Lattice distorsions in the tight-binding model of graphene

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joint work with D. Gontier and T. Roussigné

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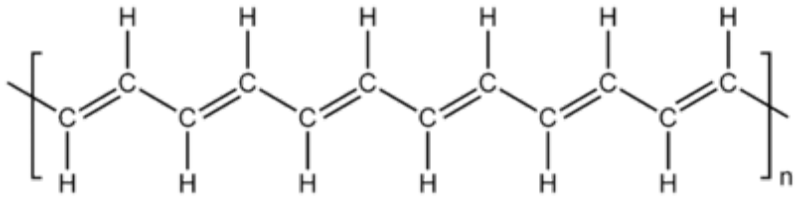
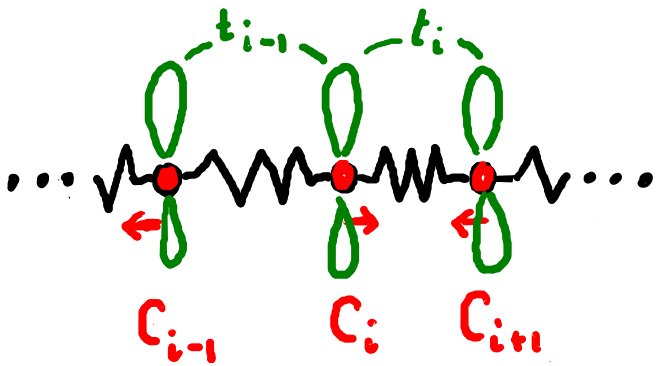
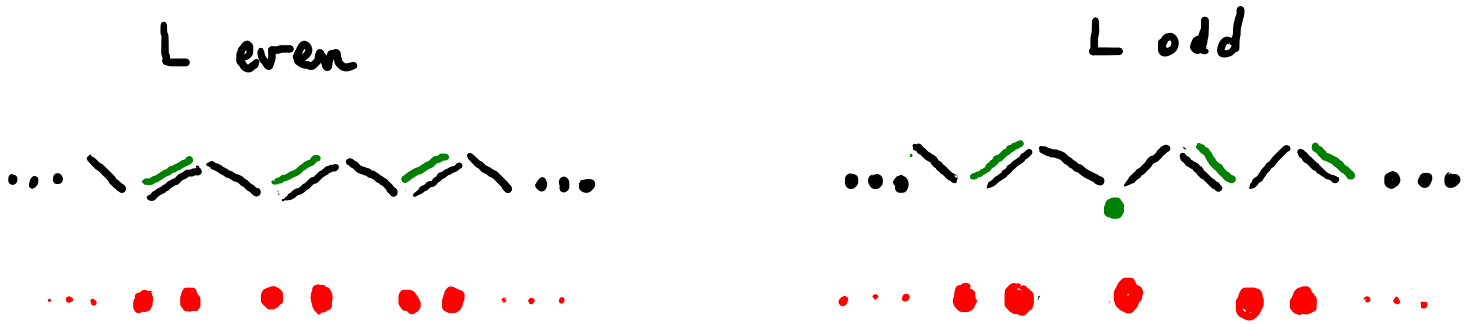
One dimension: example of the polyacetylene chain

Structural formula of polyacetylene:



Tight-binding model of closed polyacetylene chain with L carbon atoms:





Discrete model of polyacetylene: the Hamiltonian

The π electrons live in the Hilbert space $\mathbb{C}^L \otimes \mathbb{C}^2$.

The Hamiltonian $T \otimes \mathbb{1}_{\mathbb{C}^2}$ depends on a vector $\boldsymbol{t} \in \mathbb{R}^L$ of hopping amplitudes:

$$T = T(\boldsymbol{t}) := \begin{pmatrix} 0 & t_1 & 0 & 0 & \cdots & t_L \\ t_1 & 0 & t_2 & \cdots & 0 & 0 \\ 0 & t_2 & 0 & t_3 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & \cdots & t_{L-2} & 0 & t_{L-1} \\ t_L & 0 & \cdots & 0 & t_{L-1} & 0 \end{pmatrix}.$$

Electronic energy at half-filling

The π electrons occupy all the negative energy states.Their energy is

$$K(\boldsymbol{t}) = -2\mathrm{Tr}\left(T^{-}\right) = -\mathrm{Tr}\left(|T|\right).$$

With $\gamma(\boldsymbol{t}) := \mathbb{1}_{(-\infty,0)}(T)$, one also has

$$K(\boldsymbol{t}) = 2\mathrm{Tr}\left(\gamma(\boldsymbol{t})\,T\right) = 4\sum_{i\in\mathbb{Z}/L\mathbb{Z}} t_i\,\gamma(\boldsymbol{t})_{i,i+1}\,.$$

Total energy at half-filling

In addition, the chain has the elastic energy $\frac{\mu}{2}\sum_{i=1}^{L}(t_i-1)^2 \quad (\mu>0)$.

Total energy of the chain:

$$\boxed{\mathcal{E}^{(L)}(\mathbf{t}) = \frac{\mu}{2}\sum_{i=1}^{L}(t_i-1)^2 - \mathrm{Tr}\left(|T|\right).}$$

Any minimizer must satisfy the system of Euler-Lagrange equations $\frac{\partial \mathcal{E}^{(L)}}{\partial t_i} = 0$, which takes the self-consistent form

$$t_i = 1 + \frac{4}{\mu}\gamma(\boldsymbol{t})_{i,i+1}\,, \quad \forall i \in \mathbb{Z}/L\mathbb{Z}\,.$$

Dimerization (Peierls instability) for L even

Theorem (Kennedy-Lieb, PRL 1987)

If $L = 2N$, the only configurations minimizing $\mathcal{E}^{(L)}$ are

$$t_i^+ = W_N + (-1)^i \delta_N \quad \text{and} \quad t_i^- = W_N - (-1)^i \delta_N$$

where $W_N > \delta_N \geq 0$ depend only on N and μ. When $N \to \infty$ (μ fixed) one has $W_N \to W$ and $\delta_N \to \delta$ with $W > \delta > 0$.

The property $\delta > 0$ called Peierls instability was proved independently by Fröhlich '54 and Peierls '55.

Kivelson-Heim '82 showed that for N even, one always has $\delta_N > 0$.

For N odd and small, one may have $\delta_N = 0$ (example: Benzene $\mathrm{C_6H_6}$).

The main argument of Kennedy-Lieb

Key observation: $\mathbf{t}$ is 2-periodic $\Longleftrightarrow$ T^2 commutes with all translations.

Theorem

Let I be an interval and $\varphi : I \to \mathbb{R}$ a convex function. Let $\mathcal{I}$ be the convex set consisting of Hermitian matrices A of order L such that $\sigma(A) \subset I$. Then the map $A \in \mathcal{I} \mapsto \mathrm{Tr}\,(\varphi(A))$ is convex.

Kennedy-Lieb take $I = \mathbb{R}_+$ and $\varphi(x) = -\sqrt{x}$. They write $|T| = \sqrt{T^2}$ and

$$-\mathrm{Tr}\,(|T|) = \frac{1}{2N}\sum_{k=1}^{2N} \mathrm{Tr}\left(-\sqrt{\Theta_k T^2 \Theta_k^{-1}}\right) \geq \mathrm{Tr}\left(-\sqrt{< T^2 >}\right),$$

with $< T^2 > := \frac{1}{2N}\sum_{k=1}^{2N} \Theta_k T^2 \Theta_k^{-1}$, Θ_k being the shift of k units.

Proof of Peierls instability in the limit $L \to \infty$

The limit $\underline{\mathcal{E}} := \lim_{L\to\infty} \frac{1}{L}\mathcal{E}_L$ (energy per unit cell) is well-defined:

$$\begin{aligned}\underline{\mathcal{E}}(W,\delta) &= \frac{\mu}{2}\left[(W-1)^2+\delta^2\right] - \frac{2}{\pi}\int_0^{\frac{\pi}{2}} \sqrt{4W^2\cos^2(k)+4\delta^2\sin^2(k)}\,dk \\ &= \underline{\mathcal{E}}(W,0) + \frac{\mu}{2}\delta^2 + \frac{2\delta^2}{\pi W}\log\left(\frac{\delta}{2W}\right) + o(\delta^2).\end{aligned}$$

Conclusion: For all $\mu > 0$, taking a small $\delta > 0$ decreases the energy, as first observed by Fröhlich and Peierls: cost $\sim \delta^2$ in elastic energy, gain $\sim \delta^2 \log(\delta)$ in quantum energy.

Heteroclinic configuration for $L = 2N+1 \to \infty$

When $L = 2N >> 1$, there are two minimizers $\boldsymbol{t}^{\pm}$ with $\boldsymbol{t}_i^{\pm} = W \pm (-1)^i \delta$.

When $L = 2N+1 >> 1$, the minimizers "interpolate" between these two configurations.

Theorem (Garcia Arroyo - S., Gontier-Kouande-S.)

*If $L = 2N+1$, minimizers look like «*kinks*» :*
If $\boldsymbol{t}(N)$ is a minimiser, then, up to space translation and extraction of a subsequence, $\lim_{N\to\infty} \boldsymbol{t}(N)_i =: t_i$ exists, and

$$|t_{-i} - W + (-1)^i \delta| + |t_i - W - (-1)^i \delta| \leq C e^{-\rho i}, \quad \forall i > 0 .$$

Moreover one has

$$t_i = 1 + \frac{4}{\mu} \gamma(\boldsymbol{t})_{i,i+1}, \quad \forall i \in \mathbb{Z},$$

where $\gamma(\boldsymbol{t}) := \mathbb{1}_{(-\infty,0)}(T)$.

The spectral gap ($L = 2N$ finite)

For $L = 2N$ and $t_i = W_N + (-1)^i \delta_N$, we have

$$T = \begin{pmatrix} 0 & a & 0 & 0 & \cdots & b \\ a & 0 & b & \cdots & 0 & 0 \\ 0 & b & 0 & a & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & \cdots & b & 0 & a \\ b & 0 & \cdots & 0 & a & 0 \end{pmatrix}, \quad \sigma(T) = \bigcup_{\omega^N = 1} \{\pm |a + b\omega|\}, \quad \begin{cases} a = W_N + \delta_N \\ b = W_N - \delta_N. \end{cases}$$

Spectral gap around the origin of size $4\delta_N$ for N even (slightly larger than $4\delta_N$ for N odd).

Spectral gap (L infinite)

When L is infinite, T becomes an operator acting in $\ell^2(\mathbb{Z}, \mathbb{C})$.

- If $t_i^{\pm} = W \pm (-1)^i \delta$ with $W > \delta \geq 0$, the spectrum of $T^{\pm}$ is

$$\sigma(T^{\pm}) = [-2W, -2\delta] \cup [2\delta, 2W] \,.$$

- The interval $(-2\delta, 2\delta)$ is a spectral gap when $\delta > 0$. At zero temperature the lower band is occupied, the upper band is empty (insulator).

- The gap closes when $\delta = 0$ (metallic state).

- If $\lim_{i \to \pm\infty}(t_i - t_i^{\pm}) = 0$ and $W > \delta > 0$ (heteroclinic configuration) then

$$\sigma_{\mathrm{ess}}(T) = [-2W, -2\delta] \cup [2\delta, 2W]$$

and 0 is an eigenvalue of multiplicity one.

Two dimensions: the example of graphene

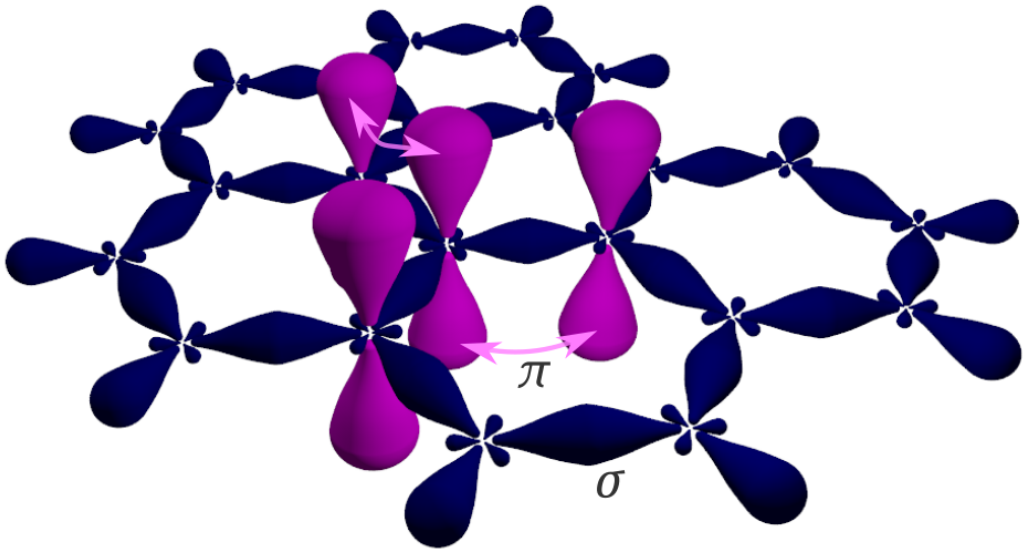
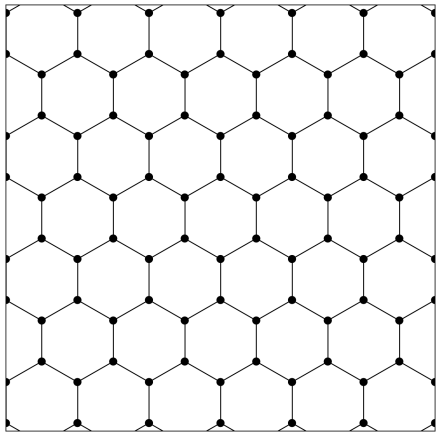


Figure: **Graphene:** a 2-d carbon allotrope with a honeycomb lattice, first isolated by Geim and Novoselov in 2004.

Structural formula of graphene

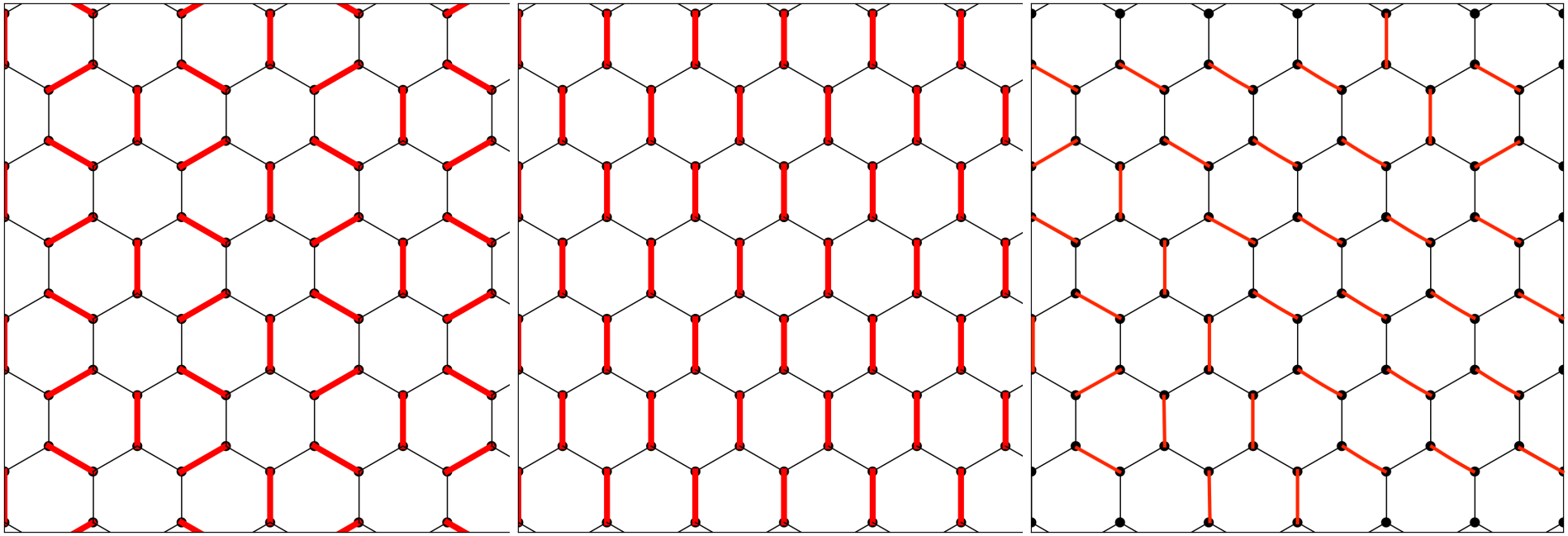
Usually represented as a **regular** honeycomb lattice:



There are no double bonds, π electrons are completely delocalized.

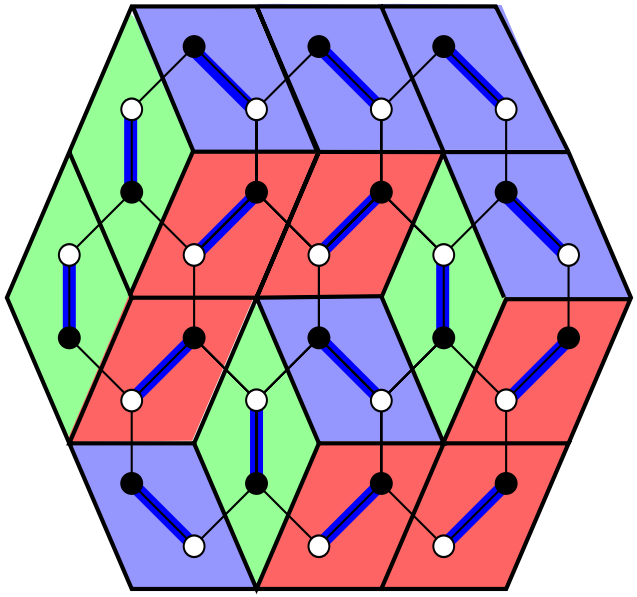
$\Longrightarrow$ no spectral gap: high conductivity.

Adding a fourth bond to each carbon atom

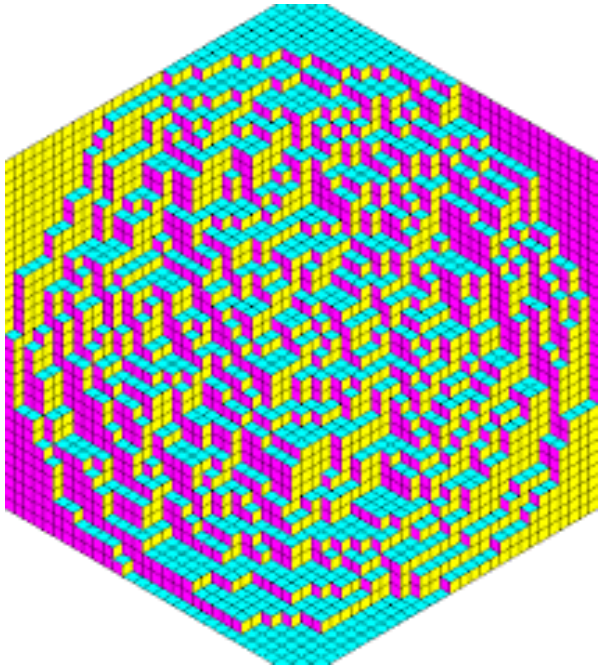


Many possible Kekulé distortions *a priori*.

Link with the theory of *dimers* and *random surfaces*



Courtesy of B. Laslier



Question: Is graphene distorted? What is its distortion pattern?

The discrete model of graphene

We consider a nearest-neighbour tight-binding model for the π electrons, with hopping amplitudes $\mathbf{t}$ that are affine functions of the bond lengths $\mathbf{d}$ between atoms, as in the case of polyacetylene.

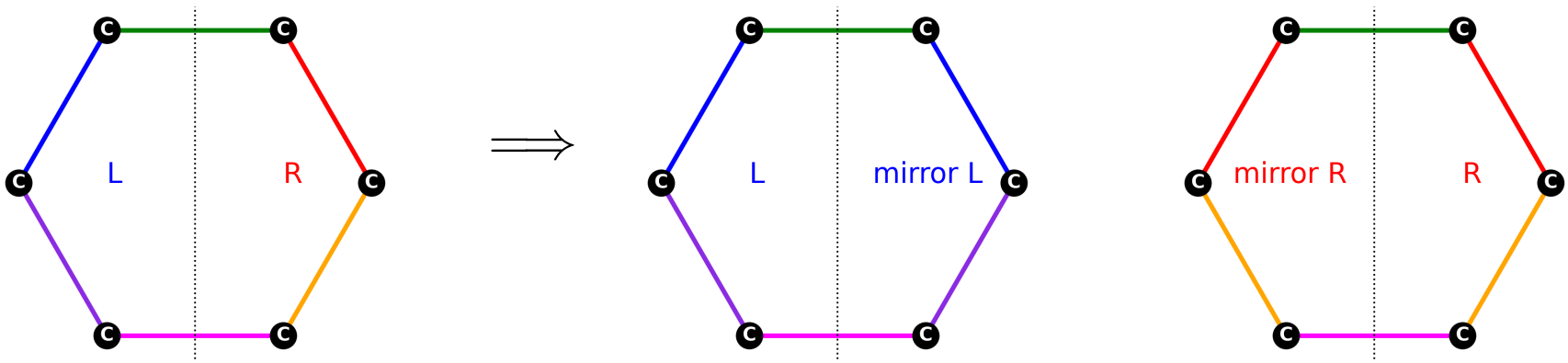
We represent the carbon sites by greek letters. The pairs of neighboring sites are denoted by $< \alpha\beta >$.

To get a finite energy, we consider a periodized honeycomb lattice, with large period L. The energy depends on the vector $\mathbf{t} = (t_{<\alpha\beta>})$ of hopping amplitudes between neighboring sites:

$$E^{(L)}(\mathbf{t}) = \frac{\mu}{2} \sum_{<\alpha\beta>} (t_{<\alpha\beta>} - 1)^2 - \mathrm{Tr}\left(|\, T(\mathbf{t})|\right)$$

where $T(\mathbf{t})$ is the Hamiltonian acting on complex vectors $\psi = (\psi_\gamma)$. The matrix of $T(\mathbf{t})$ has nonzero coefficients only for the pairs of neighboring carbon sites $< \alpha\beta >$: these coefficients are the scalars $t_{<\alpha\beta>}$.

Reflexion positivity in 1D (Lieb–Nachtergaele 1995)



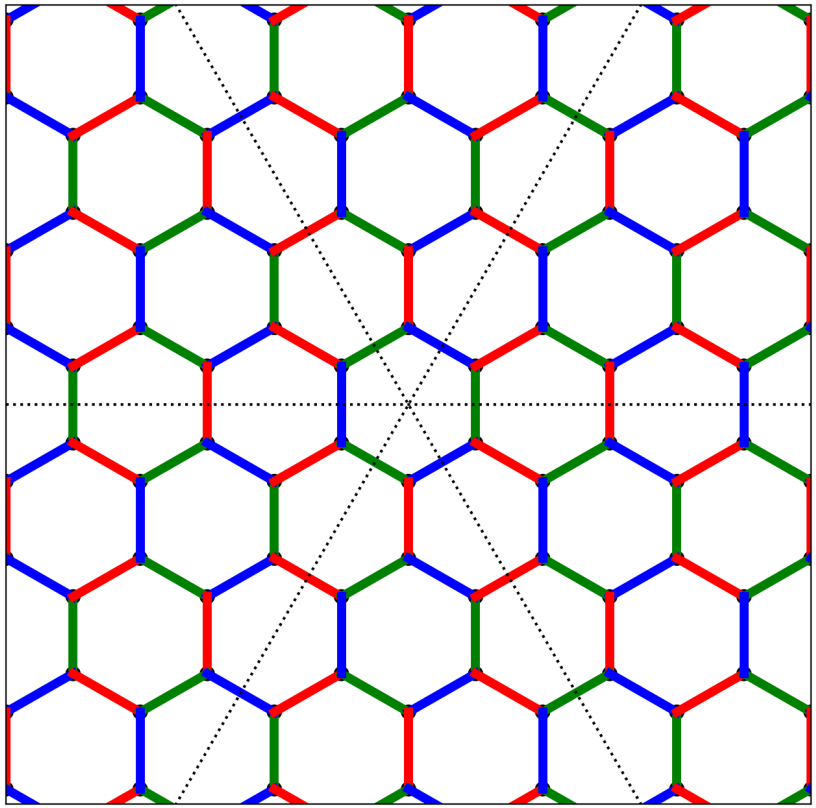
Reflection Positivity:

$$\mathcal{E}(t_L, t_{\rm cut}, t_R) \geq \frac{1}{2}\left(\mathcal{E}(t_L, t_{\rm cut}, \widetilde{t}_L) + \mathcal{E}(\widetilde{t}_R, t_{\rm cut}, t_R)\right).$$

So, there exists a minimising configuration which is symmetric with respect to **all** cuts

$\Longrightarrow$ 2–periodicity for polyacetylene (modulo a uniqueness problem).

Reflection Positivity for graphene (Frank–Lieb '12).



There is a 3-periodic energy minimizer in which at most 3 different hopping parameters/distances t_1, t_2, t_3 appear.

This configuration cannot be 1–periodic Kekulé or "random" Kekulé, but it is "Kekulé-O" (3-periodic) if 2 of the 3 parameters are equal.

Kekulé-O distortion or no distortion

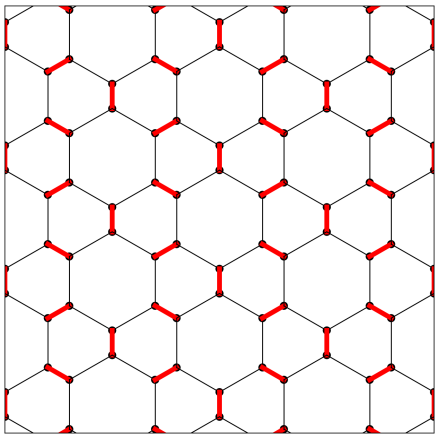
Denote by $t_1 \leq t_2 \leq t_3$ the three remaining hopping parameters.

Theorem (Gontier, Roussigné, S. '25)

If $L >> 1$ there are $0.888 \approx \mu_c \leq \mu_c' \leq 1.114$ such that:

(i) *For all $0 < \mu < \mu_c$, the Frank-Lieb minimizers satisfy $t_1 = t_2 < t_3$ (up to permutation): they are strictly "Kekulé-O", and their tight-binding Hamiltonian T is gapped, satisfying $0 \notin \sigma(T)$ (insulating phase).*

(ii) *For all $\mu \geq \mu_c'$, the minimizer of $E^{(L)}$ is unique with no distorsion: $t_1 = t_2 = t_3 = t_*$. In this case, $0 \in \sigma(T)$ (conducting phase).*



Kekulé-O, exaggerated

We conjecture that $\mu_c' = \mu_c$.
The experimental value of μ for graphene seems much larger.

Idea of proof: $t_1 = t_2$

In the limit $L = \infty$ we write the Bloch wave decomposition of the operator T (here $\mathbf{k} \in B$ with B a compact subset of $\mathbb{R}^2$ called *Brillouin zone*):

$$T^{t_1,t_2,t_3}(\mathbf{k}) = \begin{pmatrix} & & & t_1 & t_3 e^{ik_2} & t_2 \\ & 0 & & t_2 & t_1 & t_3 e^{-i(k_1+k_2)} \\ & & & t_3 e^{ik_1} & t_2 & t_1 \\ t_1 & t_2 & t_3 e^{-ik_1} & & & \\ t_3 e^{-ik_2} & t_1 & t_2 & & 0 & \\ t_2 & t_3 e^{i(k_1+k_2)} & t_1 & & & \end{pmatrix}.$$

This gives the following energy per crystal cell:

$$\underline{E}(t_1, t_2, t_3) = -\int_B \mathrm{Tr}\left(\left|T^{t_1,t_2,t_3}(\mathbf{k})\right|\right)\mathbf{dk} + \frac{3\mu}{2}\sum_{i=1}^{3}(t_i - 1)^2.$$

With $\sum_{i=1}^3 t_i$, $\sum_{i=1}^3 t_i^2$ and $\mathbf{k}$ fixed, we prove that $\mathrm{Tr}\left(\left|T^{t_1,t_2,t_3}(\mathbf{k})\right|\right)$ is maximal for $t_1 = t_2$. A key point in the proof is that this trace solves an algebraic equation of degree 4 with coefficients depending on t_1, t_2, t_3.

Idea of proof: critical value μ_c

- When $t_1 = t_2 = t_3$, the band diagram (eigenvalues of $T^{t_1,t_2,t_3}(\mathbf{k})$ as functions of $\mathbf{k} \in B$) is easily computed and has two well-known Dirac cones.
- Cones replaced by a gap when $t_1 = t_2 = W - \frac{\delta}{2}$ and $t_3 = W + \delta$, $\delta > 0$. For δ small, gain in quantum energy of same order δ^2 as the cost in elastic energy $\Longrightarrow$ critical value μ_c.

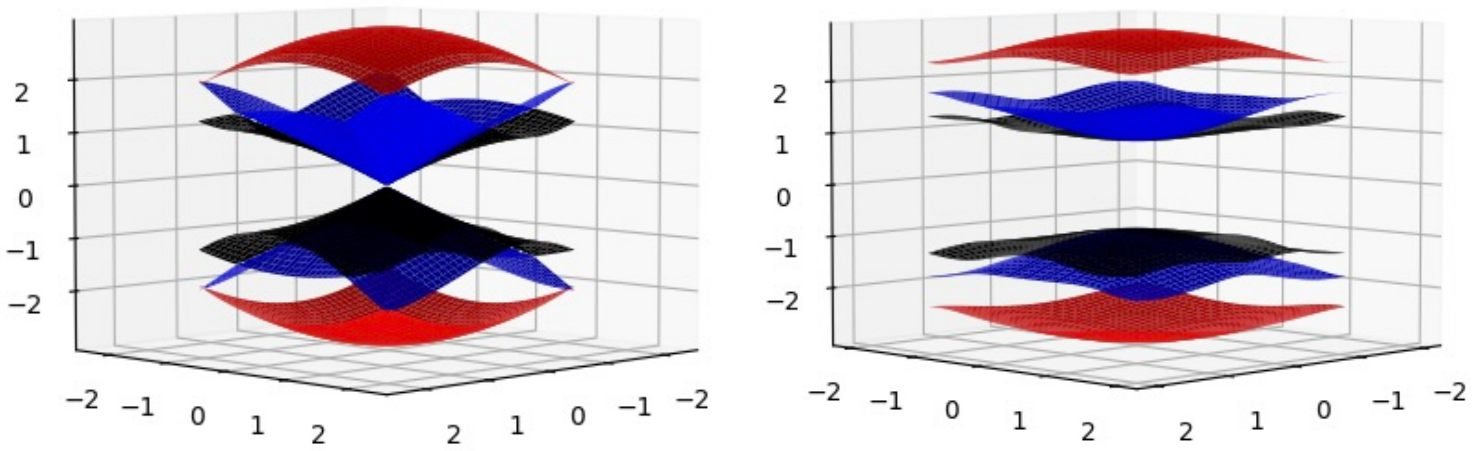


Figure: Undistorted and distorted band diagrams, plotted over the Brillouin zone.

Idea of proof: critical value μ'_c

- We call t_* be the minimizer of $\underline{E}(t,t,t)$ and $\mathbf{t}_*$ corresponding constant vector of hopping amplitudes between neighboring sites. For μ large enough our goal is to prove that for any nonzero $\mathbf{h} = (h_{<\alpha\beta>})$,

$$E^{(L)}(\mathbf{t}_* + \mathbf{h}) > E^{(L)}(\mathbf{t}_*).$$

- By convexity of $f(t) := -\sqrt{t}$, for any self-adjoint B and positive A, we have

$$-\operatorname{Tr}\sqrt{A+B} \geq -\operatorname{Tr}\sqrt{A} - \operatorname{Tr}\left(\frac{1}{2\sqrt{A}}B\right).$$

- We apply the previous inequality with

$$A = T^2(\mathbf{t}_*) \quad \text{and} \quad B = T^2(\mathbf{t}_* + \mathbf{h}) - T^2(\mathbf{t}_*).$$

- Then we show that

$$\operatorname{Tr}\left(\frac{1}{2\sqrt{A}}B\right) < \frac{\mu'_*}{2}\sum_{<\alpha\beta>}((t_* + h_{<\alpha\beta>}) - 1)^2 - (t_* - 1)^2.$$

The continuum model for graphene (formal derivation)

Let $\Delta := t_1 + jt_2 + j^2 t_3$. We work in the regime of slow variations of Δ and consider configurations close to $\mathbf{t}_*$. After change of variables and rescaling, we get the following energy:

$$\mathcal{E}(\Delta) = -\frac{1}{2}\,\mathrm{Tr}\,|\mathcal{K}_\Delta| + \frac{\nu}{2}\int_{\mathbb{R}^2/\ell\mathbb{Z}^2} |\Delta|^2(x,y)\mathrm{d}x\mathrm{d}y$$

with

$$\mathcal{K}_\Delta := \begin{pmatrix} 0 & -i\partial_x - \partial_y & \Delta & 0 \\ -i\partial_x + \partial_y & 0 & 0 & \Delta \\ \bar{\Delta} & 0 & 0 & i\partial_x - \partial_y \\ 0 & \bar{\Delta} & i\partial_x + \partial_y & 0 \end{pmatrix}$$

acting in

$$\mathcal{H}^\Lambda := \{\psi \in L^2_{\mathrm{per}}\left(\mathbb{R}^2/\ell\mathbb{Z}^2;\,\mathbb{C}^4\right)\ :\ \mathrm{supp}(\hat{\psi}) \subset [-\Lambda,\Lambda]^2\}.$$

See *e.g.* Hou-Chamon-Mudry '07 for a formal derivation of $\mathcal{K}_\Delta$.

Earlier model in 1D: Takayama, Lin-Liu, and Maki '80 for polyacetylene.

Ground state of the continuum model

Theorem (Gontier, Roussigné, S. '26)

There is $\nu_c > 0$ such that:

1. *For all $0 < \nu < \nu_c$, the minimizers of $\mathcal{E}$ are of the form $\Delta(x,y) = \Delta_0 e^{i\theta}$ where $\Delta_0 > 0$ is a unique constant and θ is an arbitrary constant. The corresponding tight-binding Hamiltonian $\mathcal{K}_\Delta$ is gapped, satisfying $0 \notin \sigma(\mathcal{K}_\Delta)$ (insulating phase).*

2. *For all $\nu \geq \nu_c$, $\Delta = 0$ is the unique minimizer of $\mathcal{E}$. It corresponds to pristine graphene, and $0 \in \sigma(\mathcal{K}_\Delta)$ (conducting phase).*

Work in progress: Graphene with localized defects

We replace the set Γ of carbon sites by $\Gamma' = (\Gamma \setminus D_-) \cup D_+$ with D_-, D_+ finite. We denote by $< \alpha', \beta' >$ the resulting pairs of neighboring atoms and by $\mathbf{t}'$ the new vectors of hopping amplitudes with associated matrices $T'(\mathbf{t}')$. For L large, we periodize the crystal as before. The energy is now

$$E'^{(L)}(\mathbf{t}') = \frac{1}{2} \sum_{<\alpha'\beta'>} \mu_{<\alpha'\beta'>}(t'_{<\alpha'\beta'>} - 1)^2 - \mathrm{Tr}\left(|T'(\mathbf{t}')|\right)$$

where $\mu_{<\alpha'\beta'>}$ are given positive numbers. Only a finite number of these parameters differ from μ. Here we assume $\mu > \mu'_c$.

Theorem (Gontier-Roussigné-S.)

For each L, let $\mathbf{t}'(\mathbf{L})$ be a minimizer of $E'^{(L)}$. Then, after extraction, for each pair $< \alpha'\beta' >$, $\lim_{L\to\infty} t'(L)_{<\alpha'\beta'>} =: t'_{<\alpha'\beta'>}$ exists, and

$$\sum_{<\alpha'\beta'>} |t'_{<\alpha'\beta'>} - t_*|^2 < \infty\,.$$

THANK YOU !