Theory seminar: Electronic properties of graphene

# Graphene nanoribbons

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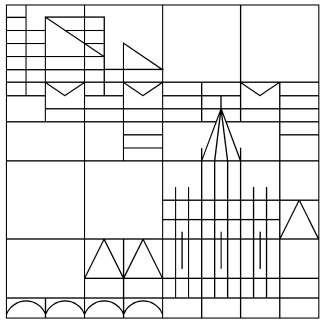
18. Mai 2009

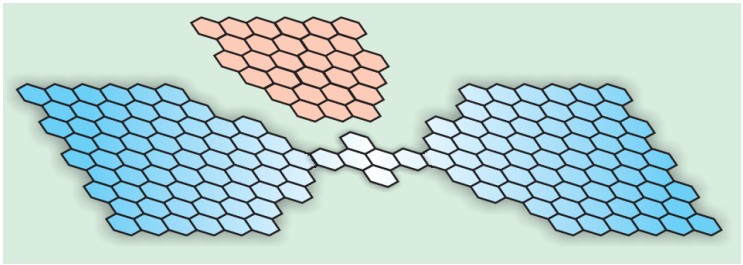


Universität Konstanz

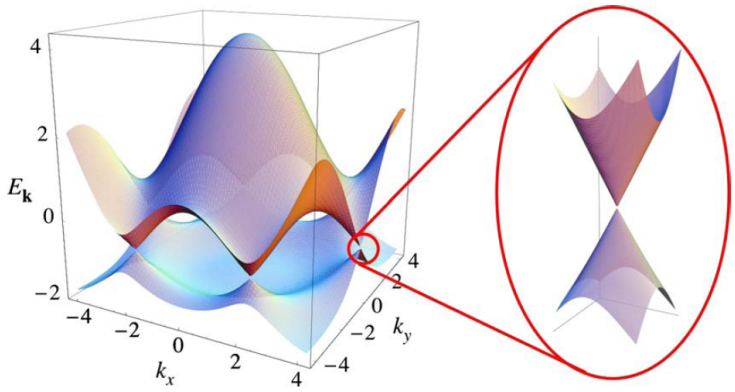
# Outline

# 1. Motivation

- Up to now: Infinite graphene layers
- Nanoelectronics based on graphene
  - electron mobility $\approx 10^4\,\mathrm{cm}^2/\mathrm{Vs}$ (Si: $10^3\,\mathrm{cm}^2/\mathrm{Vs}$)
  - the smaller the better
  - entire circuits carved out of graphene
- Electronic properties depending on size and geometry
  - bandgap in finite structures?
  - replacement for Si?



[Geim, MacDonald, 2007]




[Castro Neto et al., 2009]

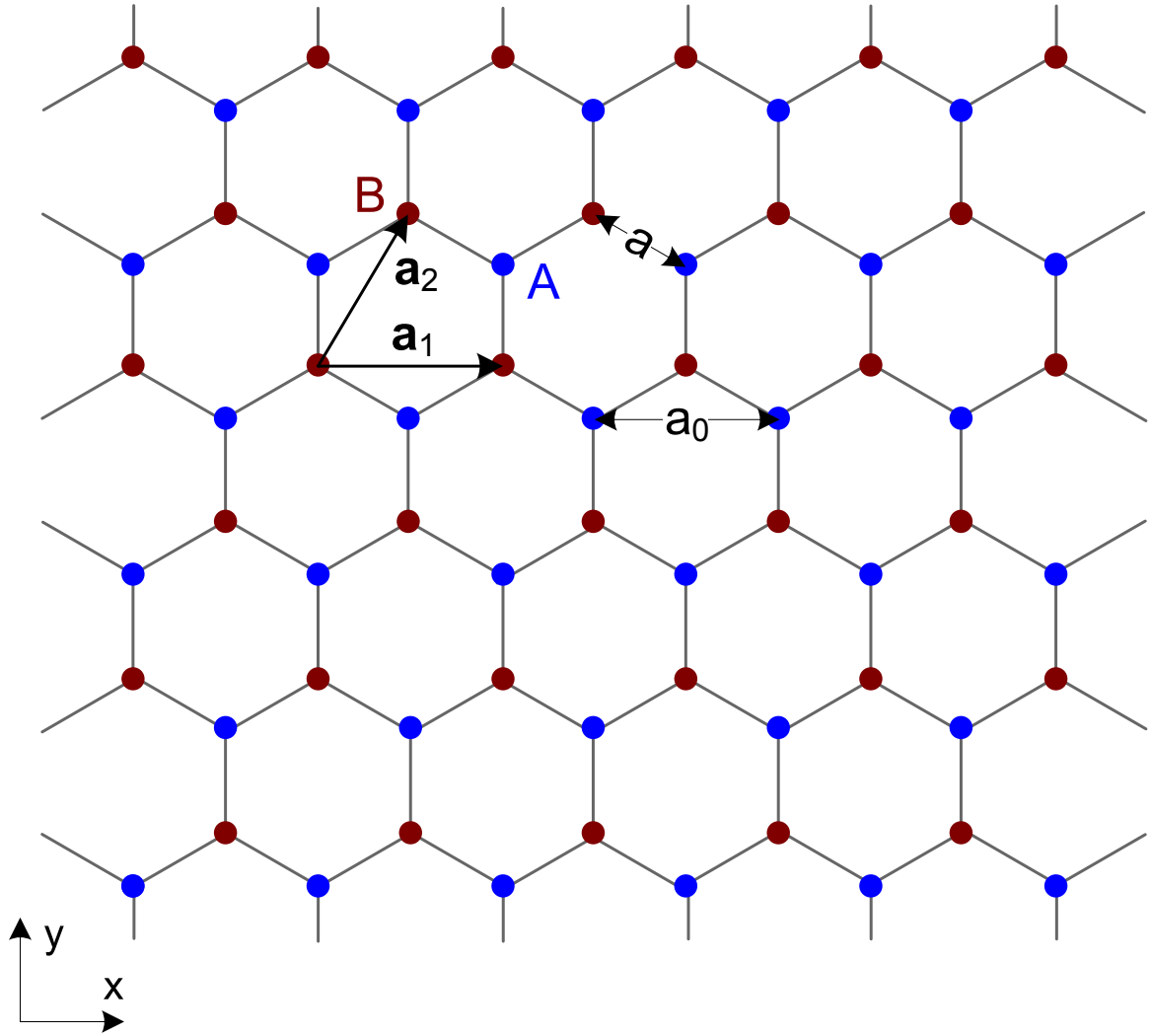
# 2. Review: Lattice structure and Dirac equation

## 2.1 Lattice, model Hamiltonian, wavefunctions

$$\mathbf{a}_1 = a_0(1, 0)$$

$$\mathbf{a}_2 = a_0(\frac{1}{2}, \frac{\sqrt{3}}{2})$$

$$a_0 = \sqrt{3}a$$



# 2. Review: Lattice structure and Dirac equation

## 2.1 Lattice, model Hamiltonian, wavefunctions

- Low-energy Dirac equation around $\mathbf{K}$ and $\mathbf{K}'$:

$$H_{\mathbf{K}}\psi(\mathbf{r}) = \gamma a_0 \begin{pmatrix} 0 & p_x - ip_y \\ p_x + ip_y & 0 \end{pmatrix} \psi(\mathbf{r}) = \varepsilon\psi(\mathbf{r})$$

$$H_{\mathbf{K}'}\psi'(\mathbf{r}) = \gamma a_0 \begin{pmatrix} 0 & p_x + ip_y \\ p_x - ip_y & 0 \end{pmatrix} \psi'(\mathbf{r}) = \varepsilon\psi'(\mathbf{r})$$

- With spinor/envelope wavefunctions

$$\psi(\mathbf{r}) = \begin{pmatrix} \psi_A(\mathbf{r}) \\ \psi_B(\mathbf{r}) \end{pmatrix} \quad , \quad \psi'(\mathbf{r}) = \begin{pmatrix} \psi'_A(\mathbf{r}) \\ \psi'_B(\mathbf{r}) \end{pmatrix}$$

and energy $\varepsilon = \pm\gamma a_0 |\mathbf{k}|$

# 2. Review: Lattice structure and Dirac equation

## 2.1 Lattice, model Hamiltonian, wavefunctions

### Wavefunctions in real space

Sublattice A:

$$\Psi_A(\mathbf{r}) = e^{i\mathbf{K}\cdot\mathbf{r}}\psi_A(\mathbf{r}) + e^{i\mathbf{K}'\cdot\mathbf{r}}\psi'_A(\mathbf{r})$$

Sublattice B:

$$\Psi_B(\mathbf{r}) = e^{i\mathbf{K}\cdot\mathbf{r}}\psi_B(\mathbf{r}) + e^{i\mathbf{K}'\cdot\mathbf{r}}\psi'_B(\mathbf{r})$$

How to deal with finite structures?

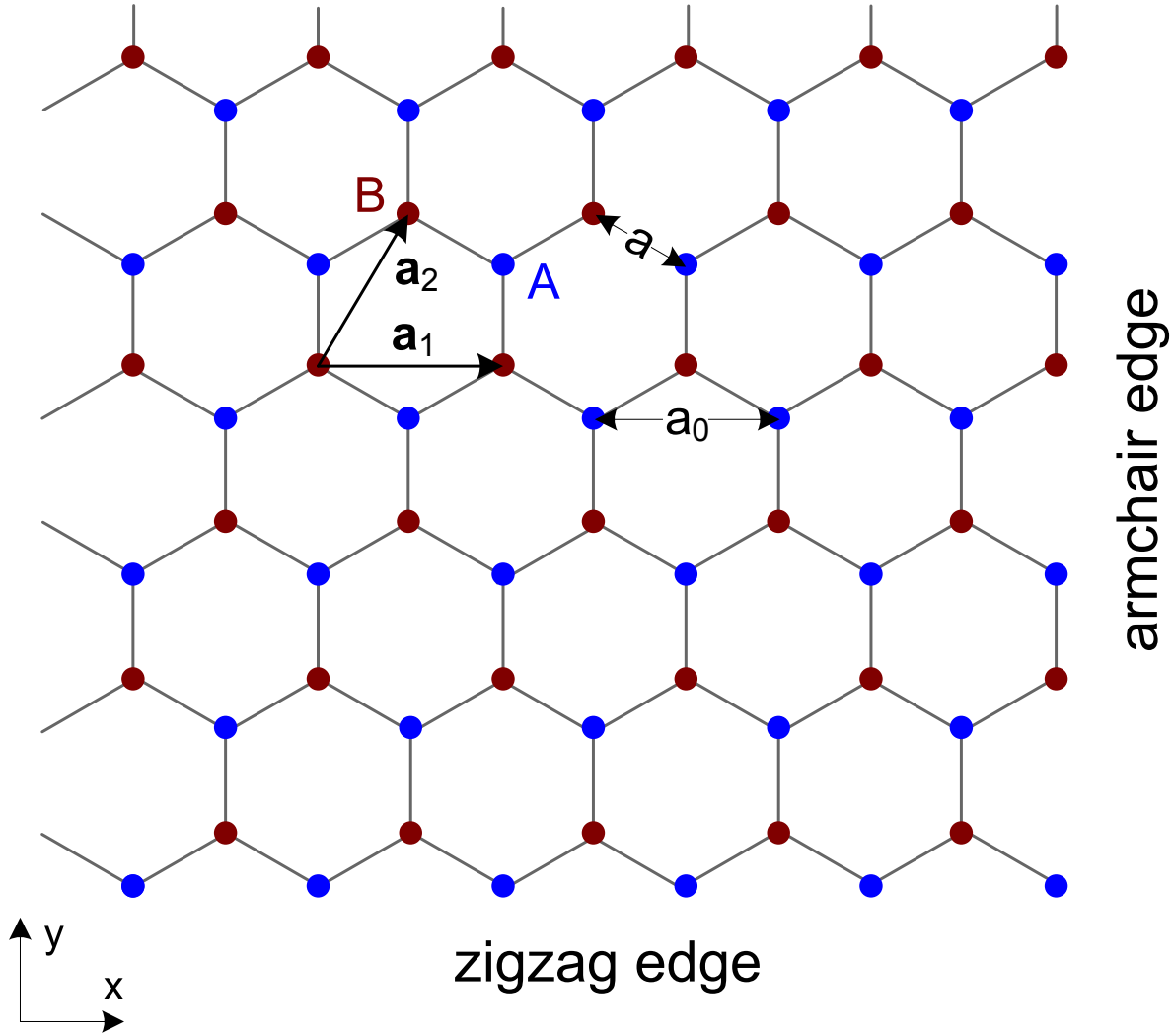
# 2. Review: Lattice structure and Dirac equation

## 2.2 Edge types

$$\mathbf{a}_1 = a_0(1, 0)$$

$$\mathbf{a}_2 = a_0(\frac{1}{2}, \frac{\sqrt{3}}{2})$$

$$a_0 = \sqrt{3}a$$



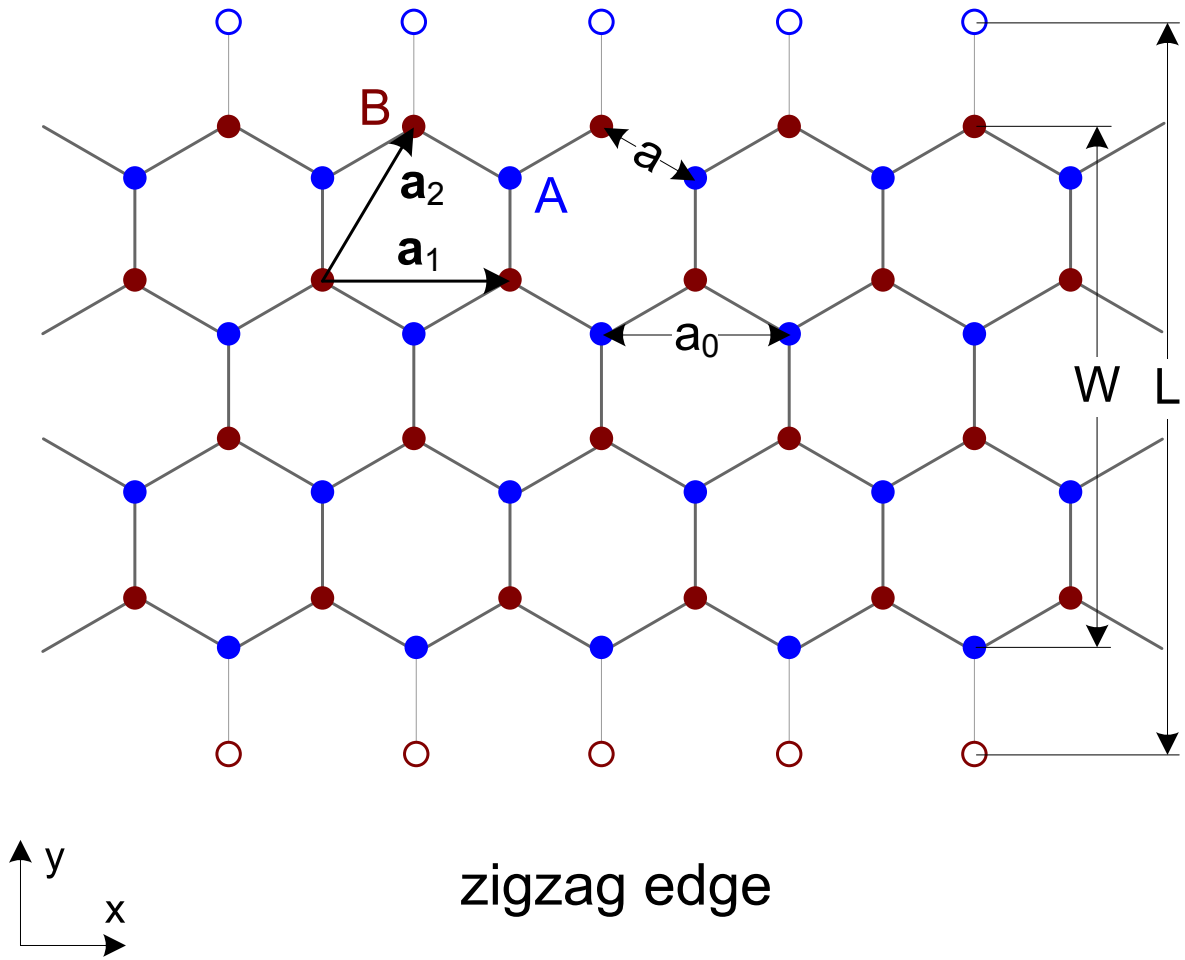
# 3. Zigzag nanoribbons

## 3.1 Spinor functions, boundary conditions

$$\mathbf{a}_1 = a_0(1, 0)$$

$$\mathbf{a}_2 = a_0(\frac{1}{2}, \frac{\sqrt{3}}{2})$$

$$a_0 = \sqrt{3}a$$



# 3. Zigzag nanoribbons

## 3.1 Spinor functions, boundary conditions

### Translational invariance in $x$-direction

$$\psi(\mathbf{r}) = \begin{pmatrix} \psi_A(\mathbf{r}) \\ \psi_B(\mathbf{r}) \end{pmatrix} = e^{ik_x x} \begin{pmatrix} \phi_A(y) \\ \phi_B(y) \end{pmatrix}$$

### Finite width $L$ in $y$-direction

$$\Psi_A(y = L) = 0 \quad , \quad \Psi_B(y = 0) = 0$$

# 3. Zigzag nanoribbons

## 3.2 Electronic dispersion

- Dirac equation ($p_j \to -i\partial_j$) for $\psi(\mathbf{r})$:

$$\begin{pmatrix} 0 & -i\partial_x - \partial_y \\ -i\partial_x + \partial_y & 0 \end{pmatrix} \psi(\mathbf{r}) = \tilde{\varepsilon}\psi(\mathbf{r})$$

with $\tilde{\varepsilon} = \frac{\varepsilon}{\gamma a_0}$

$$\begin{aligned} \Rightarrow \ (k_x - \partial_y)\phi_B &= \tilde{\varepsilon}\phi_A \\ (k_x + \partial_y)\phi_A &= \tilde{\varepsilon}\phi_B \end{aligned} \tag{1}$$

- Acting $(k_x + \partial_y)$ on (1)

$$\begin{aligned} (k_x + \partial_y)(k_x - \partial_y)\phi_B &= \tilde{\varepsilon}(k_x + \partial_y)\phi_A \\ \Leftrightarrow \ (k_x^2 - \partial_y^2)\phi_B &= \tilde{\varepsilon}^2\phi_B \end{aligned}$$

# 3. Zigzag nanoribbons

## 3.2 Electronic dispersion

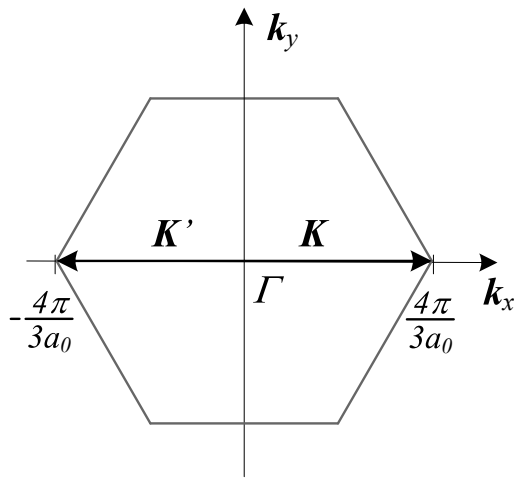
- General solution

$$\phi_B(y) = \alpha e^{zy} + \beta e^{-zy}$$
$$\Rightarrow \ \tilde{\varepsilon} = \pm\sqrt{k_x^2 - z^2}$$

- With $\mathbf{K} = (K, 0)$ and $\mathbf{K}' = (-K, 0)$ this yields

$$0 = e^{iKx} e^{ik_x x} \phi_A(L) + e^{-iKx} e^{ik_x x} \phi'_A(L)$$
$$0 = e^{iKx} e^{ik_x x} \phi_B(0) + e^{-iKx} e^{ik_x x} \phi'_B(0)$$

$$\Rightarrow \ \phi_A(L) = \phi'_A(L) = \phi_B(0) = \phi'_B(0) = 0$$



- Together with spinors

$$\phi_B(y) = \alpha e^{zy} + \beta e^{-zy} \quad \text{and} \quad \phi_A(y) = \frac{1}{\tilde{\varepsilon}}(k_x - \partial_y)\phi_B$$

$$\Rightarrow \; 0 = \alpha + \beta$$
$$0 = (k_x - z)\alpha e^{Lz} + (k_x + z)\beta e^{-Lz}$$

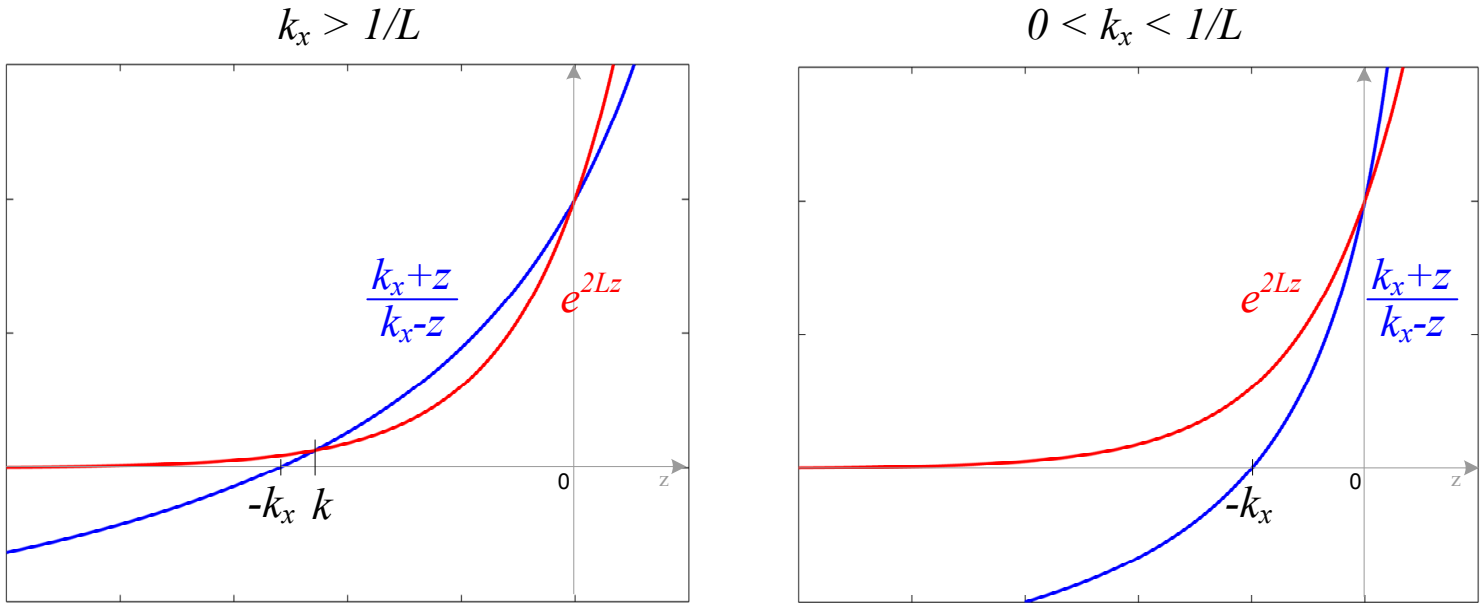
- Transcendental equation for $z$

$$\frac{k_x + z}{k_x - z} = e^{2Lz} \tag{2}$$

# 3. Zigzag nanoribbons

## 3.2 Electronic dispersion: Surface states

- Solutions of (2) for real values of $z = k$

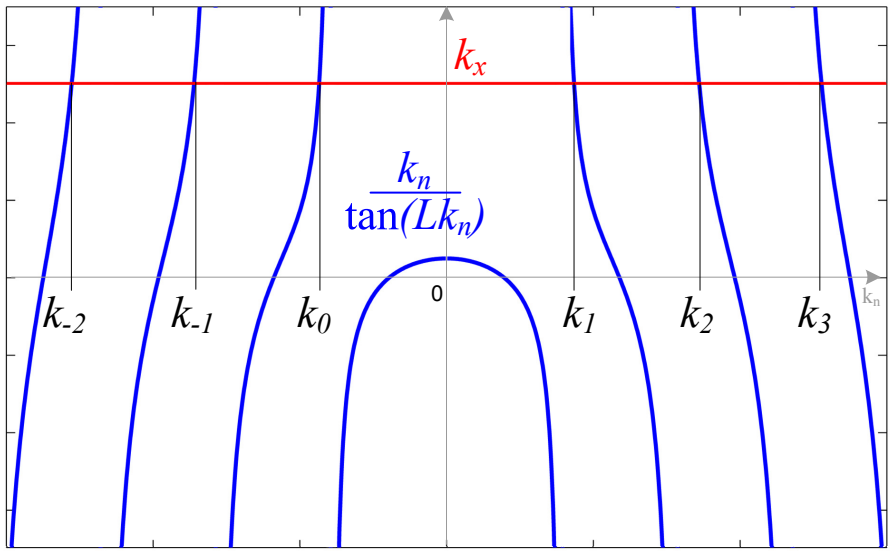



- $k_x > \frac{1}{L}$: surface states with energy $\tilde{\varepsilon}_s = \pm\sqrt{k_x^2 - k^2}$
- for large $k_x$: $\tilde{\varepsilon}_s \to 0$, degeneracy
- $k_x < \frac{1}{L}$: no states with real $z$

# 3. Zigzag nanoribbons

## 3.2 Electronic dispersion: Confined states

- Solutions of (2) for pure imaginary values of $z = ik_n$

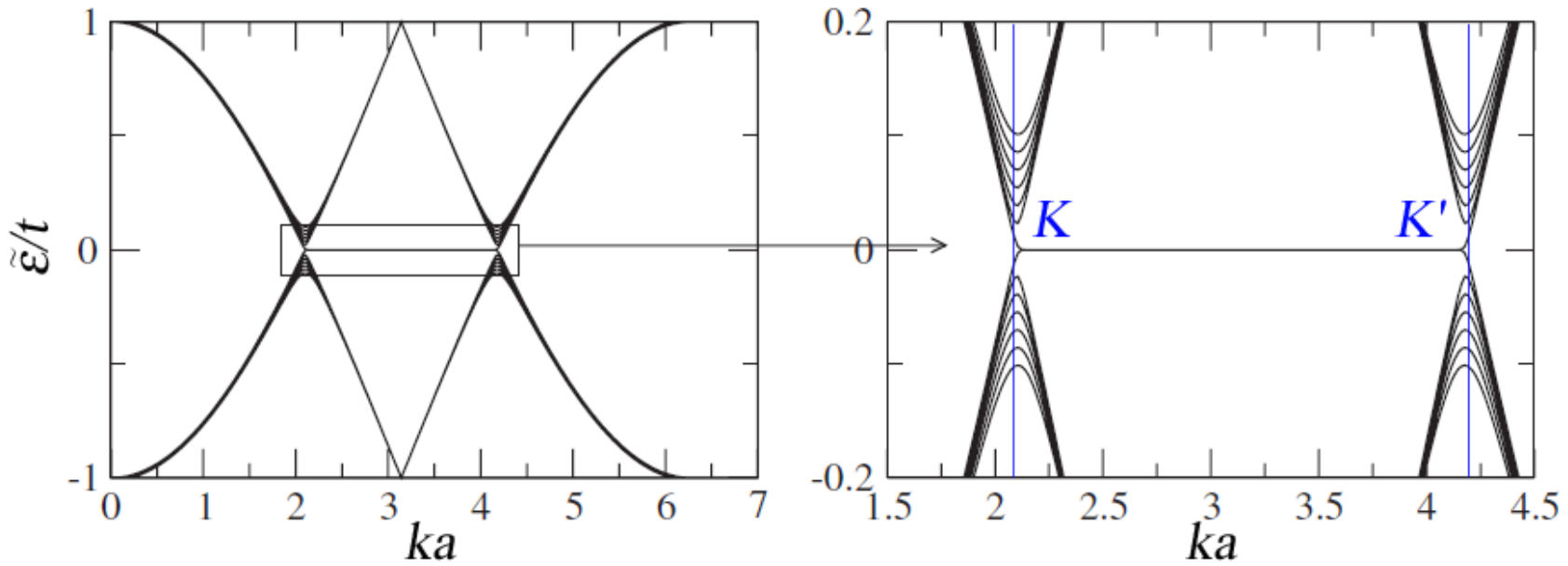



- confined states with energy $\tilde{\varepsilon}_c = \pm\sqrt{k_x^2 + k_n^2}$
- Dirac equation motivates $n \in \mathbb{Z}$
- for large $|k_x|$: $\tilde{\varepsilon}_c \propto \pm k_x$

# 3. Zigzag nanoribbons

## 3.2 Electronic dispersion

- Calculation for $\mathbf{K}'$ valley yields $k_x \to -k_x$
- Tight-binding calculation for $L = 201a_0$:




[Castro Neto et al., 2009]

# 4. Armchair nanoribbons

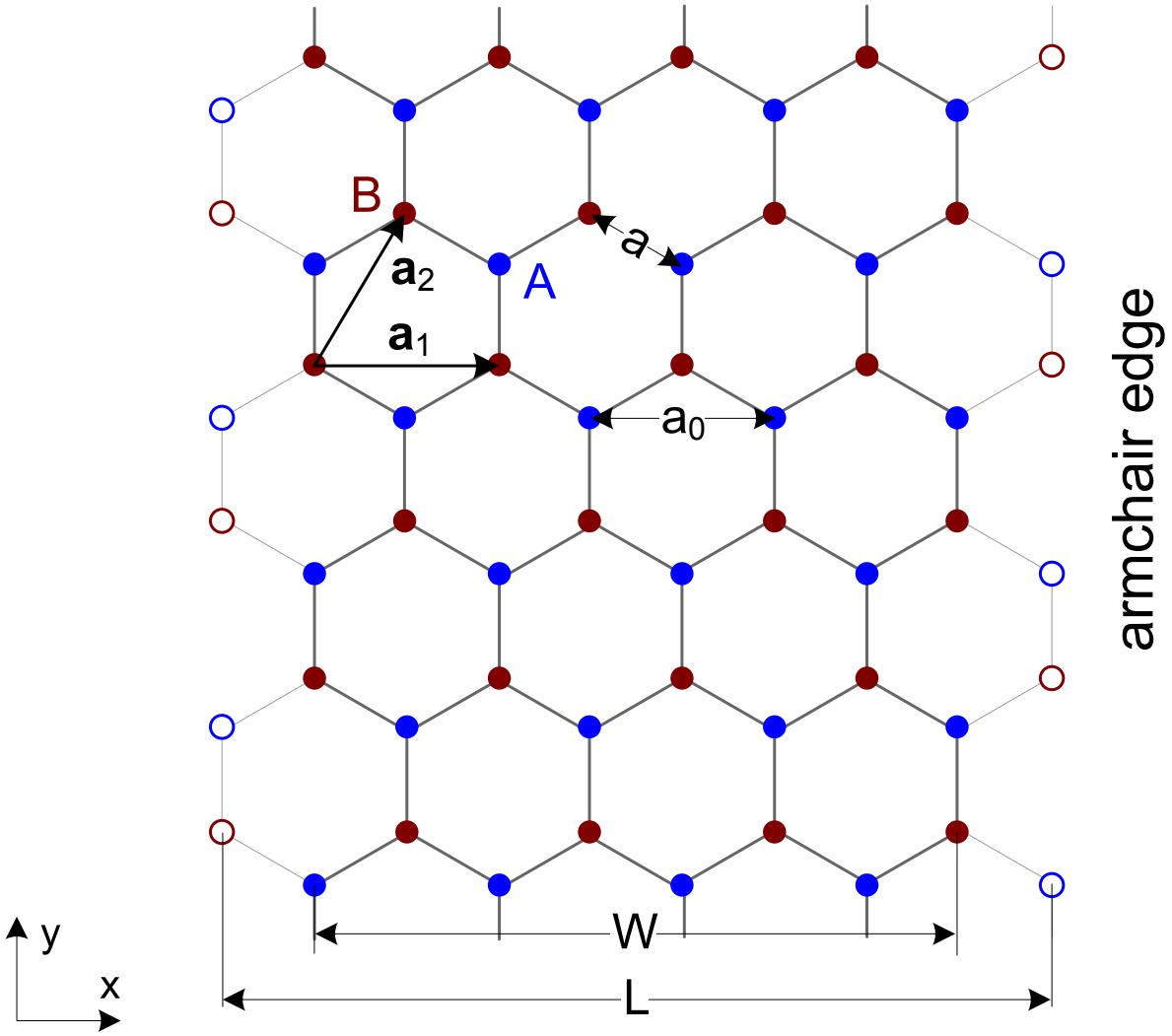
## 4.1 Spinor functions, boundary conditions

$$\mathbf{a}_1 = a_0(1,0)$$

$$\mathbf{a}_2 = a_0(\frac{1}{2}, \frac{\sqrt{3}}{2})$$

$$a_0 = \sqrt{3}a$$

$$W = L - a_0 = w\frac{a_0}{2}$$



# 4. Armchair nanoribbons

## 4.1 Spinor functions, boundary conditions

### Translational invariance in $y$-direction

$$\psi(\mathbf{r}) = \begin{pmatrix} \psi_A(\mathbf{r}) \\ \psi_B(\mathbf{r}) \end{pmatrix} = e^{ik_y y} \begin{pmatrix} \phi_A(x) \\ \phi_B(x) \end{pmatrix}$$

### Finite width $L$ in $x$-direction

$$\Psi_A(x=0) = \Psi_A(x=L) = 0 \quad , \quad \Psi_B(x=0) = \Psi_B(x=L) = 0$$

# 4. Armchair nanoribbons

## 4.2 Electronic dispersion

- Spinor wavefunctions with $z = ik_n$

$$\phi_B(x) = \alpha e^{ik_n x} + \beta e^{-ik_n x}$$
$$\phi'_B(x) = \gamma e^{ik_n x} + \delta e^{-ik_n x}$$

- Boundary conditions satisfied for $\alpha = -\delta$ and $\beta = \gamma = 0$ which leads to

$$\sin((k_n + K)L) = 0 \;\Leftrightarrow\; (k_n + K)L = \pi n$$

with $K = \frac{4\pi}{3a_0}$ and $n \in \mathbb{Z}$

- Only confined states with

$$k_n = \frac{n\pi}{L} - \frac{4\pi}{3a_0} \quad \text{and} \quad \tilde{\varepsilon} = \pm\sqrt{k_y^2 + k_n^2}$$

# 4. Armchair nanoribbons

## 4.2 Electronic dispersion: Confined states

- Width of the nanoribbon $W = L - a_0 = w\frac{a_0}{2}$
- Searching for $k_n = 0$ (metallic states)

$$0 = \frac{n\pi}{(w+2)\frac{a_0}{2}} - \frac{4\pi}{3a_0}$$

$$\Leftrightarrow \quad w = \frac{3}{2}n - 2$$

- Satisfied for $w = 1, 4, 7, \ldots$ and band index $n = 2, 4, 6 \ldots$
- For $k_y = 0$ the energy $\tilde{\varepsilon} = \pm\sqrt{k_y^2 + k_n^2}$ only vanishes if

$$w = 3m + 1 \quad \text{with} \quad m \in \mathbb{N}$$

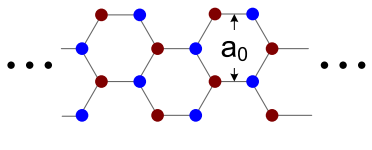
- For any other width: bandgap $E_g \propto \frac{1}{w}$!

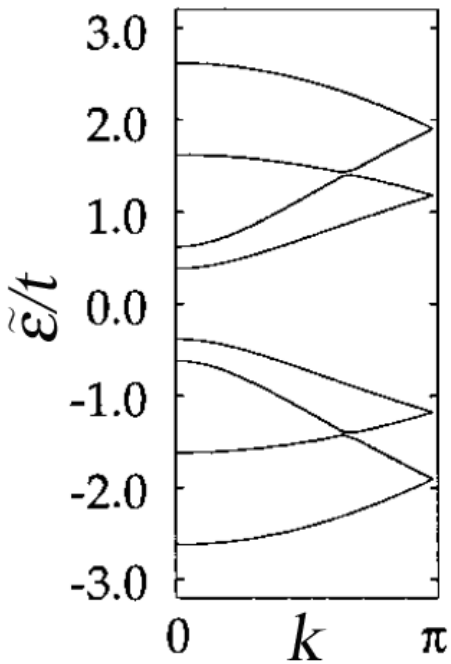
# 4. Armchair nanoribbons

## 4.2 Electronic dispersion

- Tight-binding calculation for different values of $w$:

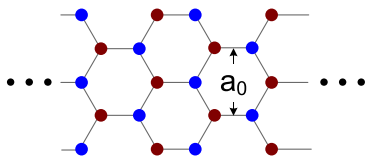
$w = 3$

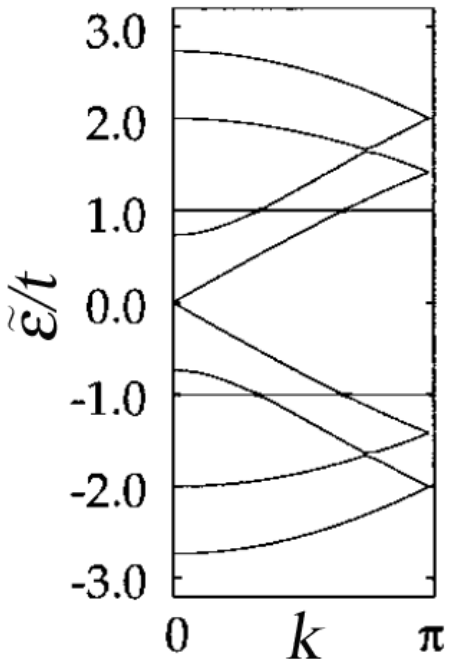


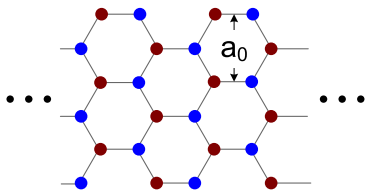

[Nakada et al., 1996]

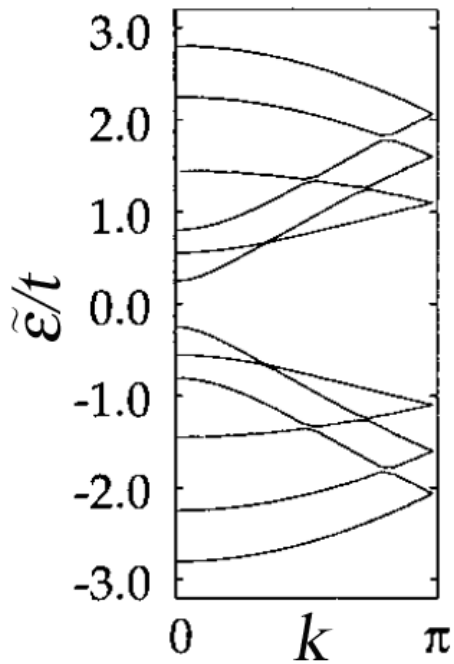
$w = 4$




$w = 5$



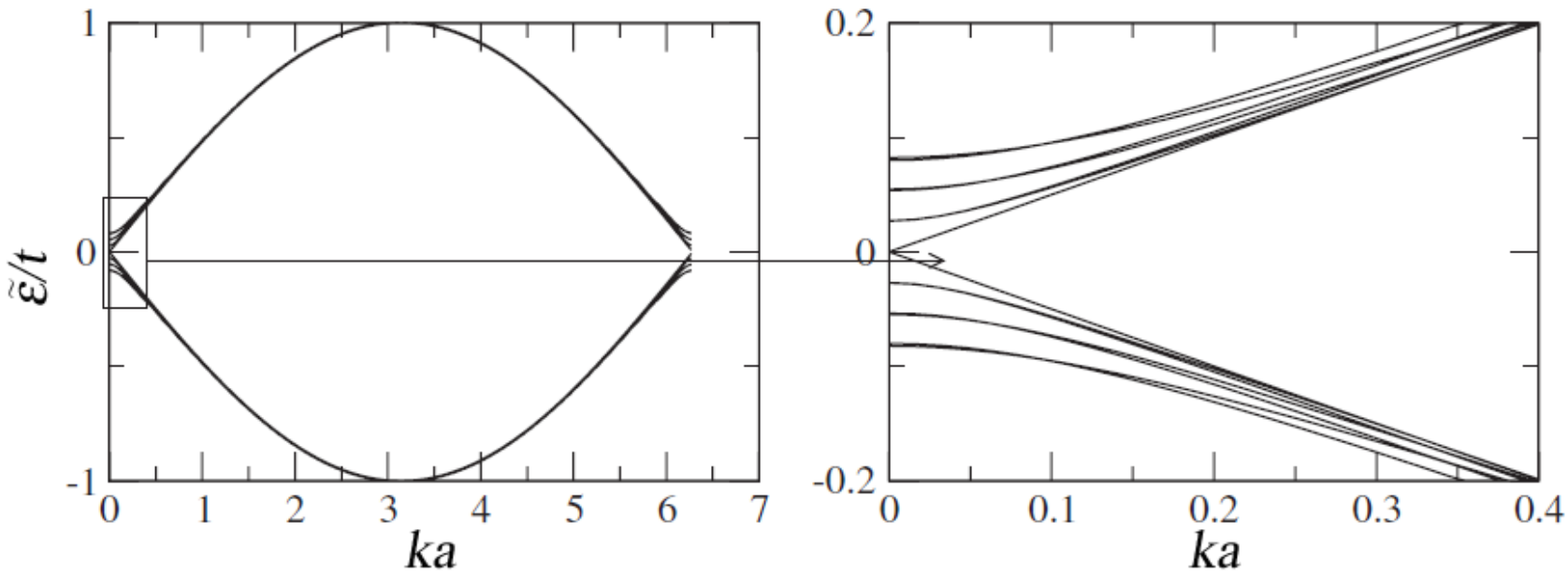
# 4. Armchair nanoribbons

## 4.2 Electronic dispersion

- Tight-binding calculation for $W = 400\frac{a_0}{2}$:

$$w = 3m + 1 \;\Rightarrow\; m = 133$$

No gap!

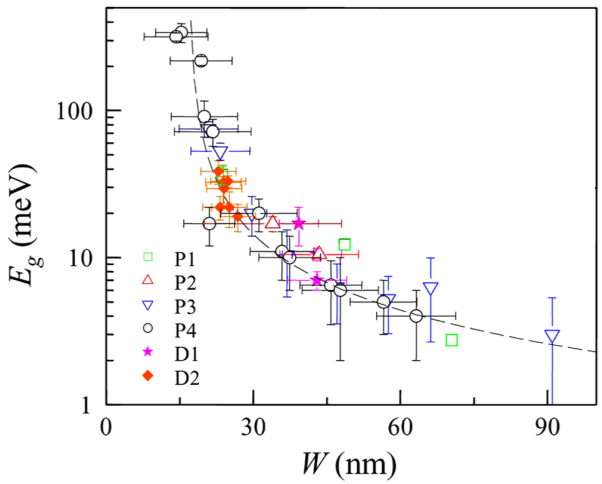



[Castro Neto et al., 2009]

# 5. Summary

- Electronic properties of graphene nanoribbons depend critically on their geometry and size

- Zigzag nanoribbons:
  - localized zero energy surface states, degeneracy
  - delocalized confined states
  - zero gap semiconductor



[Han et al., 2007]

- Armchair nonoribbons:
  - no surface states, only delocalized confined states
  - zero gap semiconductor or **band gap** depending on the width

- Application in semiconductor physics? Spin qubits?

# References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