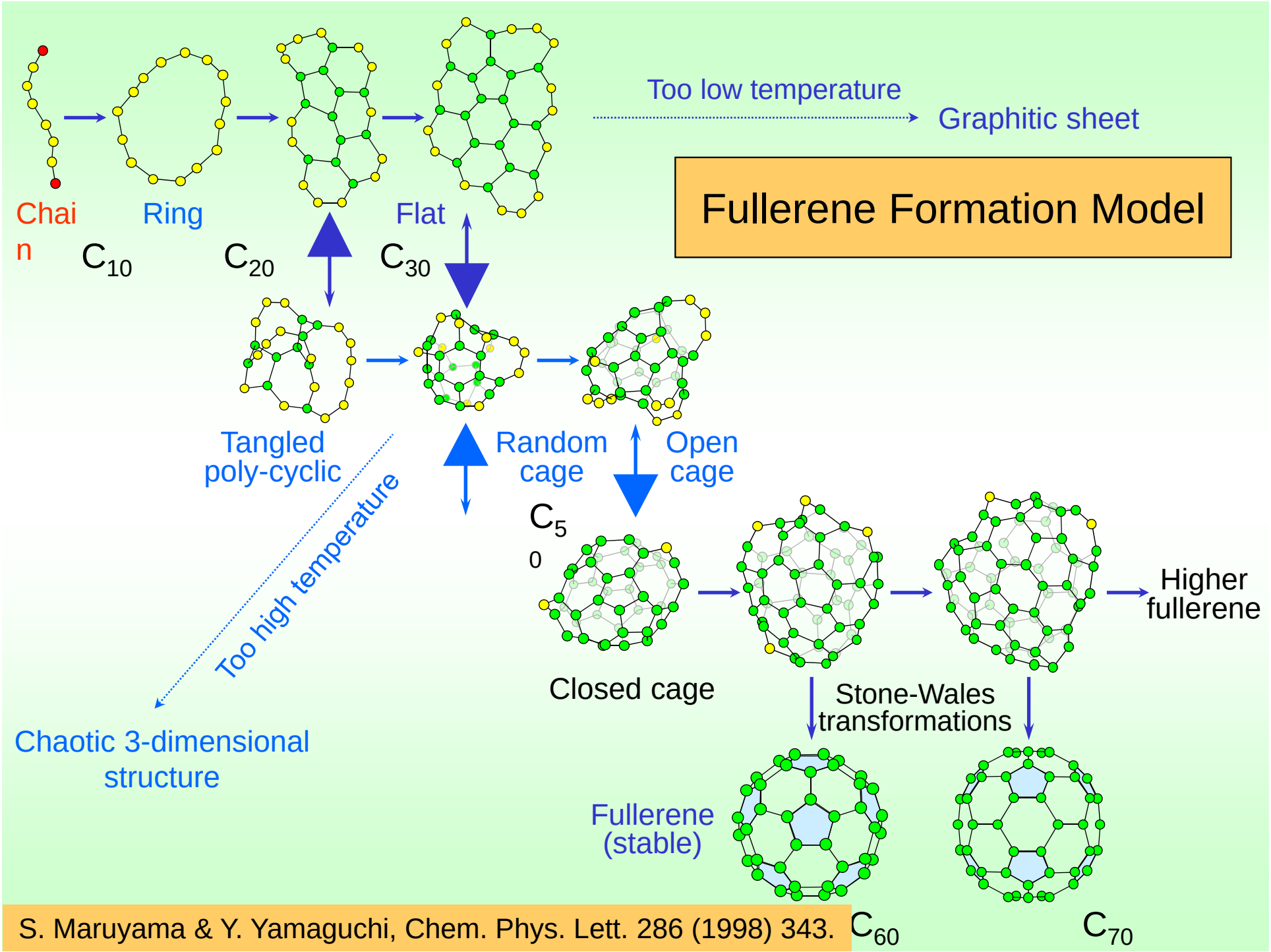




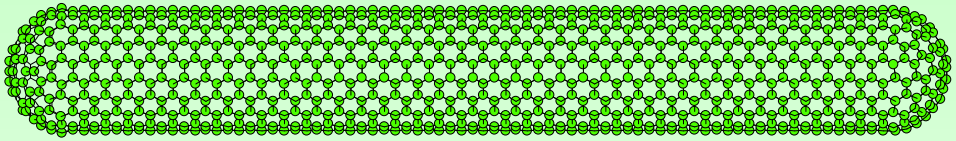


S.Maruyama & Y.Yamaguchi,
Chem. Phys. Lett., **286**, 343 (1998).

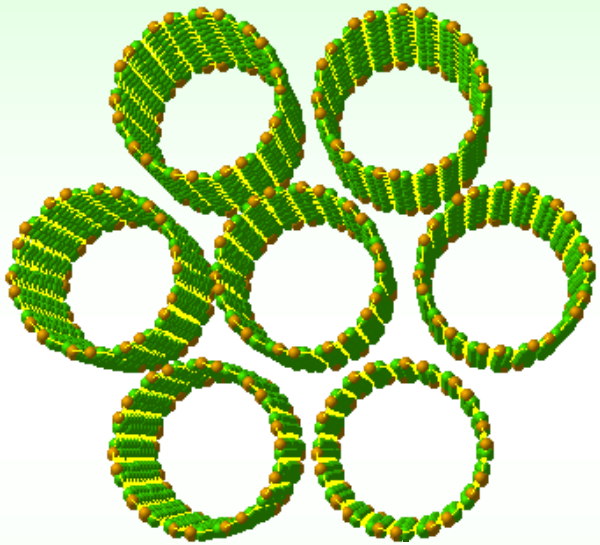
Annealing Process to perfect C_{60}

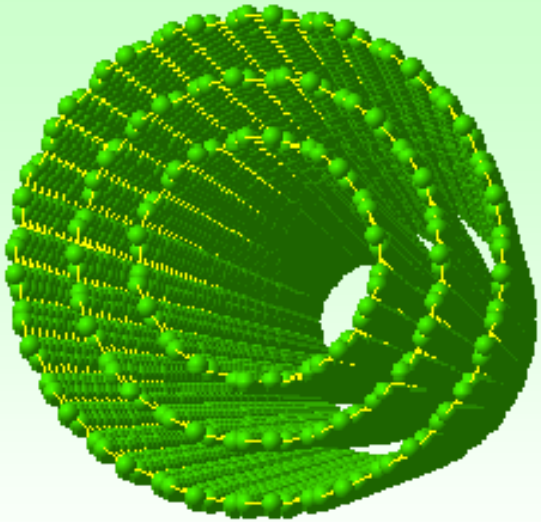


S. Maruyama & Y. Yamaguchi, Chem. Phys. Lett. 286 (1998) 343.

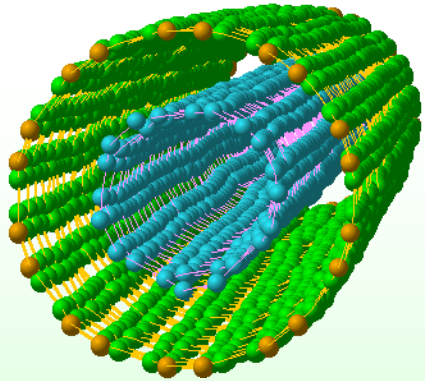


Single-Walled Carbon Nanotube, SWNT

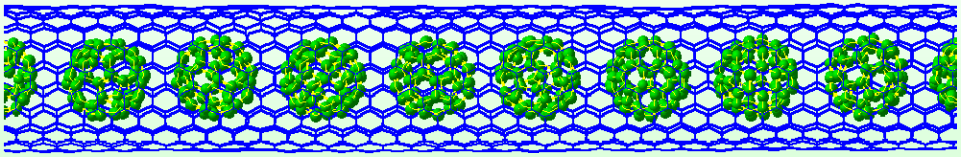




Multi-Walled Carbon Nanotubes
MWNT



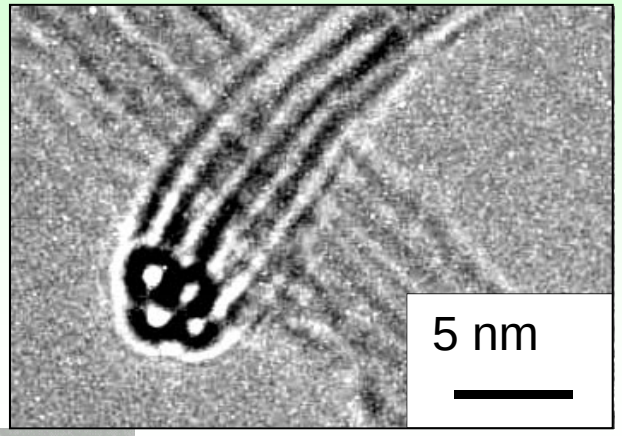
Double-Walled Carbon Nanotubes
DWNT



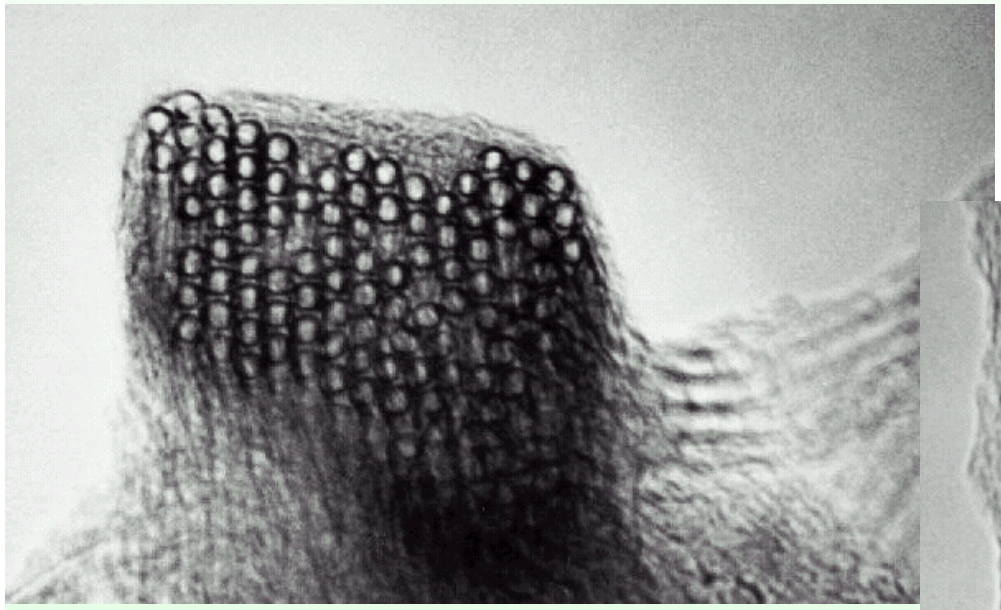
Peapod

Carbon Nanotubes

TEM Pictures of SWNT Ropes



By ACCVD

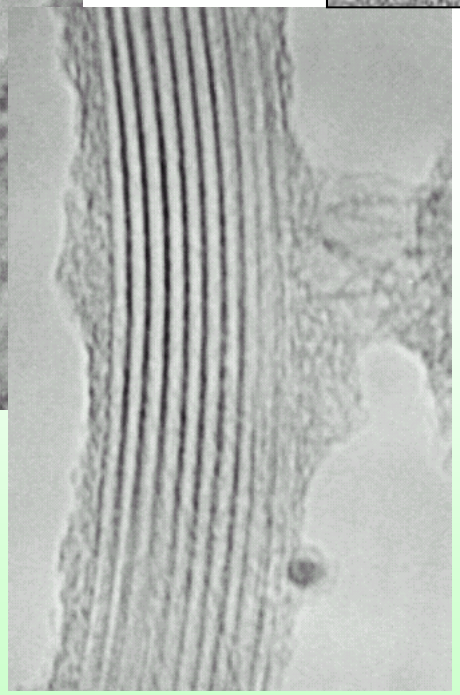


About 100 SWNTs

Individual tube diameter: 1.3 nm

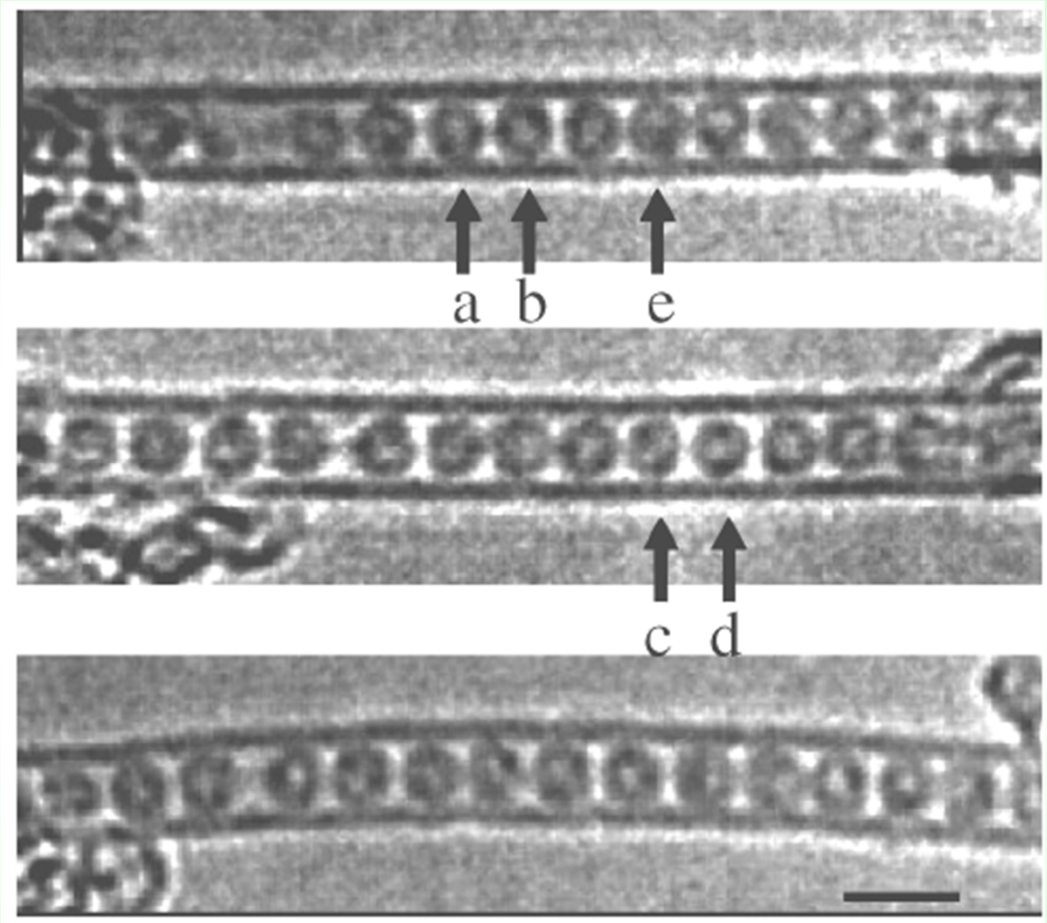
Spacing: 0.34 nm

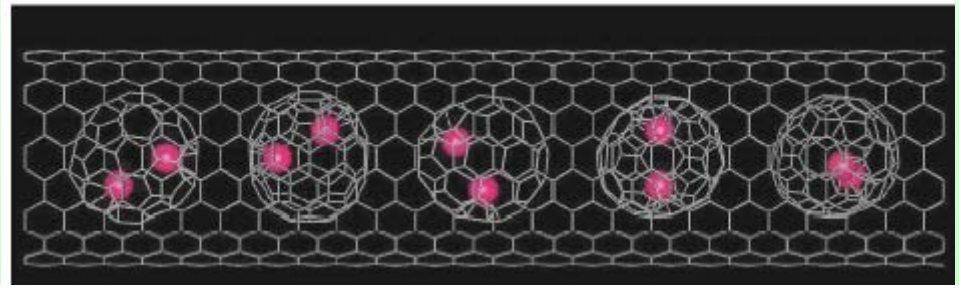
Misalignments and Terminations



TEM from Smalley et al. at Rice University

Peapods

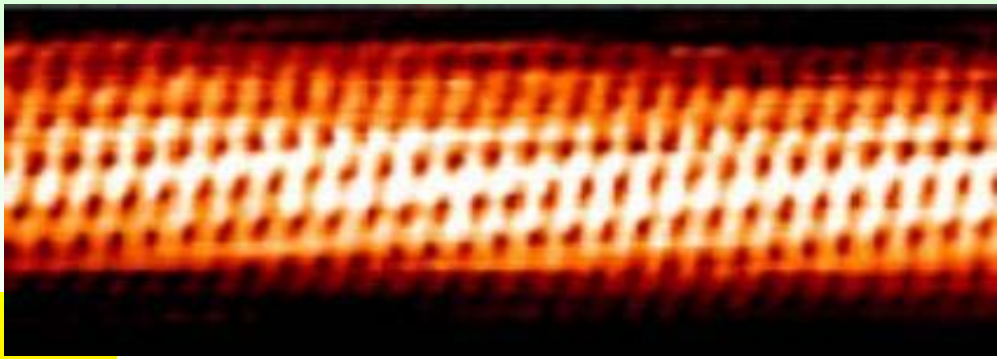


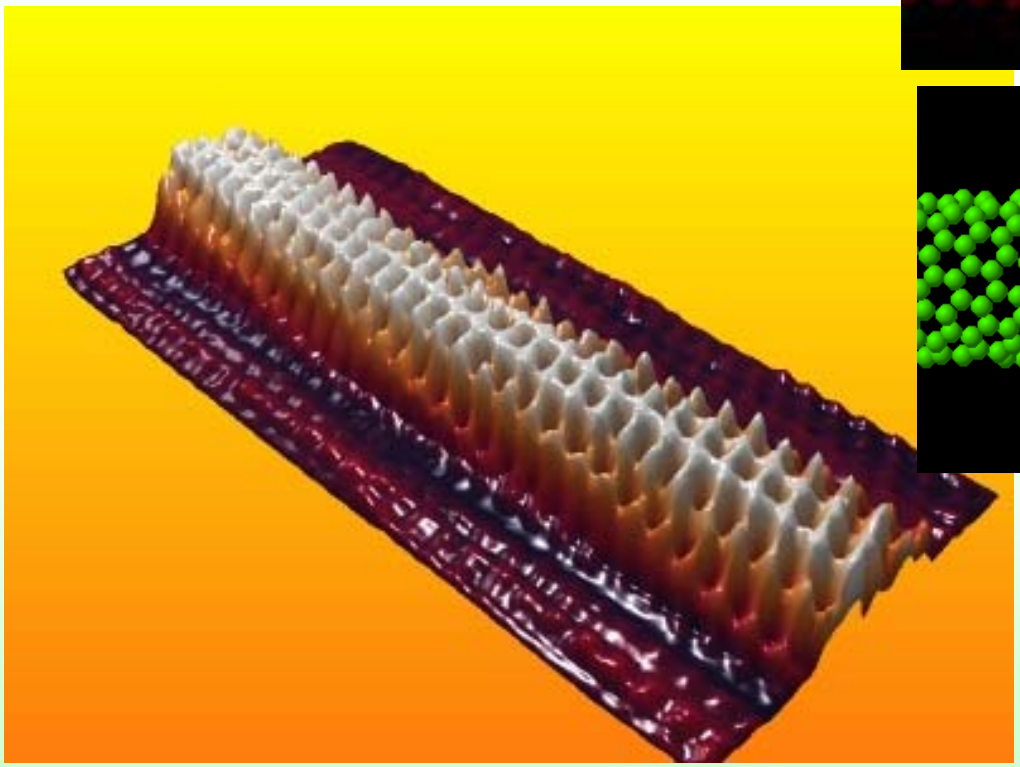


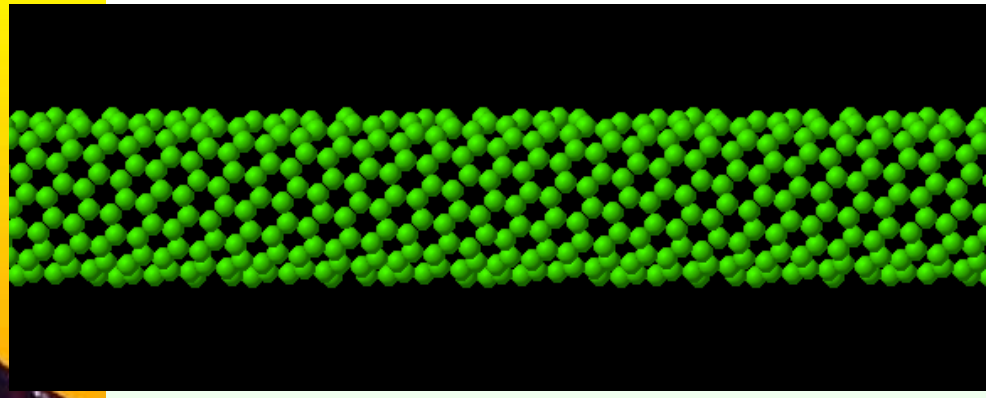
Peapod with $Sc_2@C_{84}$

Suenaga et al., PRL 2003

STM Image of Individual Atoms

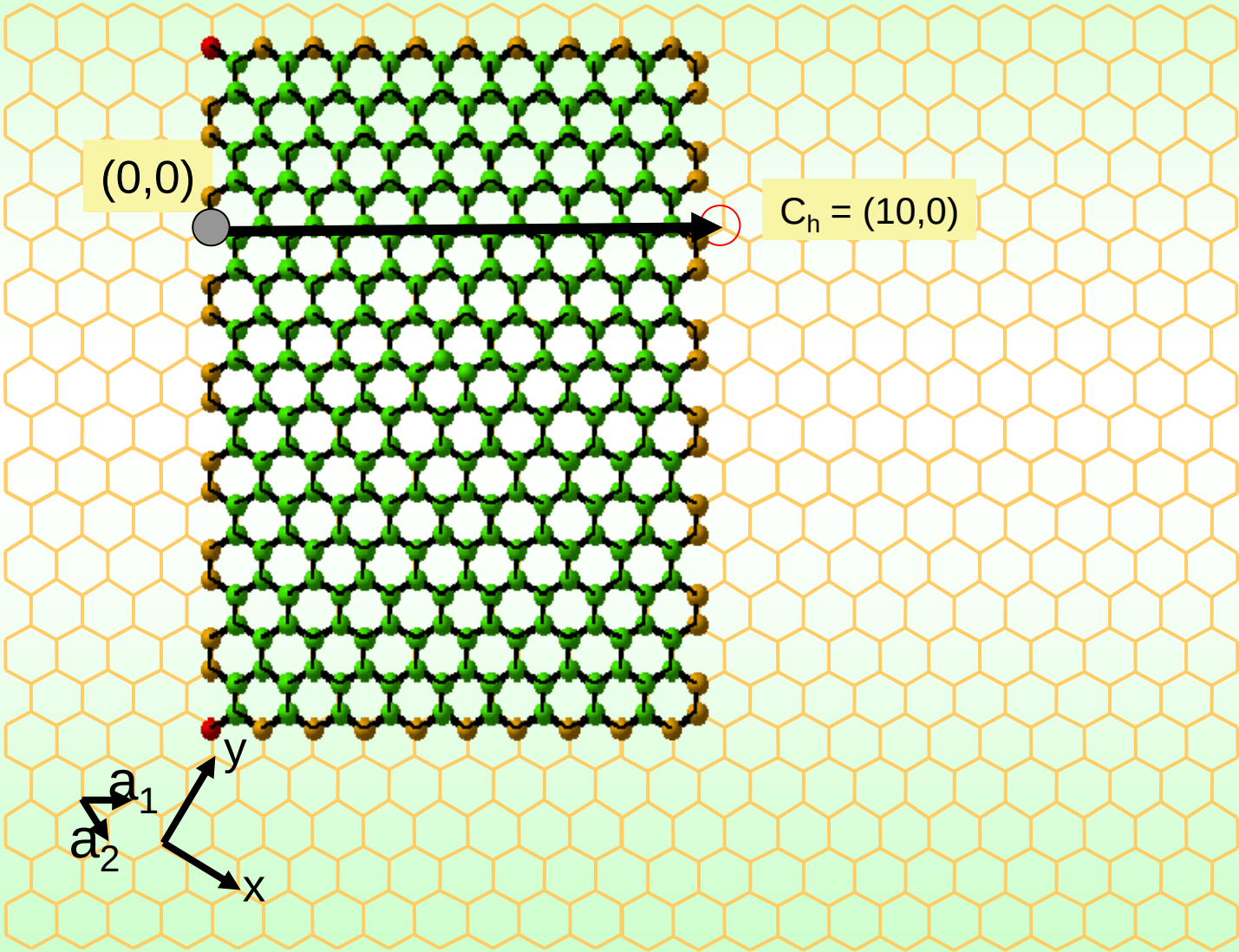




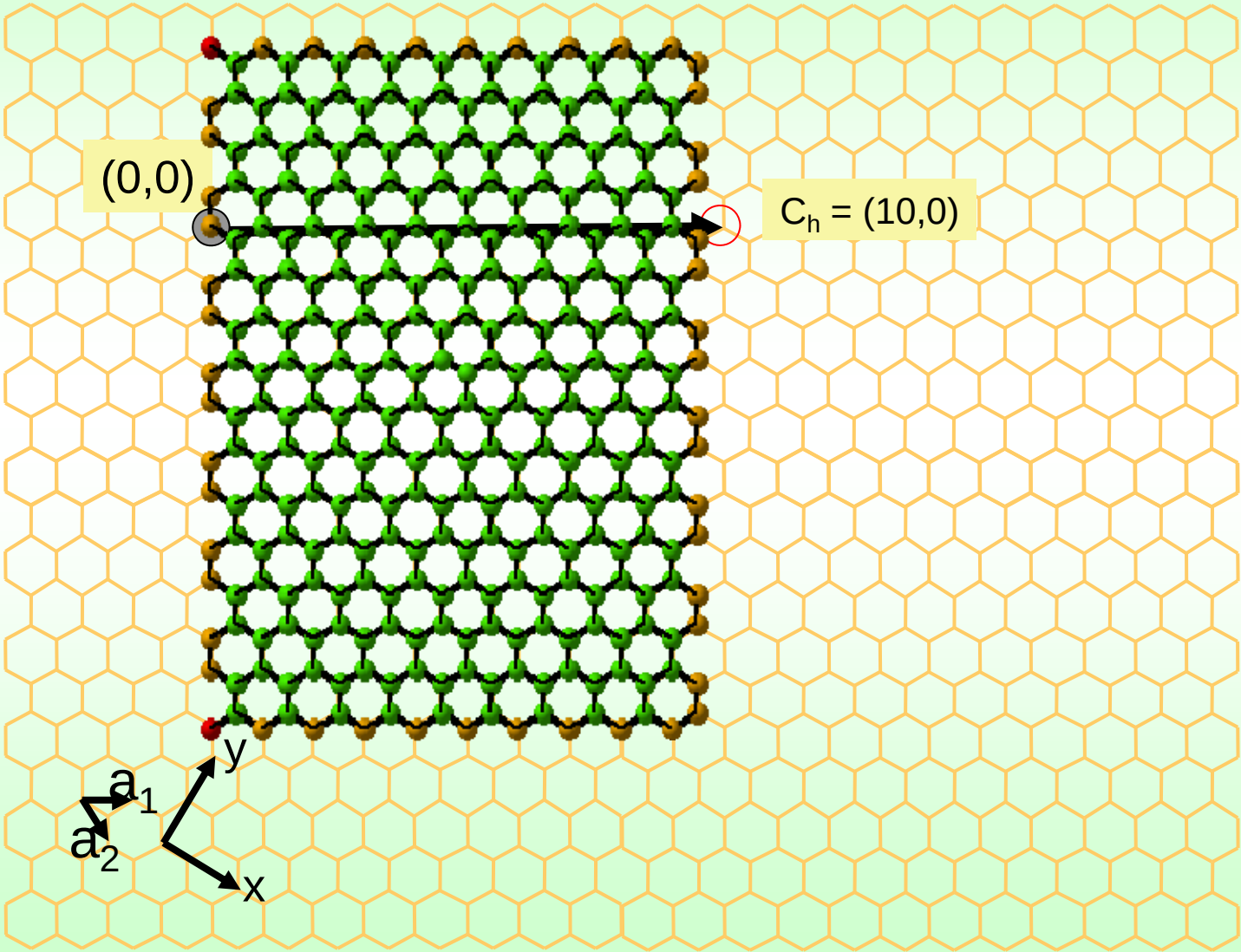


http://vortex.tn.tudelft.nl/~dekker/nanotubes.html

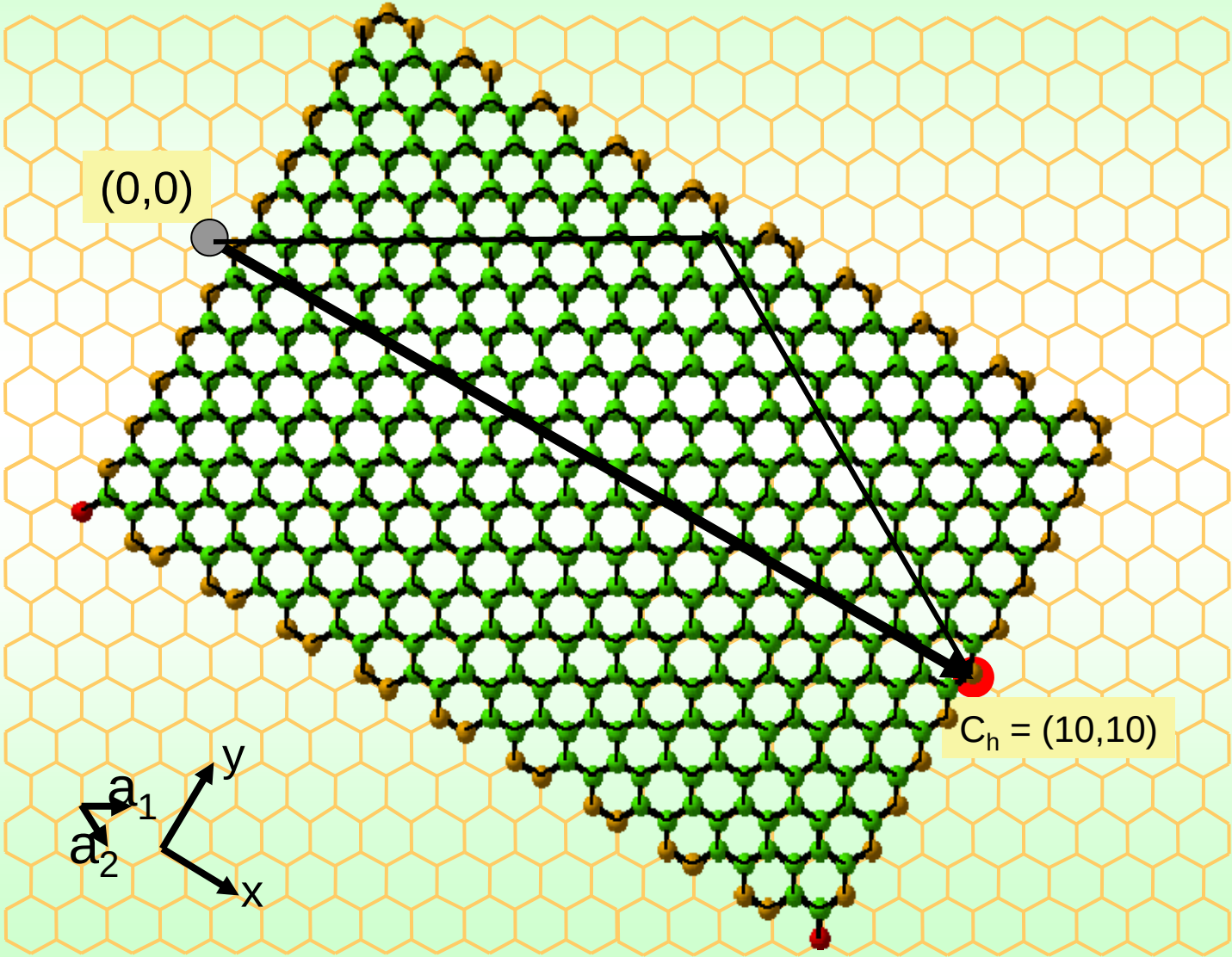
Wrapping (10,0) SWNT (zigzag)



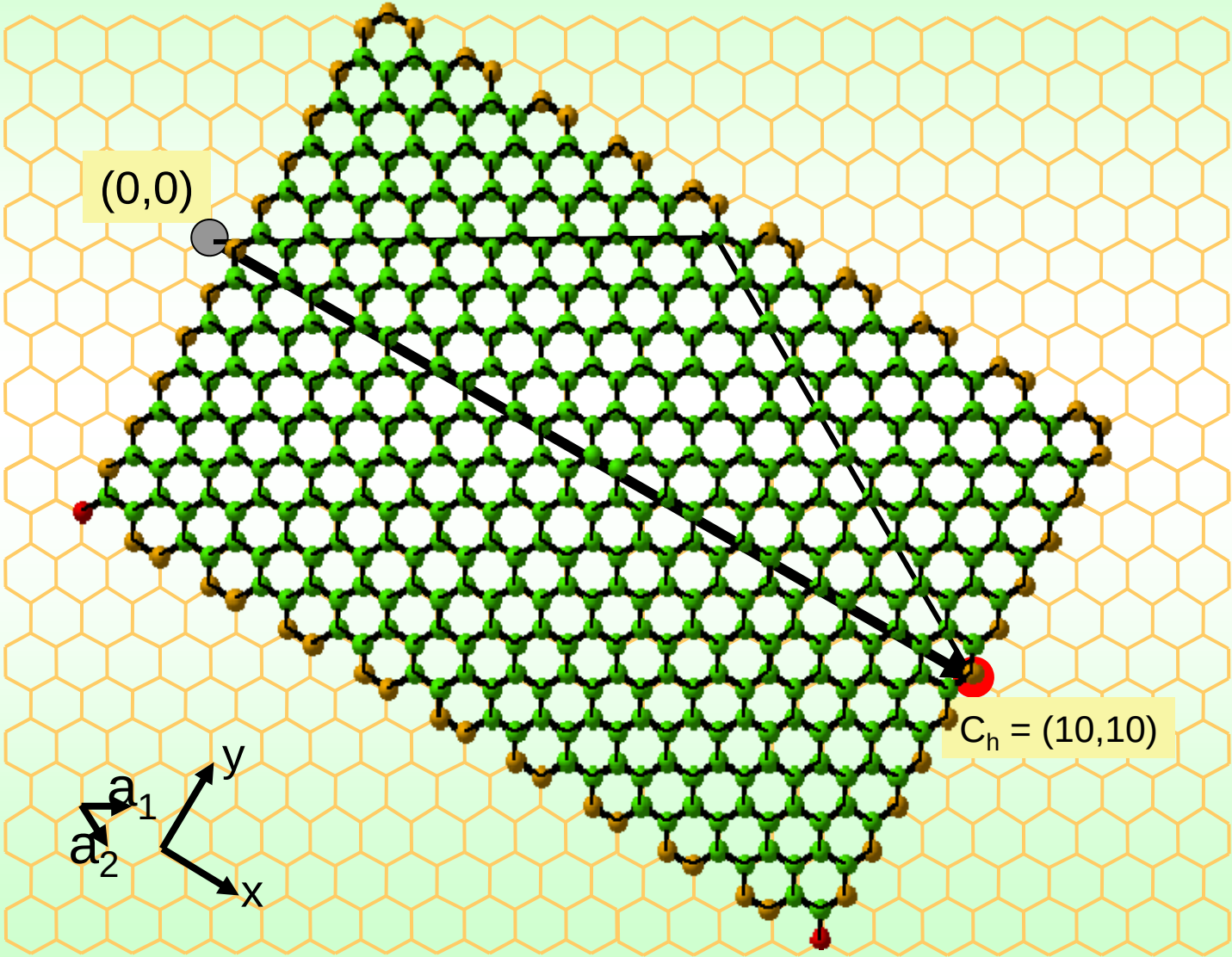
Wrapping (10,0) SWNT (zigzag)



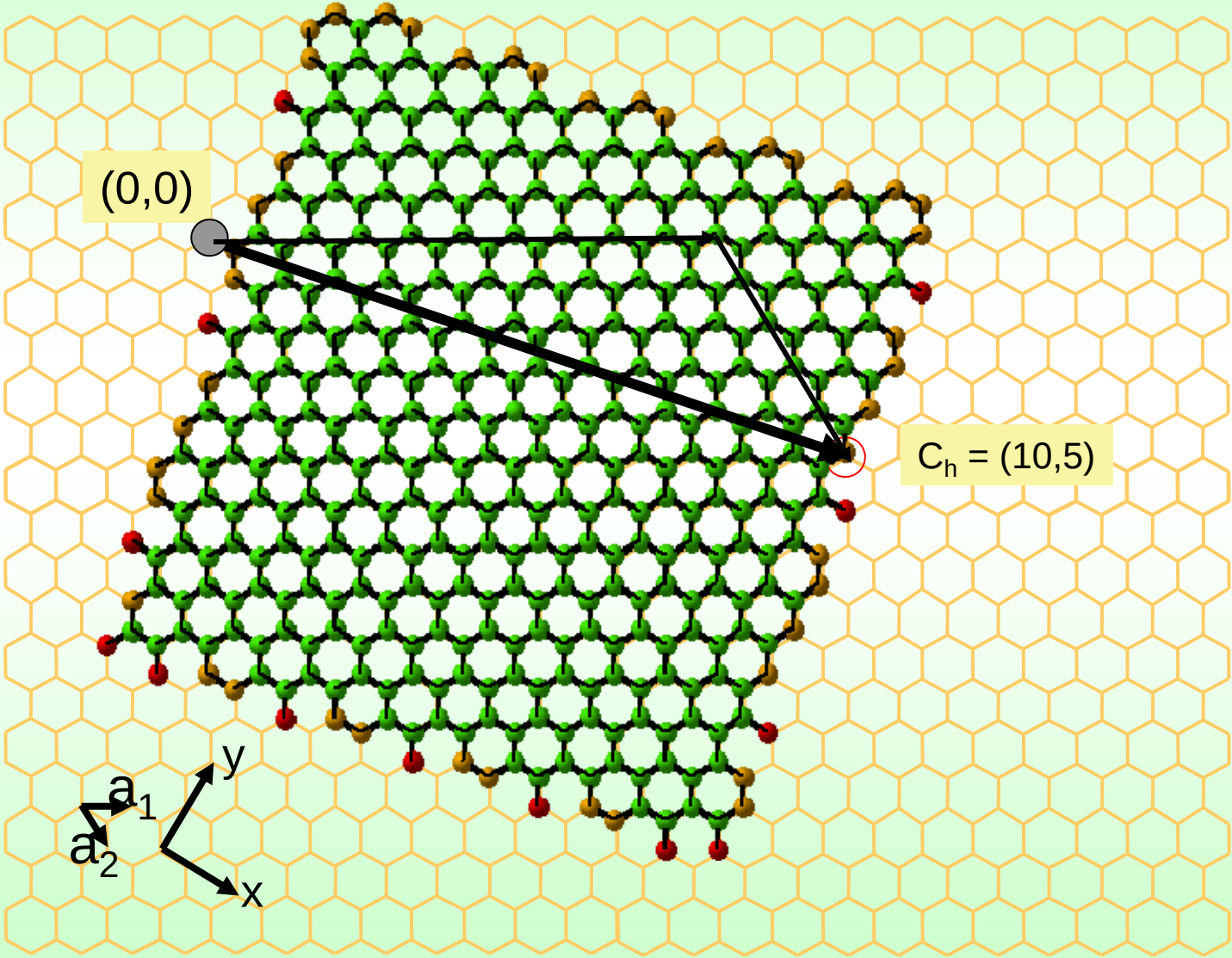
Wrapping (10,10) SWNT (armchair)



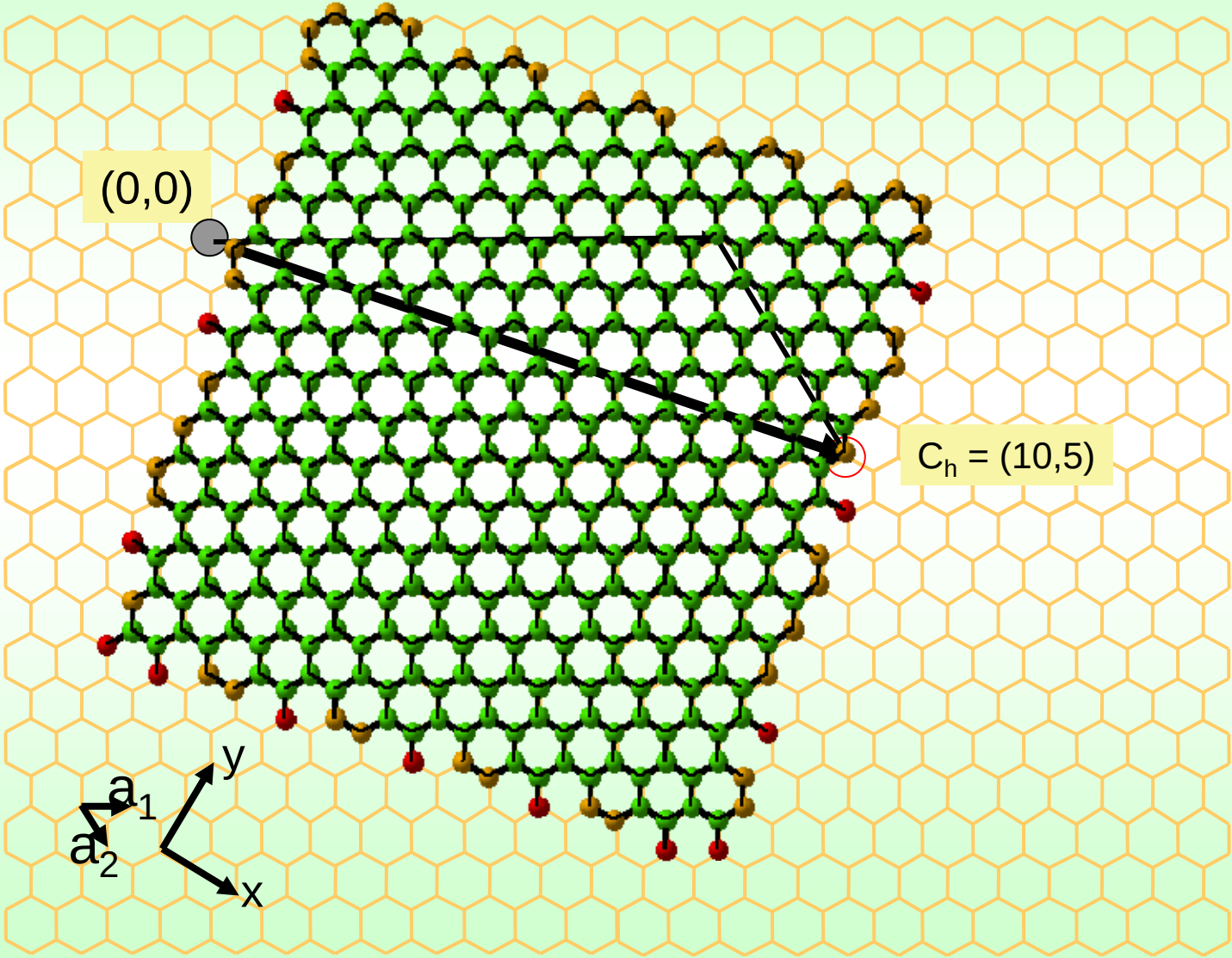
Wrapping (10,10) SWNT (armchair)



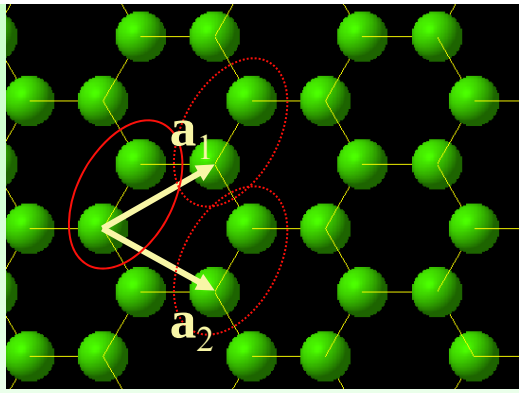
Wrapping (10,5) SWNT (chiral)

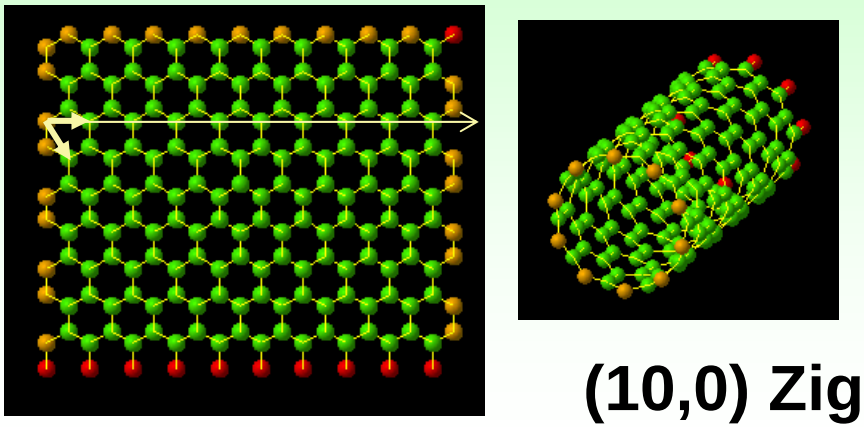


Wrapping (10,5) SWNT (chiral)

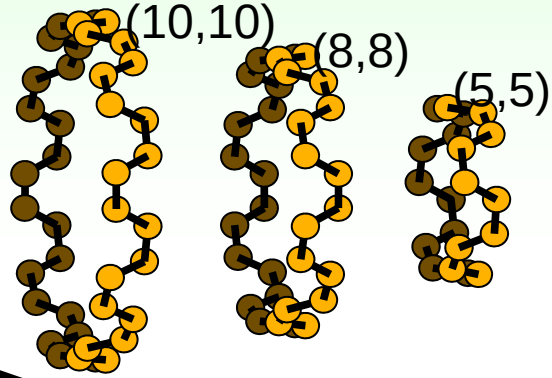


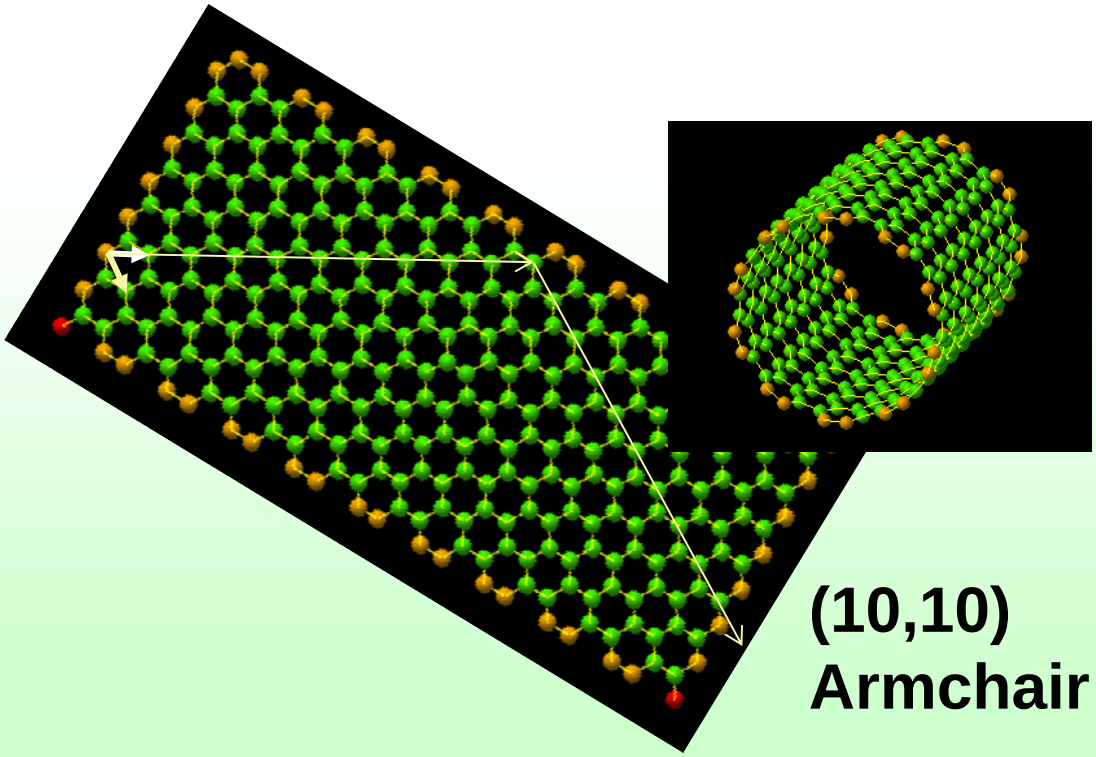
Chirality and Radius of SWNT



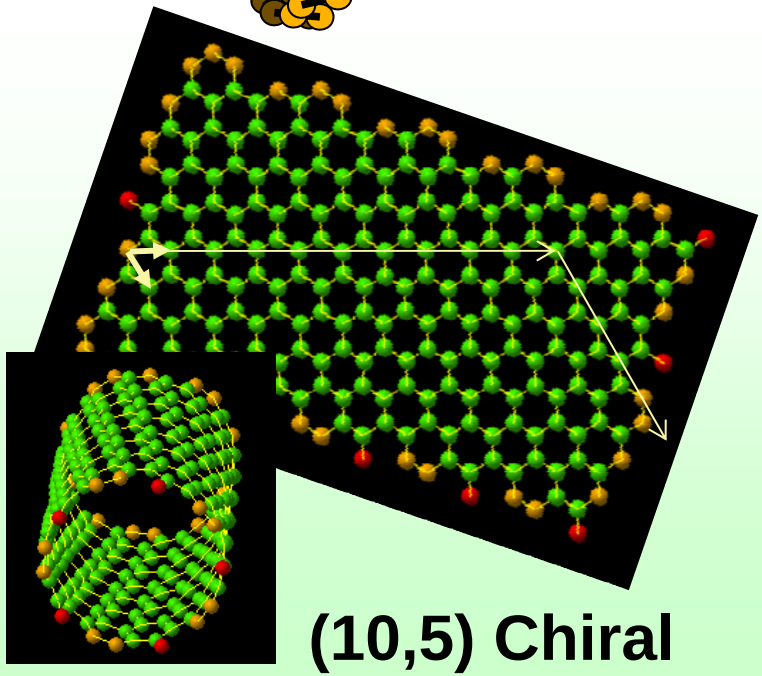


(10,0) Zigzag



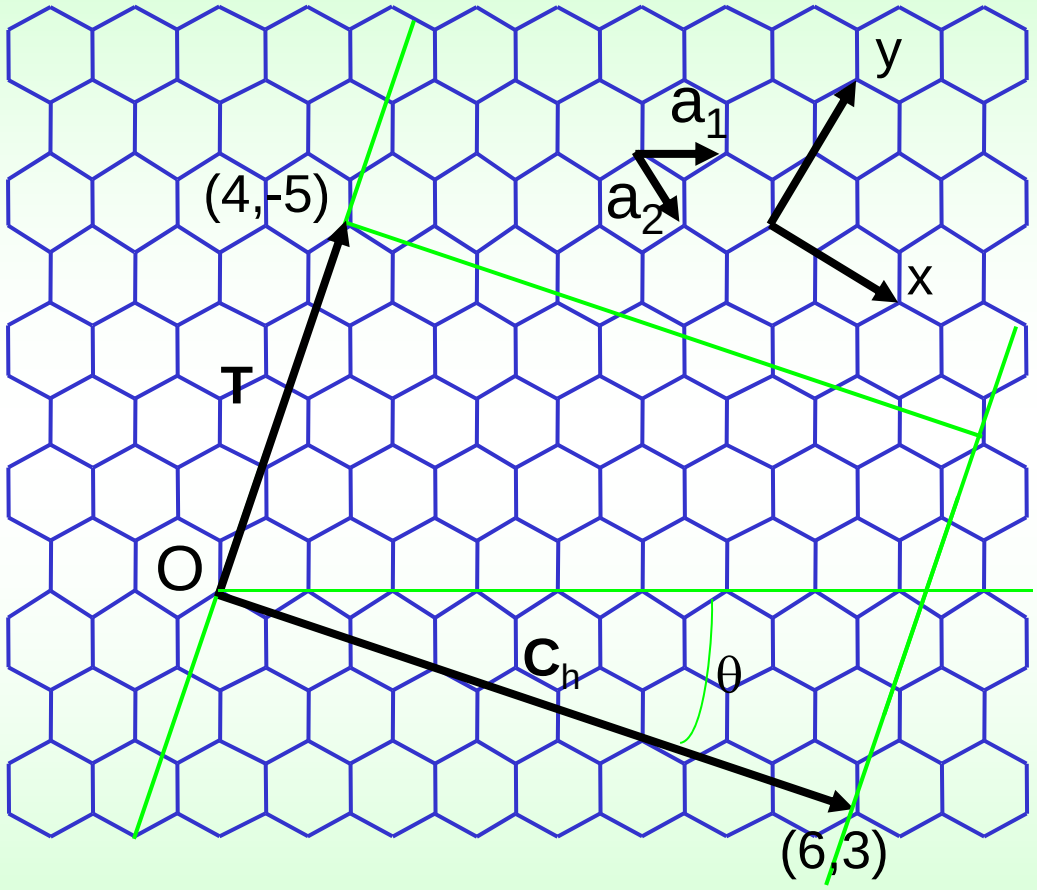


(10,10) Armchair



(10,5) Chiral

Hexagonal Lattice (Definition of Vectors)



Chiral vector

$$\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2$$

$$\mathbf{a}_1 = (\frac{3}{2}a_{cc}, \frac{\sqrt{3}}{2}a_{cc})$$

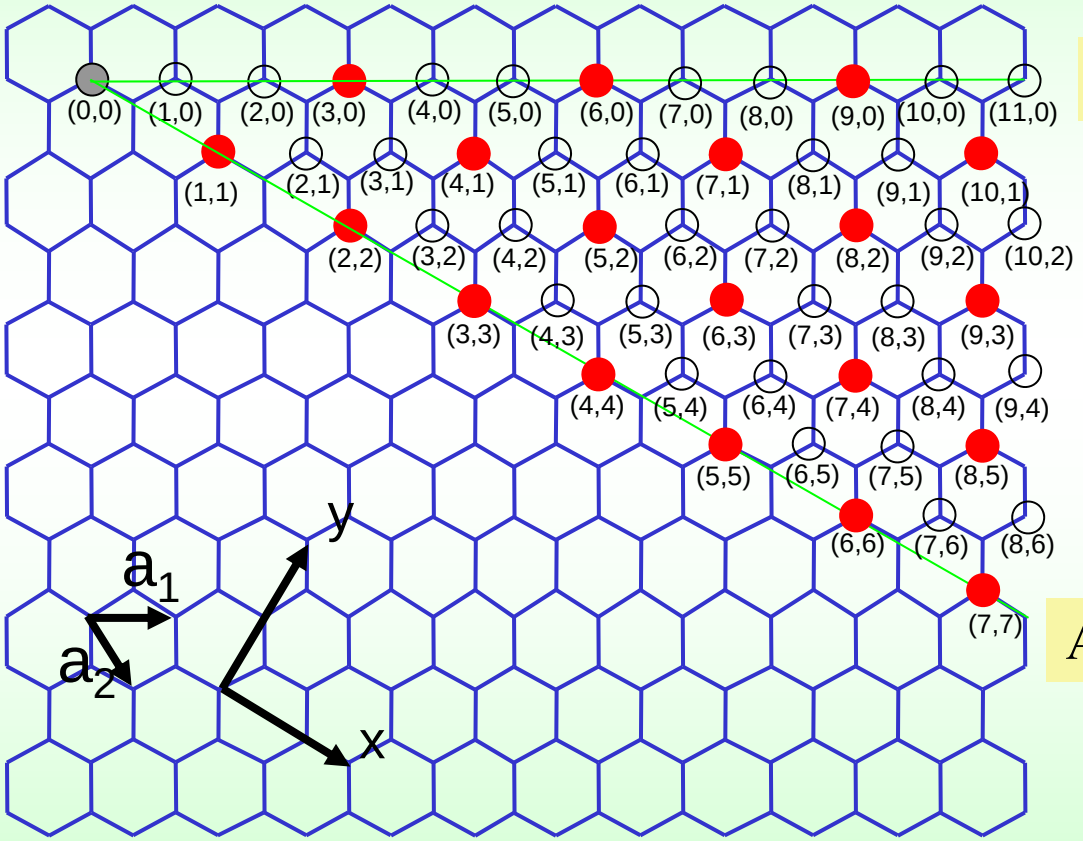
$$\mathbf{a}_2 = (\frac{3}{2}a_{cc}, -\frac{\sqrt{3}}{2}a_{cc})$$

$$|\mathbf{a}_1| = |\mathbf{a}_2| = \sqrt{3}a_{cc} \equiv a$$

$$\mathbf{a}_1 = (\frac{\sqrt{3}}{2}, \frac{1}{2})a$$

$$\mathbf{a}_2 = (\frac{\sqrt{3}}{2}, -\frac{1}{2})a$$

Hexagonal Lattice (n,m) nanotubes



Zigzag

Armchair

n - m = 3q (q: integer): metallic

n - m ≠ 3q (q: integer): semiconductor

(n,m) Symmetry

Chiral vector $\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2$

Diameter of Tube $d_t = \frac{C_h}{\pi} = \frac{\sqrt{3}a_{c-c}}{\pi}\sqrt{n^2 + nm + m^2}$

$d_t = \frac{3n}{\pi}a_{c-c}$ Armchair

Chiral angle $\theta = \tan^{-1}\left[\sqrt{3}m/(m+2n)\right]$

Lattice Vector $\mathbf{T} = \left[(2m+n)\mathbf{a}_1 - (2n+m)\mathbf{a}_2\right]/d_R$

$T = \sqrt{3}C_h / d_R$

$$d_R = \begin{cases} d & \text{if } n-m \text{ is not a multiple of } 3d \\ 3d & \text{if } n-m \text{ is a multiple of } 3d \end{cases}$$

d: highest common divisor of (n,m)

Number of hexagons per unit cell: $N = \frac{2(m^2 + n^2 + nm)}{d_R}$

Electric DOS of Graphite

幾何学構造と同様に，SWNTの電子構造はグラフェン
（グラファイト1層）の電子構造を基礎として理解できる.
そこで，最初にグラフェンの電子構造について復習する.

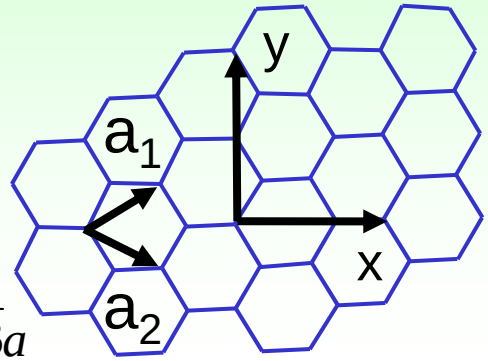
炭素のπ電子の挙動が問題となる.
電子の波動関数を波数(kx, ky)の平面波で展開し，
6角形のブリリアンゾーンにおける分散関係を求める.
グラフェンは，ゼロバンドギャップ半導体であり，K点とM点で
のみ，π電子とπ＊電子の分散関係が接する.

Reference

P. R. Wallace, *Phys. Rev*, **71** 622 (1947).

Reciprocal Lattice Vector

逆格子ベクトル　Reciprocal Lattice Vector



$$Per_x = 3a_{cc} = \sqrt{3}a$$

$$Per_y = \sqrt{3}a_{cc} = a$$

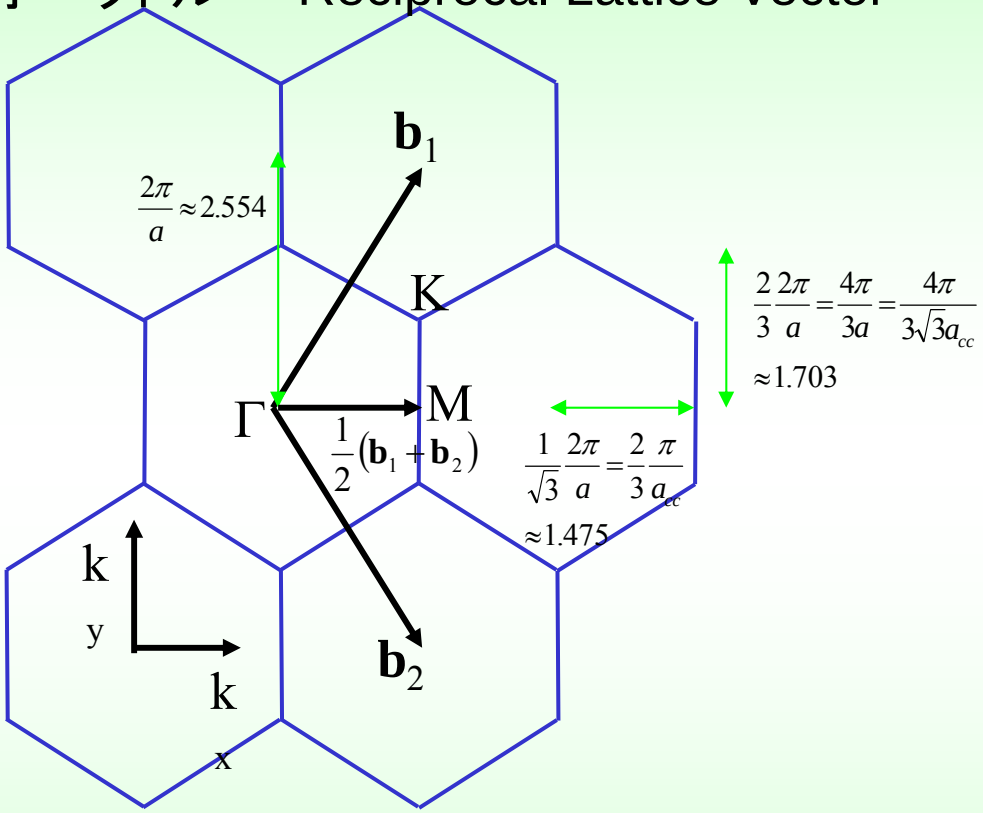
$$\mathbf{a}_1 = (\frac{\sqrt{3}}{2}, \frac{1}{2})a \qquad |\mathbf{a}_1| = |\mathbf{a}_2| = \sqrt{3}a_{cc} \equiv a$$

$$\mathbf{a}_2 = (\frac{\sqrt{3}}{2}, -\frac{1}{2})a \qquad \mathbf{b}_1 = 2\pi/\mathbf{a}_1,\ \mathbf{b}_2 = 2\pi/\mathbf{a}_2$$

$$\mathbf{a}_1 \cdot \mathbf{b}_1 = 2\pi, \mathbf{a}_2 \cdot \mathbf{b}_2 = 2\pi$$

$$\mathbf{b}_1 = (\frac{1}{\sqrt{3}}, 1)\frac{2\pi}{a} = (\frac{1}{2}, \frac{\sqrt{3}}{2})\frac{4\pi}{\sqrt{3}a}$$

$$\mathbf{b}_2 = (\frac{1}{\sqrt{3}}, -1)\frac{2\pi}{a} = (\frac{1}{2}, -\frac{\sqrt{3}}{2})\frac{4\pi}{\sqrt{3}a}$$

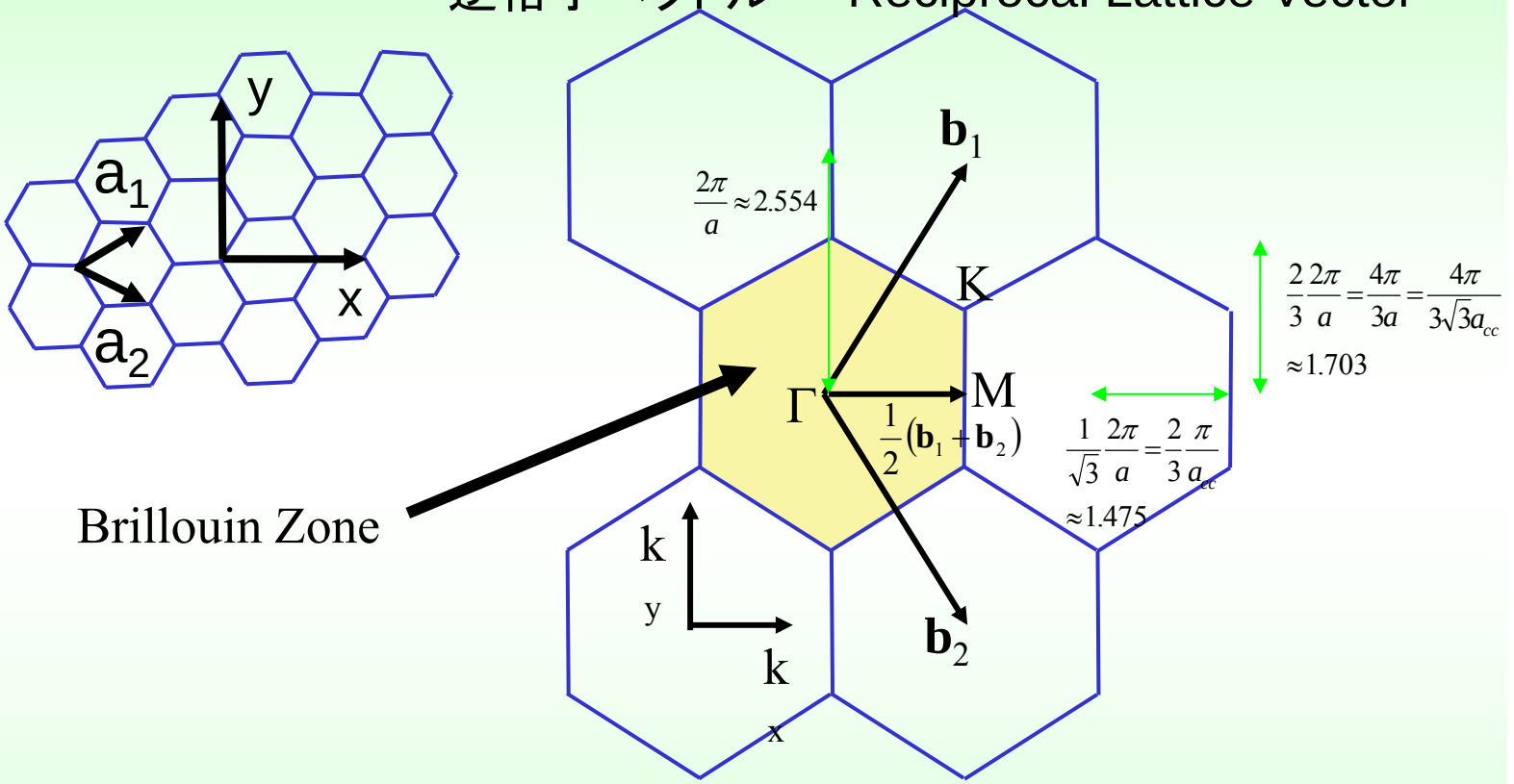


Brillouin Zone

$$\left|\mathbf{k}\cdot\frac{\mathbf{b}_1}{|\mathbf{b}_1|}\right| \le \frac{2\pi}{\sqrt{3}a} \cap \left|\mathbf{k}\cdot\frac{\mathbf{b}_2}{|\mathbf{b}_2|}\right| \le \frac{2\pi}{\sqrt{3}a} \cap |\mathbf{k}\cdot(1,0)| \le \frac{2\pi}{\sqrt{3}a}$$

Brillouin Zone

逆格子ベクトル　Reciprocal Lattice Vector



波長kx, kyで表現した位相空間を逆格子空間という.
電子の平面波の高波数の上限は(π／格子定数)で表せる.
このような上限波数範囲を逆格子空間で表したものをブリリアンゾーンとよぶ.
6角格子の場合には，ブリリアンゾーンも6角形となる．方向が90度
ずれていることに注意！

Plane Wave Representation and Tight-Binding Wave Function

Schrödinger Equation $H\Psi = E\Psi$

Plane Wave $e^{i\mathbf{kr}}$

G: reciprocal vector

Plane Wave Representation $\Psi_{\mathbf{k}}(\mathbf{r}) = \sum_G C_G e^{i(\mathbf{k}+G)\mathbf{r}}$

Fourier Transform of wave function

Tight-binding wave function

$$\Psi_{\mathbf{k}}(\mathbf{r}) = \sum_i C_i \Phi_i(\mathbf{k},\mathbf{r})$$

$$\Phi_i(\mathbf{k},\mathbf{r}) = \frac{1}{\sqrt{N_u}} \sum_{\mathbf{R}} e^{i\mathbf{kR}} \varphi(\mathbf{r}-\mathbf{R})$$

Bloch orbital

Tight-Binding Method

Functional Method

Instead of Solving Schrödinger Equation

$$H\Psi = E\Psi$$

Find best Ψ which minimize $E = \dfrac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}$

With Tight-binding wave function

$$E = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{\sum_{i,j} C_i^* C_j H_{ij}}{\sum_{i,j} C_i^* C_j S_{ij}}$$

Here,

$$H_{ij} = \langle \Phi_i | H | \Phi_j \rangle \qquad S_{ij} = \langle \Phi_i | \Phi_j \rangle$$

Hamiltonian Matrix Overlap Integral

Tight-Binding Method 2

$$\frac{\partial E(\mathbf{k})}{\partial C^*_i} = 0$$

$$\frac{\partial E(\mathbf{k})}{\partial C^*_i} = \frac{\sum_j C_j H_{ij}}{\sum_{i,j} C_i^* C_j S_{ij}} - \frac{\left(\sum_{i,j} C_i^* C_j H_{ij}\right)\left(\sum_j C_j S_{ij}\right)}{\left(\sum_{i,j} C_i^* C_j S_{ij}\right)^2} = 0$$

$$\left(\sum_j C_j H_{ij}\right) - \frac{\left(\sum_{i,j} C_i^* C_j H_{ij}\right)}{\left(\sum_{i,j} C_i^* C_j S_{ij}\right)}\left(\sum_j C_j S_{ij}\right) = 0$$

$$\sum_j H_{ij} C_j = E(\mathbf{k}) \sum_j S_{ij} C_j$$

2-D Electronic Energy Dispersions of Graphite

$$H = \begin{pmatrix} \varepsilon_{2p} & -\gamma_0 f(k) \\ -\gamma_0 f(k)^* & \varepsilon_{2p} \end{pmatrix}$$

$$S = \begin{pmatrix} 1 & sf(k) \\ sf(k)^* & 1 \end{pmatrix}$$

H: (2x2) Hamiltonian
S: (2x2) Overlap integral matrix
ε_{2p}: Site Energy of 2p atomic orbital

where $f(k) = e^{-k_x a/\sqrt{3}} + 2e^{-k_x a/2\sqrt{3}} \cos\frac{k_y a}{2}$

$$a = \sqrt{3} a_{C-C}$$

Secular equation (永年方程式) $\det(H - ES) = 0$

$$E_{g2D}{}^{\pm}(\mathbf{k}) = \frac{\varepsilon_{2p} \pm \gamma_0 w(\mathbf{k})}{1 \mp s w(\mathbf{k})}$$

where $w(\mathbf{k}) = \sqrt{|f(\mathbf{k})|^2} = \sqrt{1 + 4\cos\frac{\sqrt{3}k_x a}{2}\cos\frac{k_y a}{2} + 4\cos^2\frac{k_y a}{2}}$

2-D Energy dispersion relation for graphite

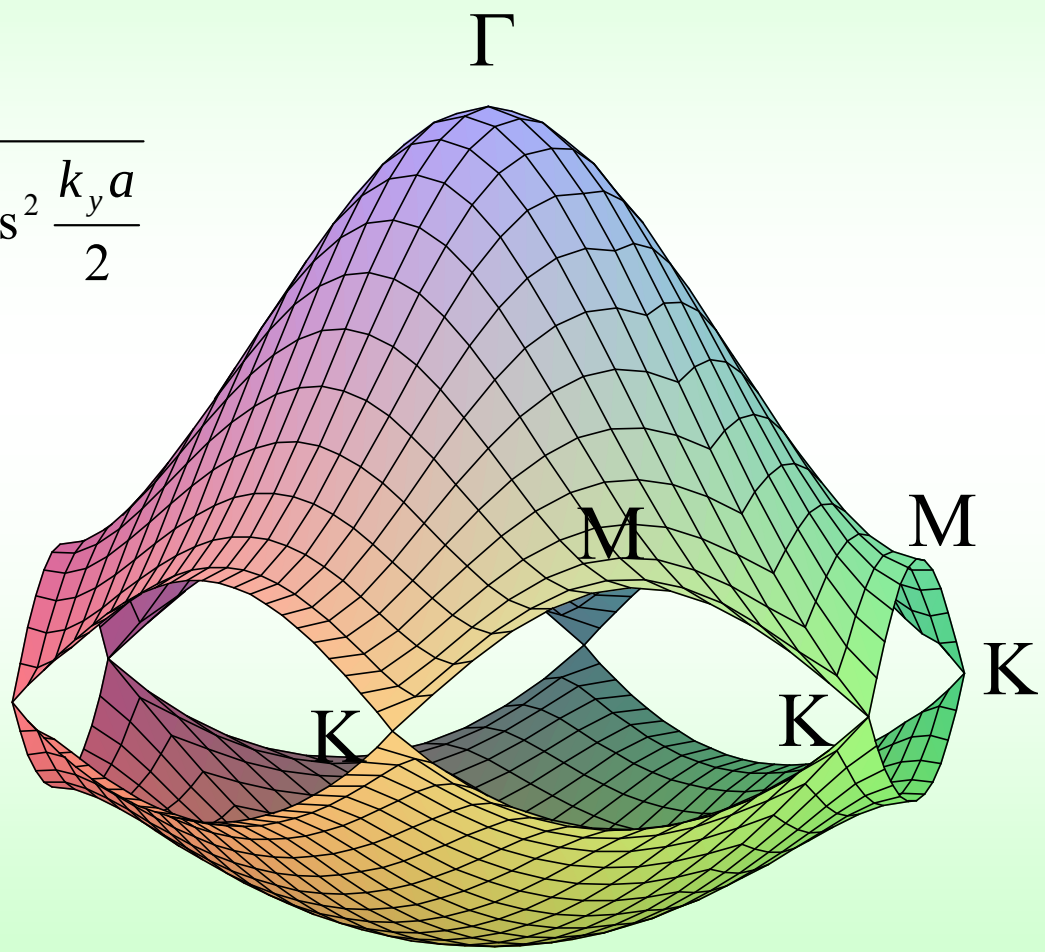
$$E_{g2D}{}^{\pm}(\mathbf{k}) = \frac{\varepsilon_{2p} \pm \gamma_0 w(\mathbf{k})}{1 \mp s w(\mathbf{k})}$$

$$w(\mathbf{k}) = \sqrt{1 + 4\cos\frac{\sqrt{3}k_x a}{2}\cos\frac{k_y a}{2} + 4\cos^2\frac{k_y a}{2}}$$

Overlap integral: s=0.129

C-C interaction energy: γ_0=2.9eV

$\varepsilon_{2p} = 0$



From: R. Saito, G. Dresselhaus, and M. S. Dresselhaus, Trigonal warping effect of carbon nanotubes, Physical Review B, vol. 61, no. 4, 2981 (2000).
[Color picture was from Professor R. Saito]

Energy dispersion relation for π and π * bands

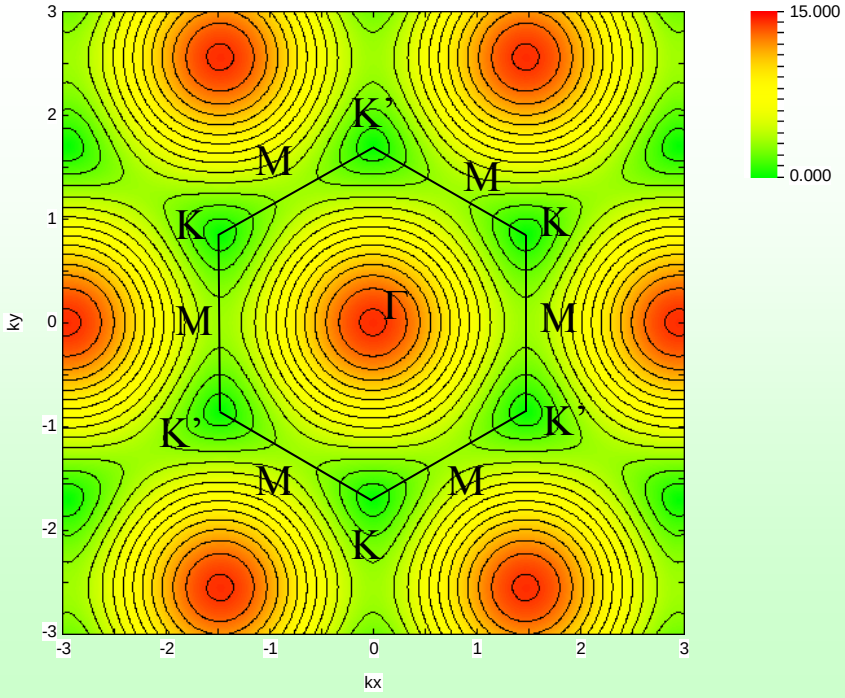
$$E_{g2D}^{\pm}(\mathbf{k}) = \frac{\varepsilon_{2p} \pm \gamma_0 w(\mathbf{k})}{1 \mp s w(\mathbf{k})}$$

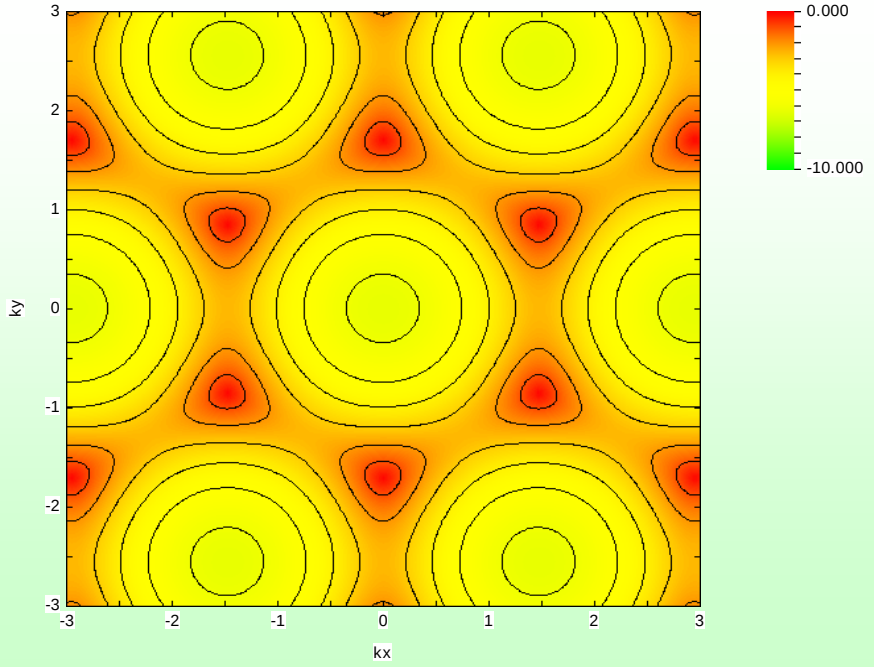
$$a = \sqrt{3} a_{C-C}$$

$$w(\mathbf{k}) = \sqrt{1 + 4\cos\frac{\sqrt{3}k_x a}{2}\cos\frac{k_y a}{2} + 4\cos^2\frac{k_y a}{2}}$$

s=0.129

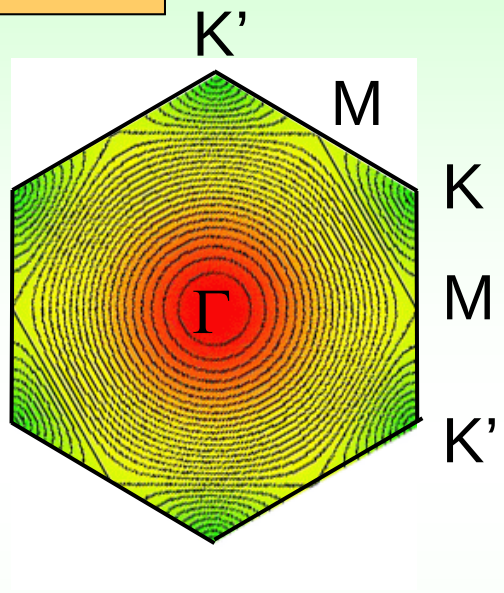
Gamma=2.9eV

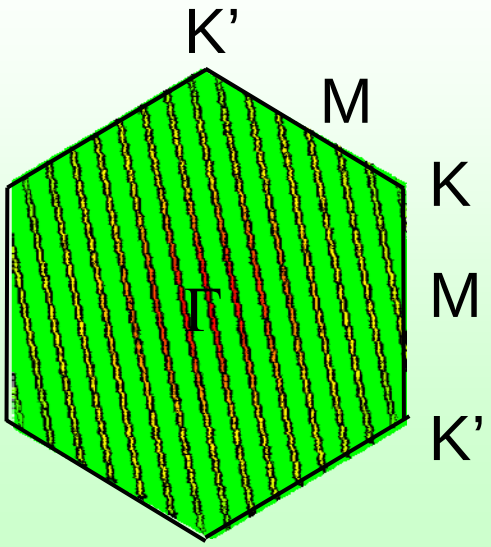




Electric DOS of Nanotube

グラフェンを巻いたSWNTの場合には，円周方向に周期境界条件を満たす電子の波動関数しか許されなくなる．このため，グラフェンの場合の6角形のブリリアンゾーン（平面）は，有限数の線となってしまう．この線が，K点かM点を通過すると金属，そうでないと半導体となる．

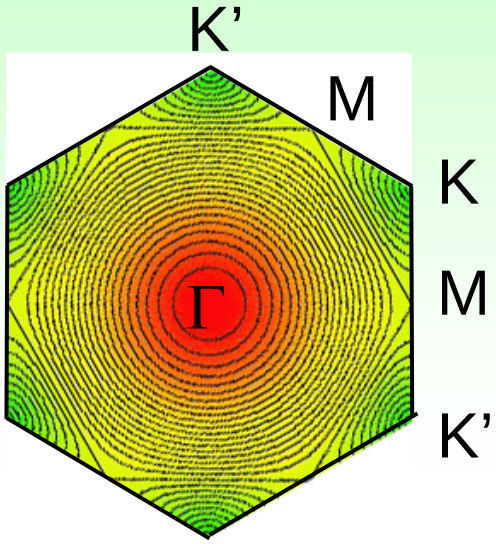


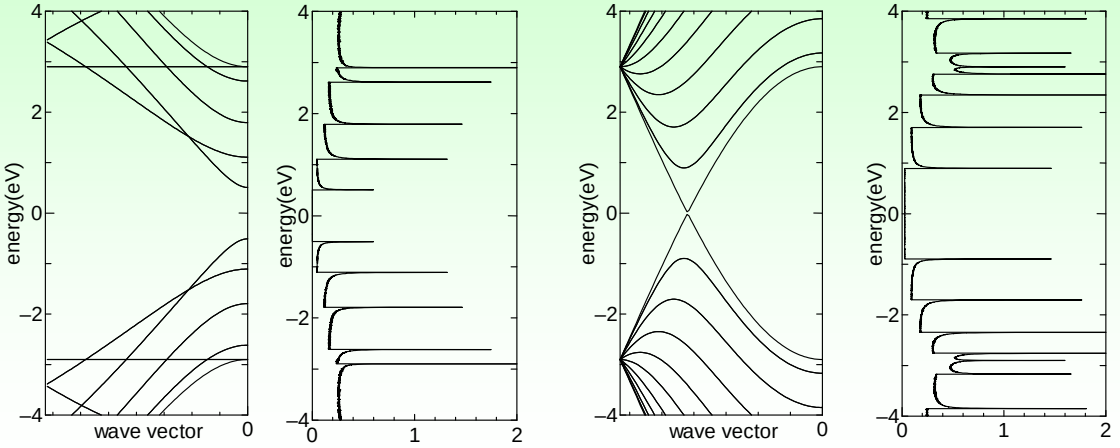


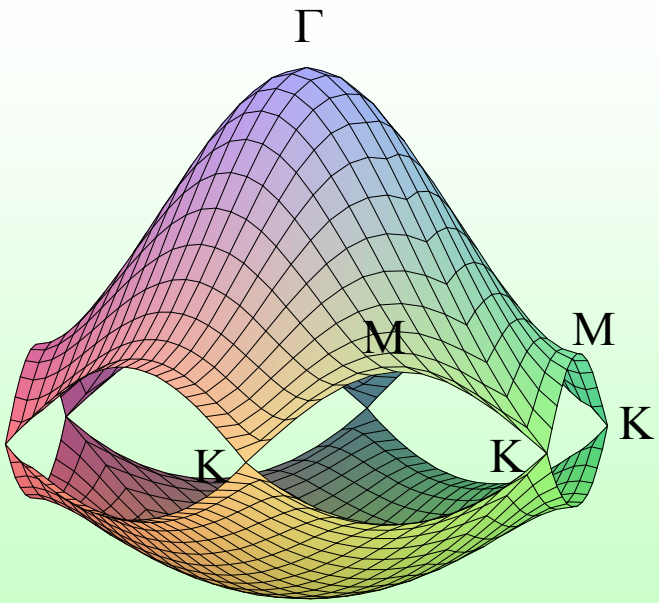
Reference
最初の理論予測：R. Saito *et al., Phys. Rev*. **B46**, 1804 (1992).

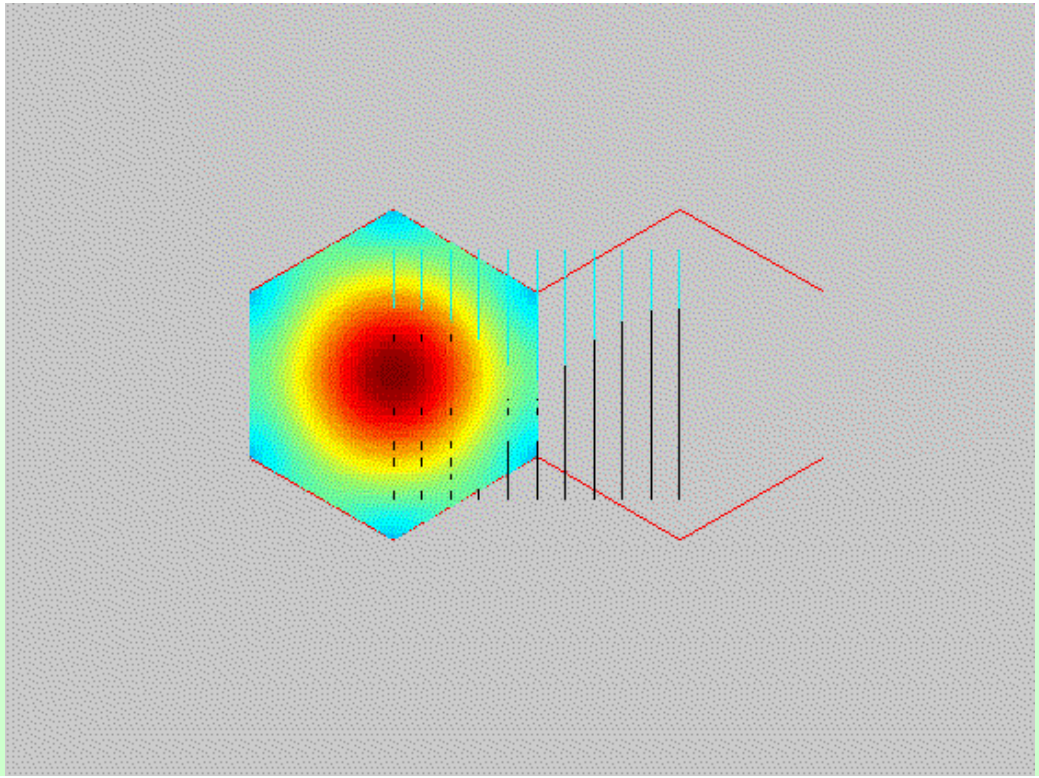
詳細かつわかりやすい論文：R. Saito, G. Dresselhaus, and M. S. Dresselhaus, Trigonal warping effect of carbon nanotubes, Physical Review B, vol. 61, no. 4, 2981 (2000).

Electric DOS of Carbon Nanotube









1D Dispersion

Lattice Vector $\mathbf{T} = \left[(2m+n)\mathbf{a}_1 - (2n+m)\mathbf{a}_2\right]/d_R$

$T = \sqrt{3}C_h / d_R$

$C_h = a\sqrt{n^2+nm+m^2}$

Discrete unit vector along the circumferential direction

$\mathbf{K}_1 = \left[(2m+n)\mathbf{b}_1 + (2n+m)\mathbf{b}_2\right]/Nd_R$

$$|\mathbf{K}_1| = \frac{2\pi}{a}2\sqrt{n^2+mn+m^2}/Nd_R$$
$$= \frac{2\pi}{a}2\sqrt{n^2+mn+m^2}/2(n^2+mn+m^2)$$
$$= \frac{2\pi}{a}\frac{1}{\sqrt{n^2+mn+m^2}}$$
$$= \frac{2\pi}{C_h}$$

Reciprocal lattice vector along the nanotube axis

$\mathbf{K}_2 = (m\mathbf{b}_1 - n\mathbf{b}_2)/N$

$$N = \frac{2(m^2+n^2+nm)}{d_R}$$

$$E_\mu(k) = E_{g2D}\left(k\frac{\mathbf{K}_2}{|\mathbf{K}_2|} + \mu\mathbf{K}_1\right) \qquad \mu = 1,2,\ldots,N$$

$$-\frac{\pi}{T} < k < \frac{\pi}{T}$$

$$|\mathbf{K}_2| = \frac{2\pi}{a}\frac{2}{\sqrt{3}}\sqrt{n^2+mn+m^2}/N$$
$$= \frac{2\pi}{a}\frac{2}{\sqrt{3}}d_R\sqrt{n^2+mn+m^2}/2(n^2+mn+m^2)$$
$$= \frac{2\pi}{a}\frac{1}{\sqrt{3}}\frac{d_R}{\sqrt{n^2+mn+m^2}}$$
$$= \frac{2\pi}{C_h}\frac{1}{\sqrt{3}}d_R = \frac{2\pi}{T}$$

Summary

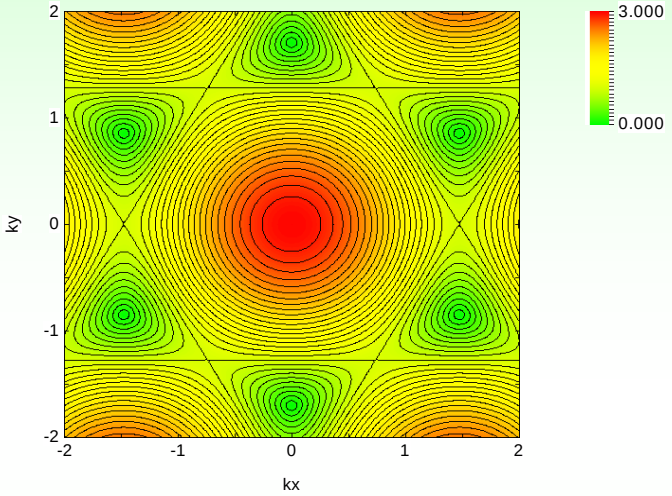
$$k\frac{\mathbf{K}_2}{|\mathbf{K}_2|}+\mu\mathbf{K}_1$$

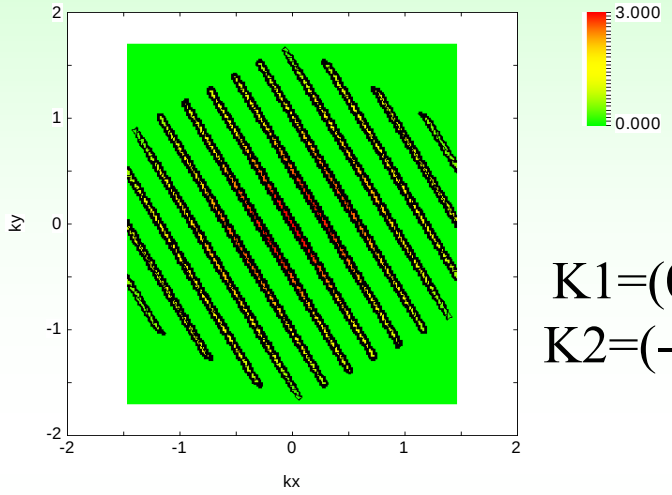
where $\mu = 1,2,\ldots,N$

$$-\frac{\pi}{T} < k < \frac{\pi}{T}$$

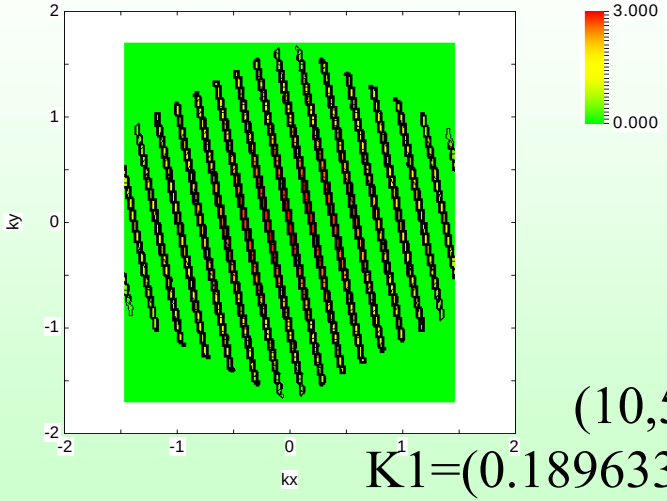
$$E_\mu(k) = E_{g2D}\left(k\frac{\mathbf{K}_2}{|\mathbf{K}_2|}+\mu\mathbf{K}_1\right)$$

Slice

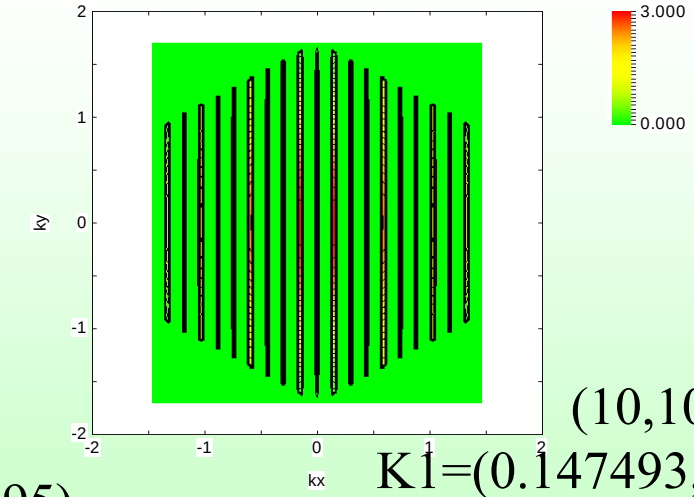




(10,0)
K1=(0.221239,0.127732)
K2=(-0.737463,1.277323)



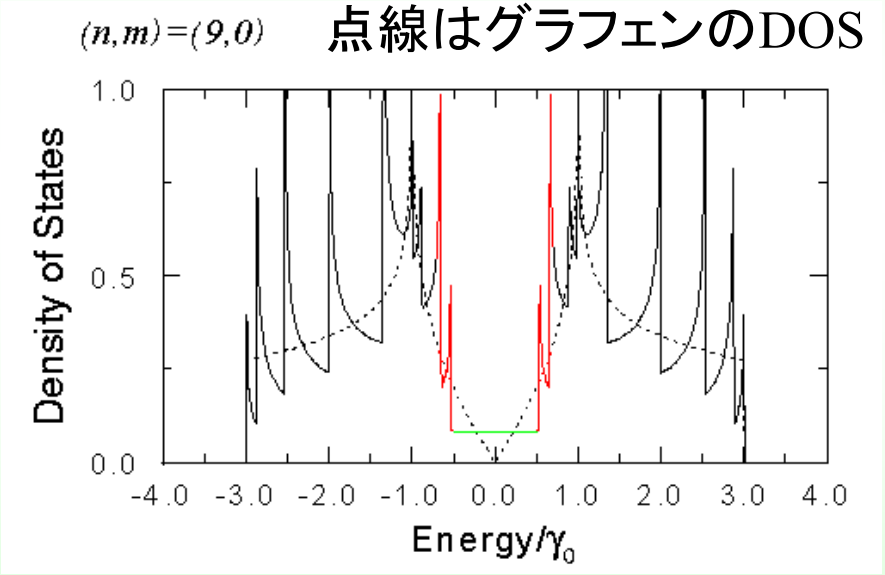
(10,5)
K1=(0.189633,0.036495)
K2=(-0.105352,0.547424)



(10,10)
K1=(0.147493,0.000000)
K2=(0.000000,2.554647)

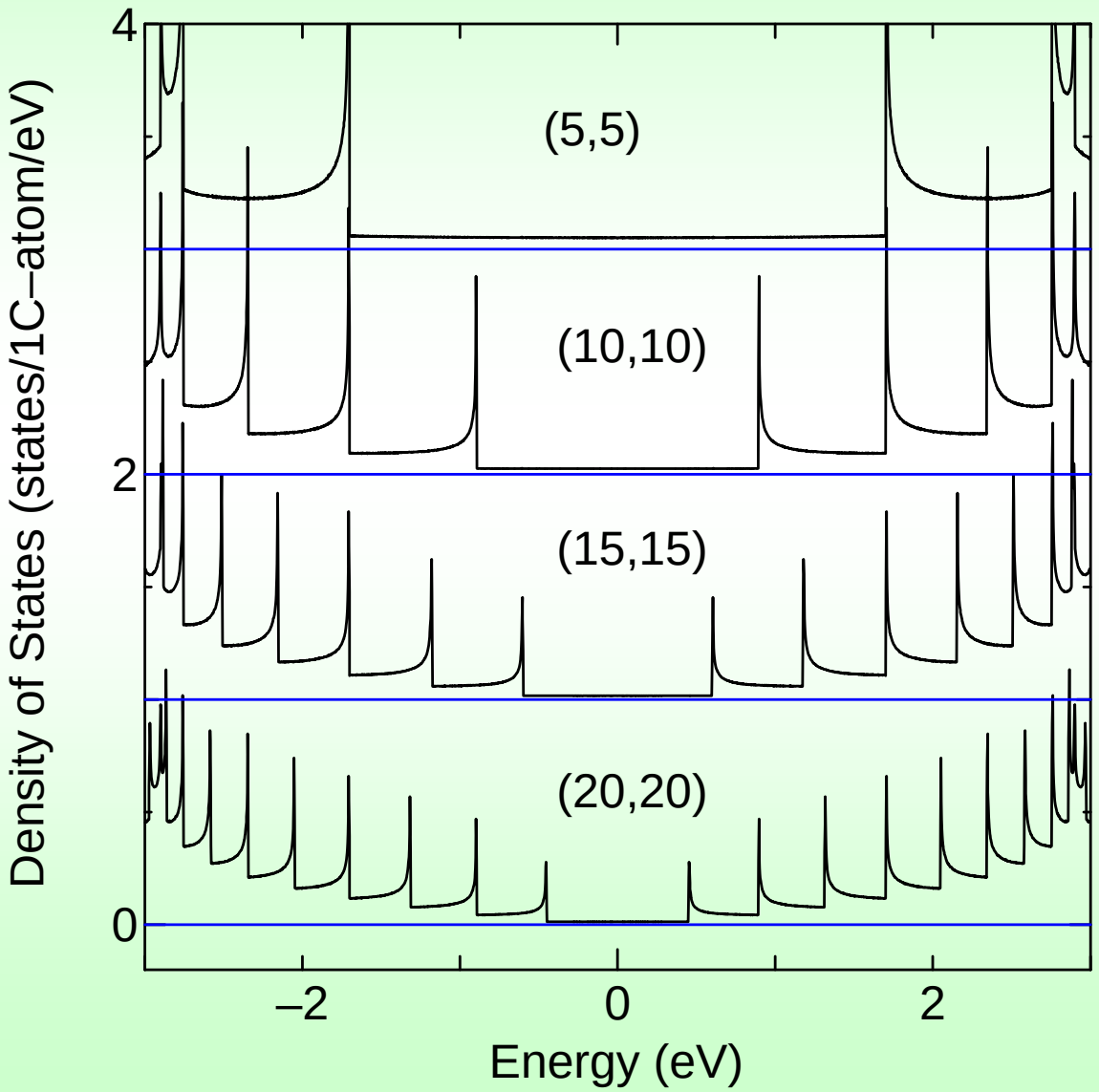
van Hove Singularity

ブリリアントゾーンを積分するといわゆる状態密度（Density of States, DOS)が求まることになる.
金属か半導体かという点以外にも，周期境界条件によって，ブリリアンゾーンが線となるために，一次元物質に特有のvan Hove特異点と呼ばれる発散するDOSとなる.

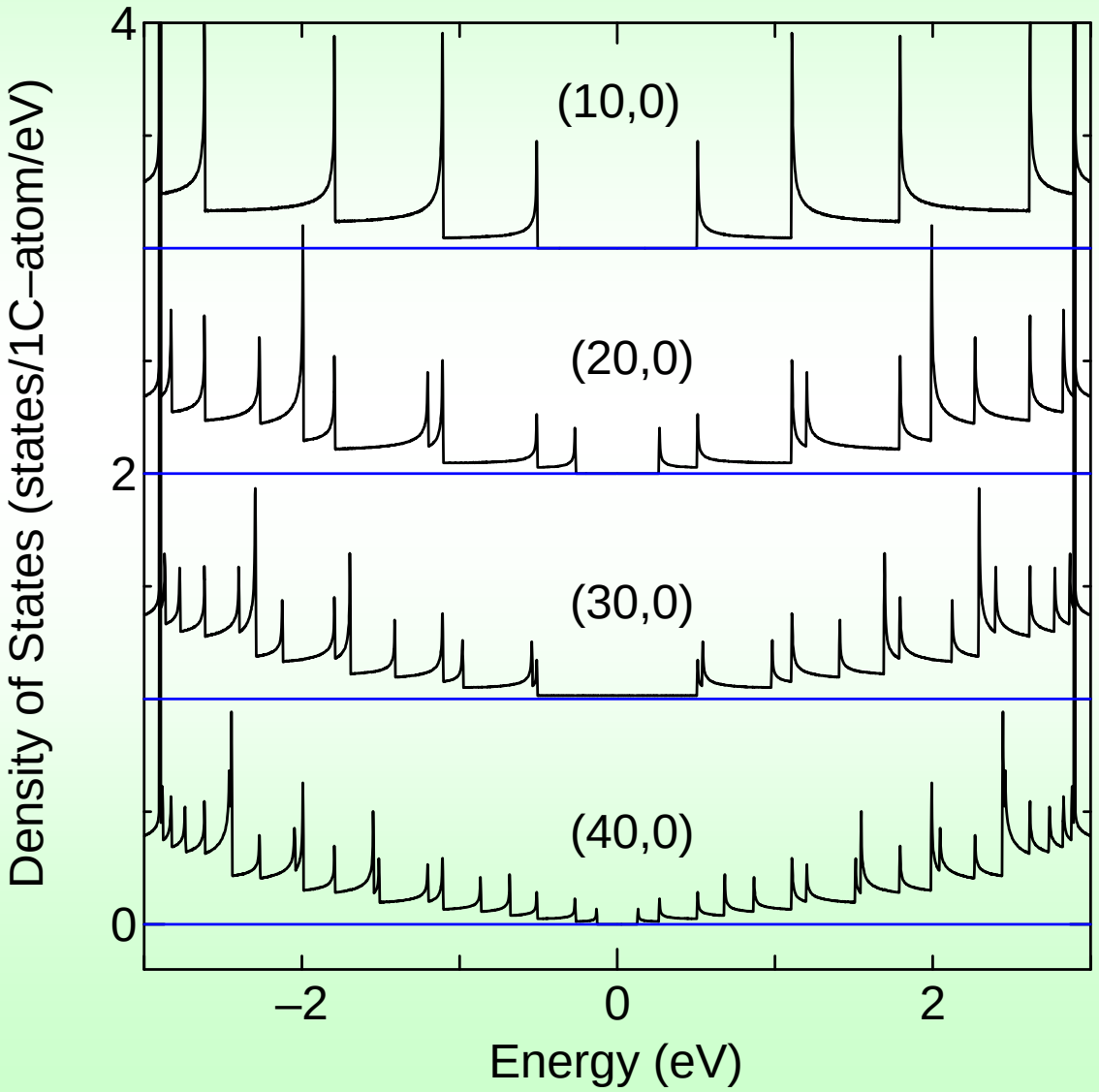


Reference
Dresselhaus, M. S. & Dresselhaus, G., Science of Fullerenes and Carbon Nanotubes, Academic Press (1996).
Saito, R., ほか2名, Physical Properties of Carbon Nanotubes, Imperial College Press (1998).

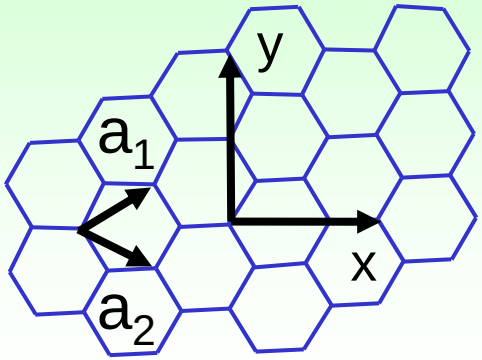
Comparison of DOS for Armchairs

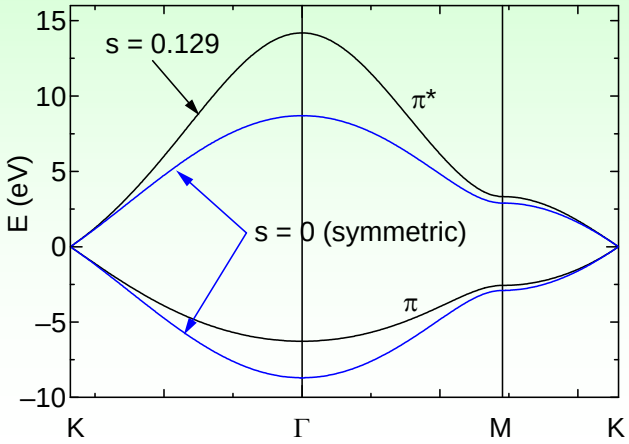


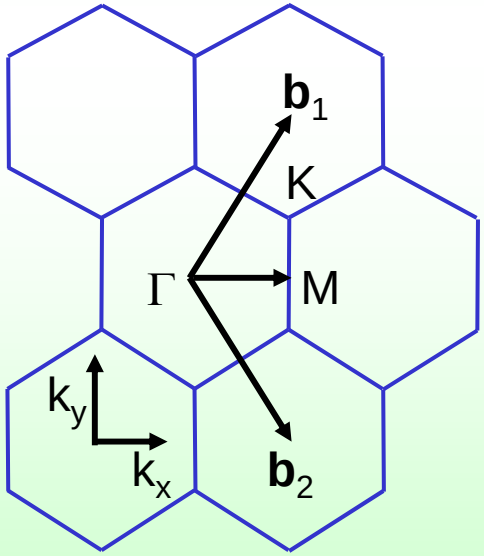
Comparison of DOS for Zig-zag

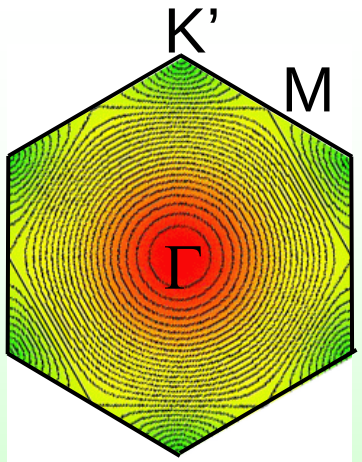


2-D Energy dispersion relation for graphite

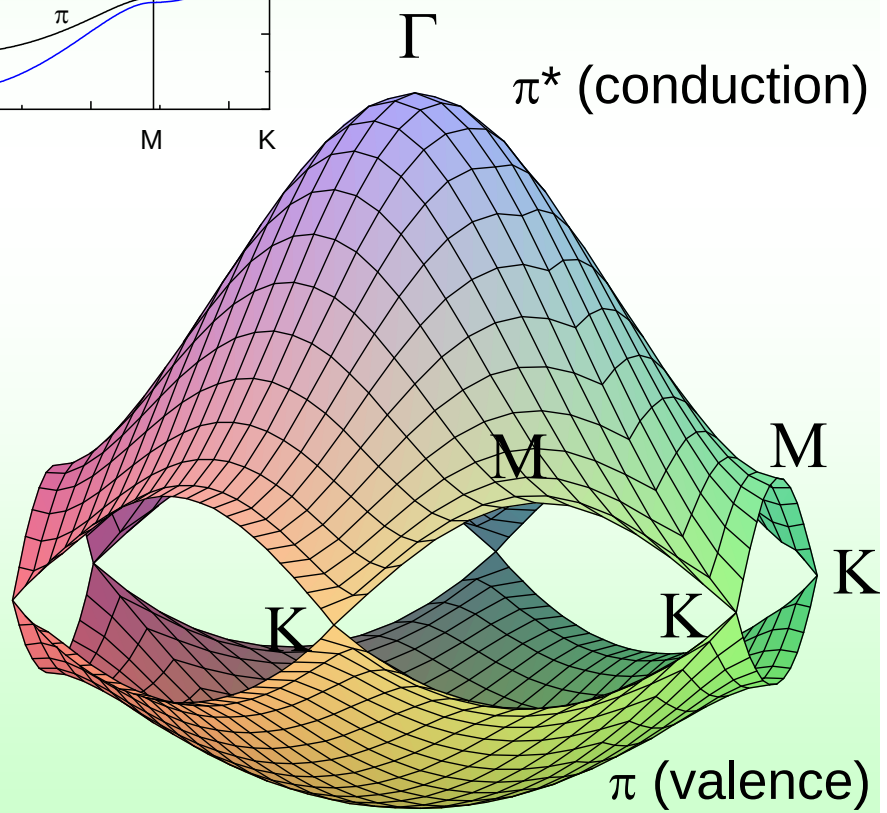








Brillouin Zone



Reciprocal Lattice Vector

From: R. Saito et al., Physical Review B (2000).