Ripples in graphene: A variational approach

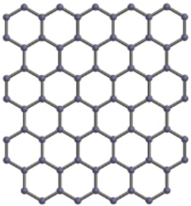
Manuel Friedrich

WWU Münster, Germany

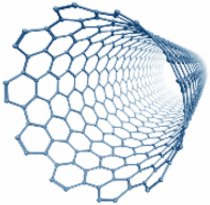
Banff, May 2018

Joint work with U. Stefanelli (Vienna)

Carbon nanostructures:



Graphene



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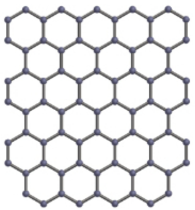

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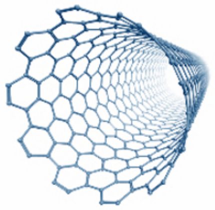

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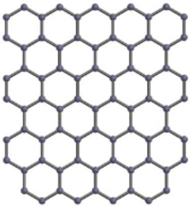

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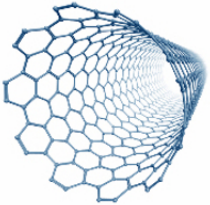

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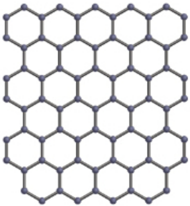
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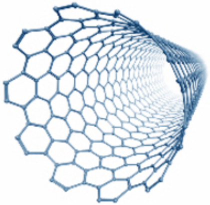
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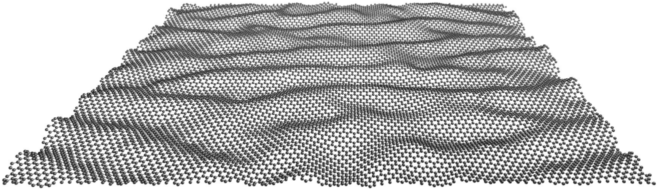
- Remarkable electro-mechanical and optical properties.
- Applications in chemistry, nano-electronics, optics, mechanics.
- Rigorous mathematical results mostly unavailable.



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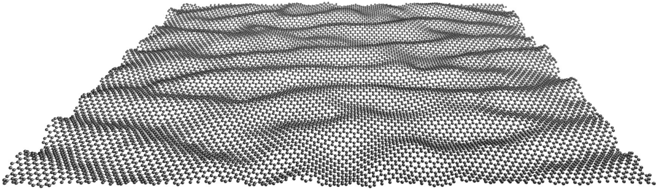
- Suspended graphene sheets are not flat but gently rippled! [Meyer et al. '07]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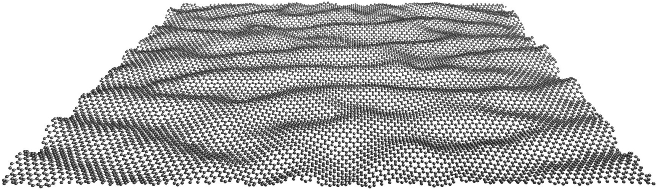

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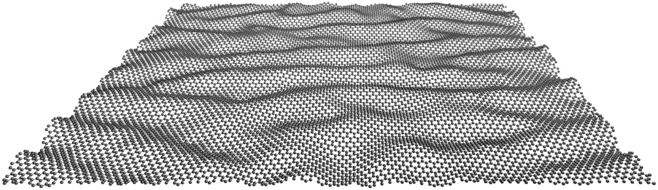

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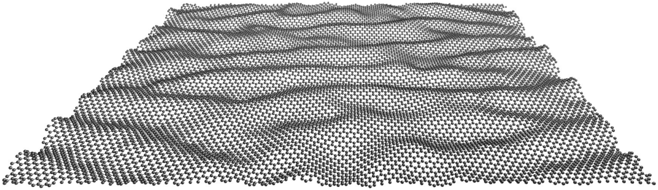

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- Waves of approximately 100 atom spacings, sample-size independent wavelength.
- Tendency to unidirectional waves (under stretching).
- Free graphene sheets tend to roll-up $\rightsquigarrow$ nanotubes/nanoscrolls.
- Reasons: Stabilization at finite temperatures, quantum fluctuations, randomly attached impurities, ...

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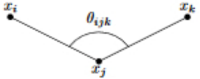
Outline:

- Phenomenological energies.
- Global vs. local minimization.
- Modeling choices ensuring nonflatness of graphene.
- Periodicity in one direction, unidirectional waves.
- Wave patterning with sample-size-independent wavelength.

Basic phenomenological energies:

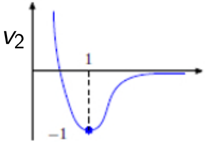
$X = (x_i)_i$ atomic positions,

θ_{ijk} angle formed by x_i, x_j, x_k.



$$E(X) = \sum_{ij \in NN} v_2(|x_i - x_j|) + \sum_{ij,jk \in NN} v_3(\theta_{ijk}).$$

Two-body interactions



Lennard-Jones

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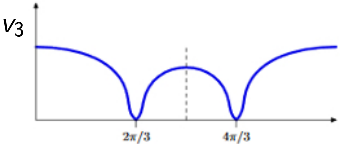


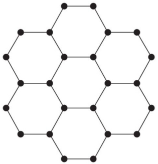
Tersoff

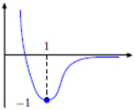
Local/global minimization:

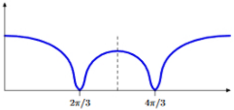
- Hexagonal lattice a strict local minimizer of E:

$$E(X') > E(X),$$

where $X' = (x_i')_i$ with $|x_i - x_i'| \leq \eta$, $\eta > 0$ small.







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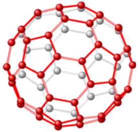
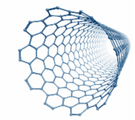
- Fullerene C_{60} and nanotubes a strict local minimizers of E



[F., Piovano, Stefanelli '16]



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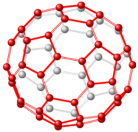

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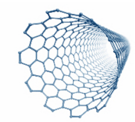
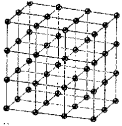


[F., Mainini, Piovano, Stefanelli '17]

- Structures are not ground states:

Bravais lattices in $\mathbb{R}^3$

are energetically favorable!



Intermediate point of view:

- H (infinite) hexagonal lattice is reference configuration, in particular all neighbors are kept fix.
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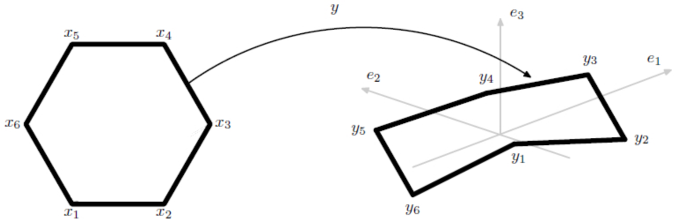
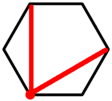


- Deformation ground state $\Leftrightarrow$ energy of every cell optimal.
- Flat hexagonal lattice unique ground state.

Refined model:

$$E_{\mathrm{ref}} = E + \rho \sum_{ij \in NNN} v_2(|x_i - x_j|), \quad \rho \text{ small.}$$



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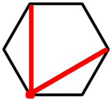

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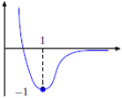
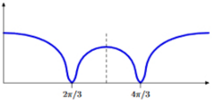
- bond length $l^* < 1$, angle $\psi^* < 2\pi/3$.





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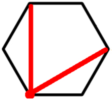

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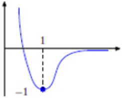
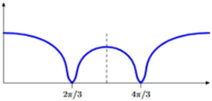
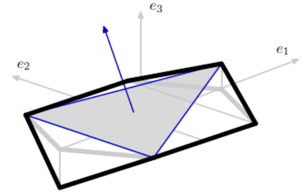
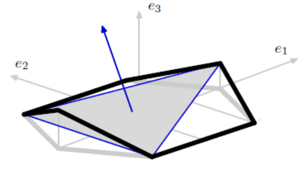




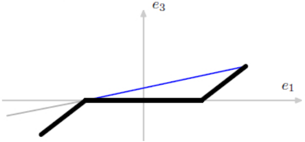
Two optimal cell geometries:

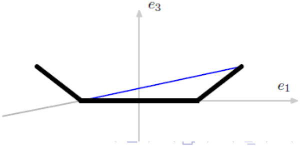
Z cell





C cell





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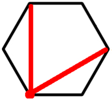

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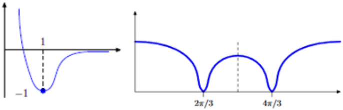

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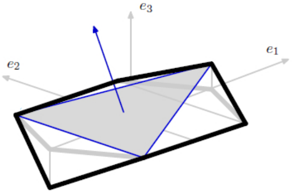

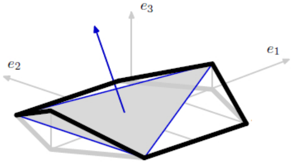

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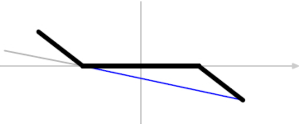
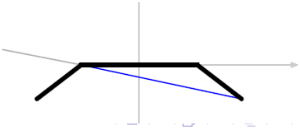
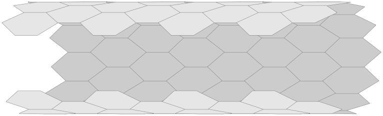




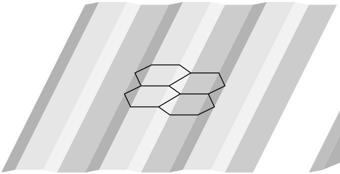
$\bar{C}$ cell

Characterization of ground states: [F., Stefanelli '18]

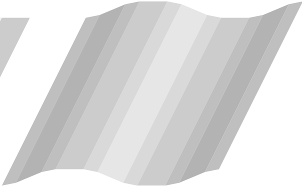
1. Roll-up structures: All cells are of type C.



2. Rippled structures: Types are constant along one direction.



$\dots, C, \bar{C}, C, \bar{C}, C, \bar{C}, \dots$



$\dots, \bar{Z}, \bar{C}, Z, C, \dots$

Proof via geometric compatibility.

- Previous result shows unidirectionality of ground states.

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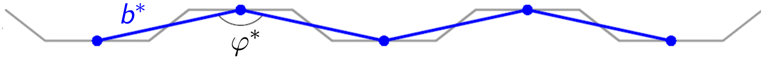
- Effective description of a section of the rippled structure:



Example for $\dots, C, \bar{C}, C, \bar{C}, C, \bar{C}, \dots$

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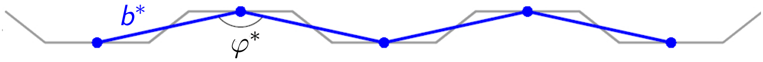

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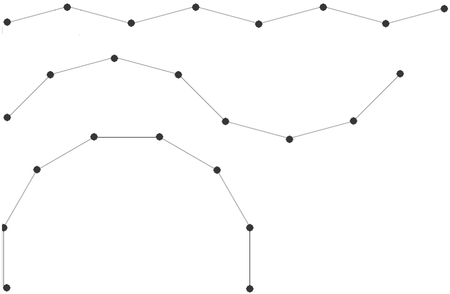
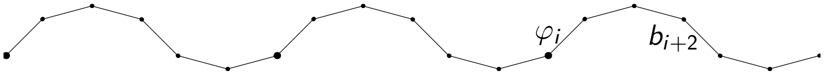


Variety of minimizers!

Suspended samples:
Specific wavelengths?

Effective 1D-to-2D model:

- Admissible configurations $y : \{1, \ldots, n\} \in \mathbb{R}^2$ with bonds $b_i = |y_i - y_{i+1}|$, angles $\varphi_i = \sphericalangle(y_{i+1} - y_i, y_{i-1} - y_i)$.



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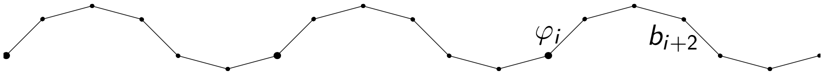

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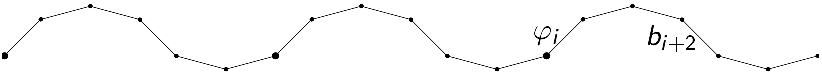
  $\rightsquigarrow$ same ground states as before with energy $(n-2)e_{\text{cell}}$.



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- Admissible configurations $y : \{1, \dots, n\} \in \mathbb{R}^2$ with bonds $b_i = |y_i - y_{i+1}|$, angles $\varphi_i = \sphericalangle(y_{i+1} - y_i, y_{i-1} - y_i)$.
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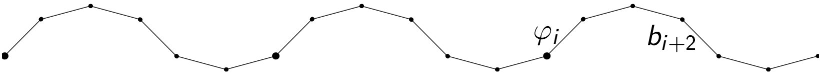

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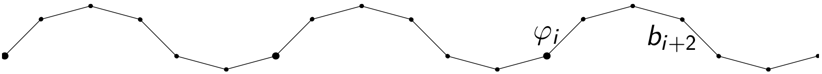

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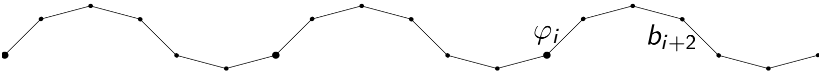

Ground-state "waves" with atomic period $\alpha = 6$ and length L_α.

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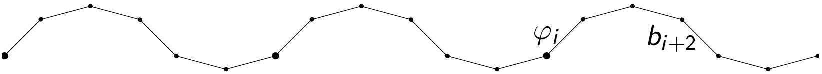

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Mean projected bond length $\lambda_\alpha = L_\alpha / \alpha$ $\rightsquigarrow$ $\lambda_\alpha = \mu$.

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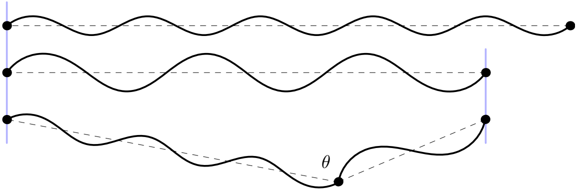

smaller α, larger λ_α

larger α, smaller λ_α

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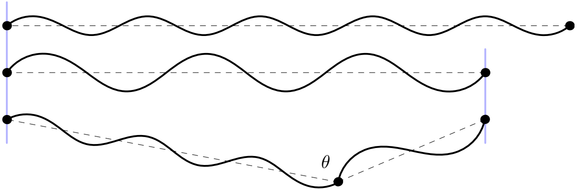

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mixed α

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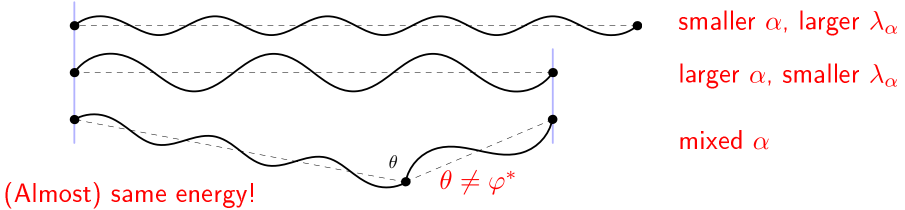
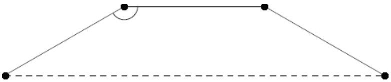
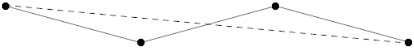


Further refinement of energy: Third neighbors!

$$E^{\text{eff}}_{\text{ref}}(y) = E^{\text{eff}}(y) + \bar{\rho} \sum_i v_2^{\text{eff}}(|y_{i+3} - y_i|), \qquad \bar{\rho} \text{ small.}$$



smaller refined energy



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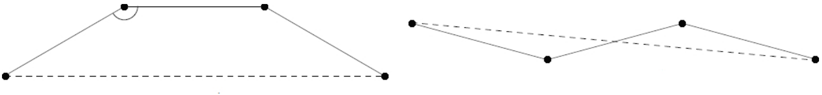

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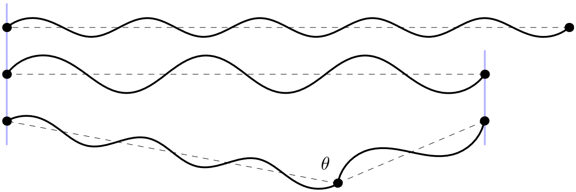

large energy

small energy

intermediate energy

Minimal energy: [F., Stefanelli' 18]

For $\mu < 1$ let $E_{\mathrm{min}}(\mu) = \frac{1}{n} \min_{y \in \mathcal{A}(\mu)} E^{\mathrm{eff}}_{\mathrm{ref}}(y)$ normalized minimal energy.

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Characterization of almost minimizers: [F., Stefanelli' 18]

Up to small portion of size $\mathrm{O}(\bar{\rho})$, almost minimizers satisfy:

- $\mu \in M_{\mathrm{res}}$: Composed of waves with atomic period α where $\lambda_\alpha = \mu$.
- $\mu \in [\mu', \mu'']$: Composed of waves with two atomic periods α', α''.

Summary:

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Thank you for your attention!