Kekulé distortions in graphene

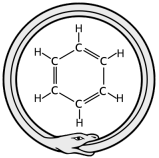
David Gontier
joint work with Adéchola Kouandé, Thaddeus Roussigné and Éric Séré

CEREMADE, Université Paris-Dauphine & DMA, École Normale Supérieure

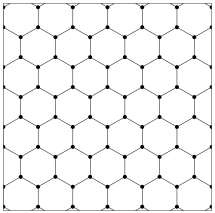
Roscoff
July 08, 2024.

Kekulé (1829-1896, German)

- Funder of the structure of molecules (atoms + covalent bonds).
- Discovered that the Carbon atom has 4 covalent bonds.
- Understood first the structure of Benzene (*out of a day–dream involving Ouroboros*).



Graphene? Usually represented with the **regular** honeycomb lattice.

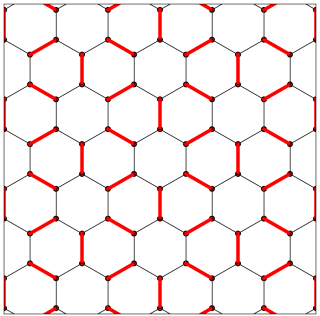


There are no double bonds!

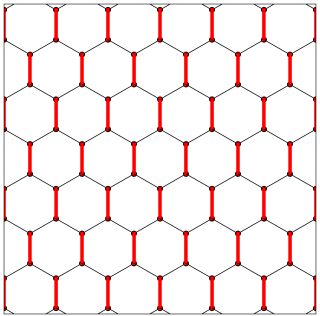
$\Longrightarrow$ responsible for the high conductivity of graphene.

Kekulé distortions $\approx$ Add the fourth bond to each Carbon atom.

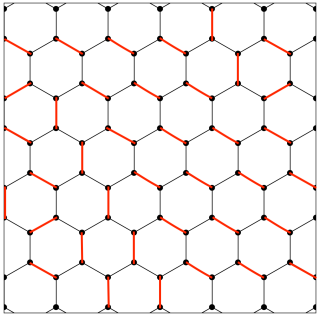
Kekulé-O (3–periodic)



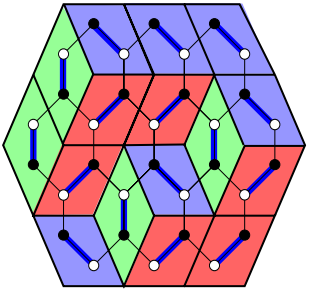
A 1–periodic Kekulé



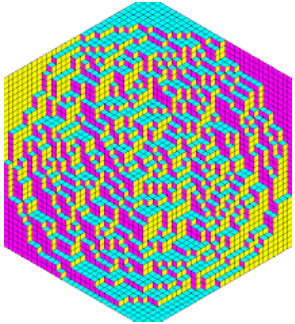
A random Kekulé



Many possible Kekulé distortions *a priori* (linked with the theory of *dimers* and *random surfaces*).



Courtesy of B. Laslier



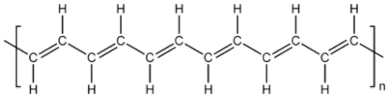
Question: Is graphene distorted?

Remarks:

- A double bond brings the atom closer;
- Electrons can jump more easily to close atoms (larger hopping parameters);
- There is a competition between the distortion energy of the lattice, and the quantum energy of the electrons.

One–dimensional graphene (*aka* polyacetylene)

Polyacetylene

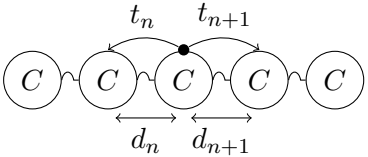


- Conductivity of undopped polyacetylene: $4.4 \times 10^{-5}\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$.
- Conductivité of dopped (with iode) polyacetylene: $38\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$.
- Nobel prize to Heeger, MacDiarmid, Shirakawa for «*conductive polymers*» (2000).

There is an insulator/metallic transition due to dopping.

Peierls/Su–Schrieffer–Heeger (SSH) model

- L *classical* atoms (Carbon), linked by springs of stiffness K and rest length $d_\sharp$.
- *Quantum* non–interacting electrons in a tight–binding Hamiltonian generated by the Carbon atoms:



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

Hopping parameters. We assume a linear relation: $(t_n - t_\sharp) = -\alpha(d_n - d_\sharp)$.

Peierls energy ($\sim$ 1930) (Peierls? Hueckel? Su-Schrieffer-Heeger (SSH)?) After rescaling and with $\mu := \frac{Kt_\sharp}{\alpha^2}$,

$$\boxed{\mathcal{E}_L(\mathbf{t}, \gamma) := \frac{\mu}{2} \sum_{n=1}^{L} (t_n - 1)^2 + 2\mathrm{Tr}\,(T\gamma)\,.}$$

We want to minimize the energy for all $t_n \in \mathbb{R}_+$ and all $0 \leq \gamma = \gamma^* \leq 1$.

Theorem (Peierls 33, Kennedy/Lieb 1987, Lieb/Nachtergaele 1995)

If $L = 2N$ is even, there are at most two optimal configurations,

$$t_n = W + (-1)^n \delta \quad \text{or} \quad t_n = W - (-1)^n \delta, \quad \text{with} \quad \delta \geq 0.$$

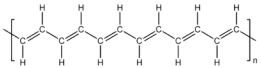
*In addition, if N is odd or if L is large enough, then $\delta > 0$ (**Peierls dimerization**).*

The corresponding Hamiltonian is of the form

$$T = \begin{pmatrix} 0 & a & 0 & 0 & \cdots & b \\ a & 0 & b & \cdots & 0 & 0 \\ 0 & b & 0 & a & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & \cdots & b & 0 & a \\ b & 0 & \cdots & 0 & a & 0 \end{pmatrix}, \qquad \sigma(T) = \bigcup_{k \in \frac{2\pi}{L}} \left\{ \pm |a + b\mathrm{e}^{\mathrm{i}k}| \right\}, \qquad \begin{cases} a = W + \delta \\ b = W - \delta. \end{cases}$$

There is a gap of size 2δ around the origin.

Case $\delta > 0$. Two distinct minimizers. The model is insulating.



Case $\delta = 0$. Unique minimizer. The corresponding model is metallic.

Proof 1 (Kennedy–Lieb 1987), with convexity

Lemma (Exercice 1)

For $T \in \mathcal{S}_L(\mathbb{C})$ *with* $\mathrm{Tr}(T) = 0$, *we have:* $\inf_{\substack{\gamma \in \mathcal{S}_L \\ 0 \leq \gamma \leq 1}} \{2\mathrm{Tr}(T\gamma)\} = -2\mathrm{Tr}(T_-) = -\mathrm{Tr}\left(\sqrt{T^2}\right)$.

The minimum is obtained for $\gamma = \mathbb{1}(T \leq 0)$.

Lemma (Exercice 2)

The map $\mathcal{S}_L^+(\mathbb{C}) \ni A \mapsto -\mathrm{Tr}\left(\sqrt{A}\right)$ *is* **convex**.

$\Longrightarrow$ The energy is **convex** it the variable T^2 $\Longrightarrow$ Minimizers are at most 2–periodic.

To study dimerization, it remains to study a functional with two variables W and δ (Peierls 1933).

Thermodynamic limit ($L \to \infty$)

We are left with only two variable in the energy, namely W and δ.
The limit $\underline{\mathcal{E}} := \lim_{L\to\infty} \frac{1}{L}\mathcal{E}_L$ (energy per unit cell) is well-defined, and given by

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

Conclusion: For all $\mu > 0$, we have $\delta > 0$.
(it costs δ^2 to open a gap δ, and we gain $\delta^2\log(\delta)$ quantum energy).

Remark (Exercice?). The gain of energy due to Peierls dimerization is of order $\Delta E \approx C\mathrm{e}^{-\frac{\pi}{2}\mu}$.

Similar results with positive temperature $\theta > 0$

Peierls free energy

$$\mathcal{E}_L^\theta(\mathbf{t},\gamma) := \frac{\mu}{2}\sum_{n=1}^{L}(t_n-1)^2 + 2\mathrm{Tr}\left(T\gamma\right) + 2\theta\mathrm{Tr}\left(\underbrace{\gamma\log(\gamma)+(1-\gamma)\log(1-\gamma)}_{\text{fermionic entropy of the electrons}}\right).$$

Lemma (Exercice 3)

For all matrix $T \in \mathcal{S}_L(\mathbb{C})$ with $\mathrm{Tr}(T) = 0$, we have

$$\inf_{\substack{\gamma\in\mathcal{S}_L\\ 0\le\gamma\le 1}} 2\left\{\mathrm{Tr}(T\gamma) + \theta\mathrm{Tr}\left(\gamma\log(\gamma)+(1-\gamma)\log(1-\gamma)\right)\right\} = \mathrm{Tr}\left[h_\theta(T^2)\right],$$

with $h_\theta(x) := -2\theta\log\left(2\cosh\left(\frac{\sqrt{x}}{2\theta}\right)\right)$. The minimum is attained for $\gamma = \left(1+\mathrm{e}^{\frac{T}{\theta}}\right)^{-1}$.

The key property is that h_θ is a convex function.

So, if $L = 2N$ is eveny, there are at most 2 minimizers, of the form

$$t_n = W + (-1)^n\delta \quad \text{ou} \quad t_n = W - (-1)^n\delta, \quad \text{with} \quad \delta \ge 0.$$

We can perform the thermodynamic limit again, and obtain the *free energy per unit cell*

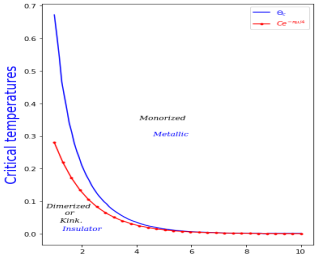
$$\underline{\mathcal{F}}(W,\delta) = \frac{\mu}{2}\left[(W-1)^2+\delta^2\right] + \frac{1}{2\pi}\int_0^{2\pi} h_\theta\left(4W^2\cos^2(s) + 4\delta^2\sin^2(s)\right)\mathrm{d}s.$$

Theorem (DG, Kouandé, Séré 2023)

For all $\mu > 0$, there is a critical temperature $\theta_c(\mu) > 0$ such that:

- *If $\theta < \theta_c(\mu)$, we have $\delta > 0$ (Peierls dimerization);*
- *Si $\theta \geq \theta_c(\mu)$, we have $\delta = 0$.*

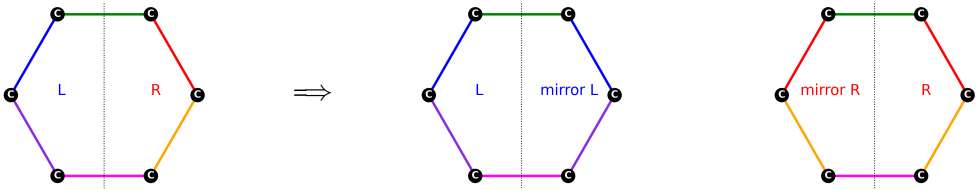
In addition, for large μ, we have $\theta_c(\mu) \sim_{\mu\to\infty} C\mathrm{e}^{-\frac{\pi}{4}\mu}$.



Phase transition due to temperature

Apparently, a reasonable value for μ is $\mu \approx 3.1$.
This gives $\theta_c(\mu) \approx 2900°K$...

Proof 2 (Lieb–Nachtergaele 1995), with Reflection Positivity



Reflection Positivity (general principle from Quantum Field Theory)

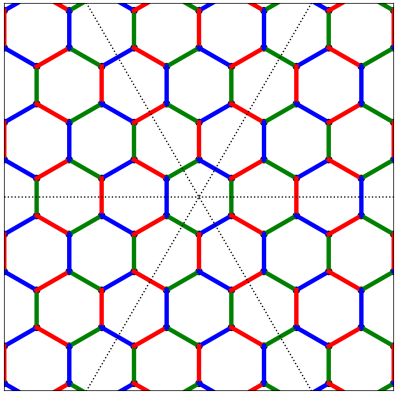
$$\mathcal{E}(t_L, t_{\text{cut}}, t_R) \geq \frac{1}{2}\left(\mathcal{E}(t_L, t_{\text{cut}}, \widetilde{t}_L) + \mathcal{E}(\widetilde{t}_R, t_{\text{cut}}, t_R)\right).$$

So, any minimising configuration should be symmetric with respect to **all** cuts

$\Longrightarrow$ 2–periodicity for polyacetylene.

Two–dimensional polyacetylene (*aka* graphene)

For graphene, Reflection Positivity applies (Frank–Lieb, 2012).



So, at most 3 different hopping parameters/distances may appear.
Graphene is **at most** 3 **periodic** (with 6 Carbon atoms per unit cell).

This already discards the 1–periodic Kekulé and other *«random»* Kekulé distortions.

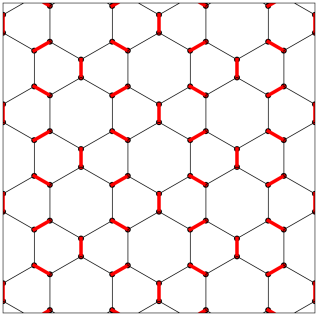
Results for the Peierls/SSH model for graphene

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

Theorem (DG, Roussigné, Séré, 2024)

There is a critical value $\mu_c > 0$ so that,

- *for $\mu \geq \mu_c$, we have $t_1 = t_2 = t_3$.* **No distortion $\implies$ no gap.**
- *for $\mu < \mu_c$, we have $t_1 = t_2 < t_3$.* **Kekulé-O distortion $\implies$ gap.**



Kekulé-O, exaggerated

We find $\mu_c = 0.88...$
...and the experimental value seems to be much greater.

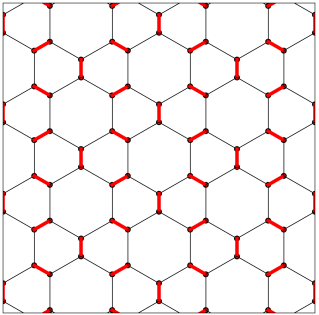
Results for the Peierls/SSH model for graphene

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

Theorem (DG, Roussigné, Séré, 2024)

There is a critical value $\mu_c > 0$ so that,

- *for $\mu \geq \mu_c$, we have $t_1 = t_2 = t_3$.* **No distortion $\implies$ no gap.**
- *for $\mu < \mu_c$, we have $t_1 = t_2 < t_3$.* **Kekulé-O distortion $\implies$ gap.**



Kekulé-O, exaggerated

We find $\mu_c = 0.88...$
...and the experimental value seems to be much greater.

Thank you for your attention.

Kinks in the Peierls/SSH model

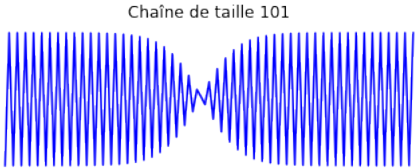
Let's go back to polyacetylene in the $\theta = 0$ case.
In the even ($L = 2N$) case, there are two minimizers $\mathbf{t}_n^{\pm} = W \pm (-1)^n \delta$.

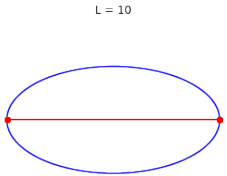
Theorem ((odd case) Garcia-Arroyo/Séré, 2011)

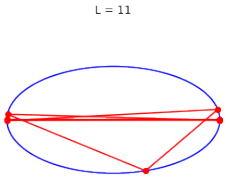
If $L = 2N + 1$ is odd, minimizers look like «kinks» :
If $\mathbf{t}(2N+1)$ is a centered *minimiser, then $\lim_{N\to\infty} \mathbf{t}(2N+1)_n =: t_n$ exists, and*

$$\lim_{n\to\infty} |t_n - t_n^+| = \lim_{n\to\infty} |t_n - t_n^-| = 0. \qquad \textit{heteroclinic configuration.}$$

Same phenomena with a billiard (maximise the periodic billiard path with L points)







Edge modes

The corresponding Hamiltonian can be seen as a junction between T^+ and T^-.

Lemma (Exercice 3)

Consider any positive sequence t_n with $\lim_{n\to\infty} |t_n - t_n^+| = \lim_{n\to\infty} |t_n - t_n^-| = 0$, and consider the corresponding tight–binding Hamiltonian $(T\psi)_n = t_n\psi_{n+1} + t_{n-1}\psi_{n-1}$. Then $0 \in \sigma(T)$.

In addition, if $\delta > 0$ (so $\mathbf{t}^+ \neq \mathbf{t}^-$), then 0 is an eigenvalue of multiplicity 1, and the corresponding eigenvector is exponentially localised (= edge mode).

Example of *topologically protected states* (Majorana states?).

Theorem (DG, Kouandé, Séré)

If (t_n) is any *(heteroclinic) positive critical point of the infinite Peierls model, then the convergence of t_n to $t_n^\pm$ at $\pm\infty$ is exponential.*