Kekulé distortions in graphene

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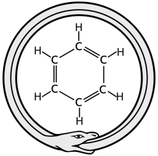
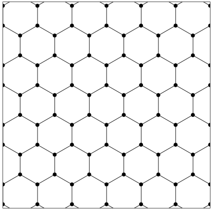
Friedrich August Kekulé von Stradonitz (1829-1896, German)

- 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 dream involving Ouroboros*).



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

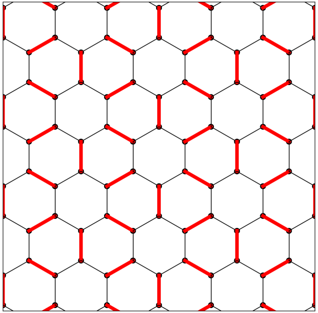


THERE ARE NO DOUBLE BONDS!

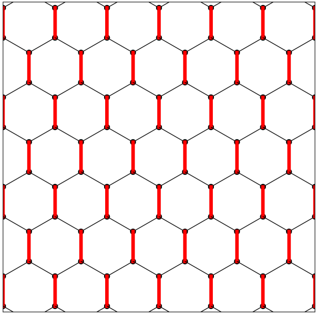
$\implies$ responsible for the high conductivity of graphene.

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

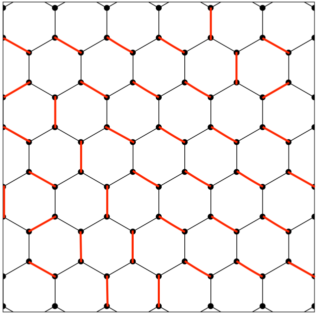
Kekulé-O (3–periodic)



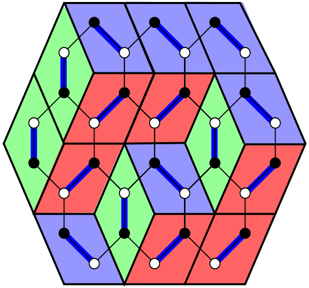
A 1–periodic Kekulé



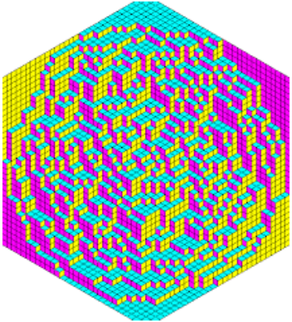
A random Kekulé



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



Courtesy of B. Laslier



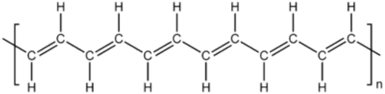
Question: Is graphene distorted?

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

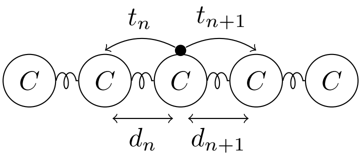


- Conductivity of undopped polyacetylene: $4.4 \times 10^{-5}\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$.
- Conductivité of dopped (with iode) polyacetylene: $38\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$.
- Nobel prize to Heeger, MacDiarmid, Shirakawa for «*conductive polymers*» (2000).

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 $\mu := \frac{K t_\sharp}{\alpha^2}$,

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

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,

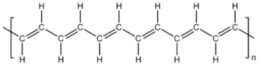
$$t_n = W + (-1)^n \delta \quad \textit{or} \quad t_n = W - (-1)^n \delta, \quad \textit{with} \quad \delta \geq 0.$$

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

The corresponding Hamiltonian is of the form

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

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:* $\inf_{\substack{\gamma \in \mathcal{S}_L \\ 0 \le \gamma \le 1}} \{2\mathrm{Tr}(T\gamma)\} = -2\mathrm{Tr}(T_-) = -\mathrm{Tr}\left(\sqrt{T^2}\right)$.

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

Lemma (Exercice 2)

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

$\implies$ The energy is **convex** in the variable T^2 $\implies$ 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 *distortion energy 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 even, 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*

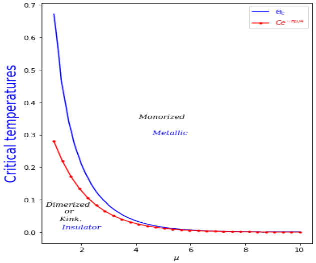
$$\underline{\mathcal{F}}(W,\delta) = \frac{\mu}{2}\left[(W-1)^2+\delta^2\right] + \frac{1}{2\pi}\int_0^{2\pi} h_\theta\left(4W^2\cos^2(s)+4\delta^2\sin^2(s)\right)\mathrm{d}s.$$

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);*
- *If $\theta \geq \theta_c(\mu)$, we have $\delta = 0$.*

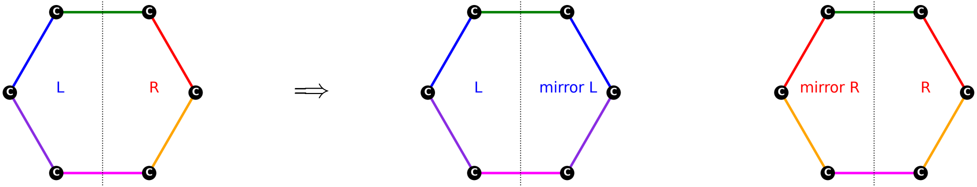
In addition, for large μ, we have $\theta_c(\mu) \sim_{\mu\to\infty} C\mathrm{e}^{-\frac{\pi}{4}\mu}$.



Phase transition due to temperature

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

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



Reflection Positivity (general principle from Quantum Field Theory)

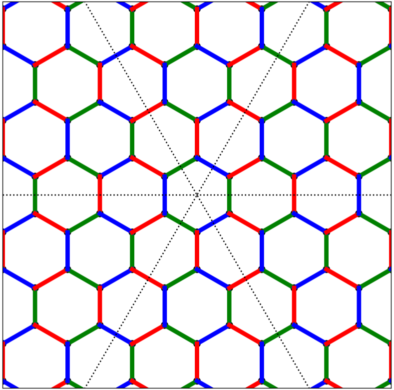
$$\mathcal{E}(t_L, t_{\mathrm{cut}}, t_R) \geq \frac{1}{2}\left(\mathcal{E}(t_L, t_{\mathrm{cut}}, \widetilde{t}_L) + \mathcal{E}(\widetilde{t}_R, t_{\mathrm{cut}}, t_R)\right).$$

So, any minimising configuration should be symmetric with respect to **all** cuts
$\implies$ 2–periodicity for polyacetylene.

Sidenote: only works if $L \equiv 2[4]$ (so $L = 6$ works: this is benzene).

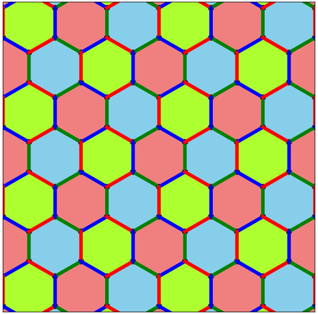
The case of graphene

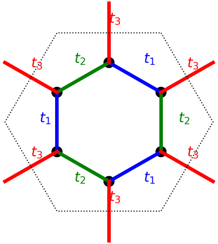
For graphene, Reflection Positivity applies (Frank–Lieb, 2012).



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.





It remains three hopping parameters: $t_1 \leq t_2 \leq t_3$

By periodicity, one can write a thermodynamic limit *energy per carbon*, of the form

$$\boxed{\underline{\mathcal{E}}(t_1, t_2, t_3) = -\fint_{BZ_6} \mathrm{Tr}\left(\sqrt{T^2}(\mathbf{k})\right) + \frac{\mu}{4}\left[(t_1-1)^2 + (t_2-1)^2 + (t_3-1)^2\right].}$$

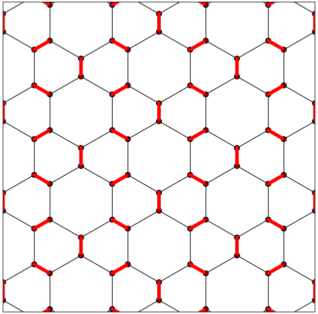
with, for instance, for $\mathbf{k} = \mathbf{0}$, $T^2(\mathbf{0}) = \begin{pmatrix} t_1^2+t_2^2+t_3^2 & t_1t_2+t_2t_3+t_3t_1 & t_1t_2+t_2t_3+t_3t_1 \\ t_1t_2+t_2t_3+t_3t_1 & t_1^2+t_2^2+t_3^2 & t_1t_2+t_2t_3+t_3t_1 \\ t_1t_2+t_2t_3+t_3t_1 & t_1t_2+t_2t_3+t_3t_1 & t_1^2+t_2^2+t_3^2 \end{pmatrix}.$

Theorem (DG, Roussigné, Séré, 2025)

At temperature $\theta = 0$*, there are critical values* $0 < \mu_c^{(1)} \leq \mu_c^{(2)} < \infty$ *so that,*

- *for* $\mu \geq \mu_c^{(2)}$*, we have* $t_1 = t_2 = t_3$. **No distortion** $\implies$ **metal** .
- *for* $\mu < \mu_c^{(1)}$*, we have* $t_1 = t_2 < t_3$. **Kekulé-O distortion** $\implies$ **insulator.**

This confirms the intuition «*2 simple bonds and 1 double bond per Carbon atom*».



Kekulé-O, exaggerated

We find $\mu_c^{(1)} = 0.88$ and $\mu_c^{(2)} = 1.11...$
...and the experimental value for graphene seems to be much greater (from 2 to 20 depending on the articles...).

Ideas of the proof that $t_1 = t_2$

Step 1

We want to compute $\sqrt{\mu_1} + \sqrt{\mu_2} + \sqrt{\mu_3}$, where μ_1, μ_2, μ_3 are the eigenvalues of $T^2(\mathbf{k})$, roots of $P(X) := \det(X - T^2(\mathbf{k}))$, which is of the form

$$P(X) = X^3 + aX^2 + bX + c \qquad \text{with} \quad \begin{cases} a & = -\mathrm{Tr}(T^2) = -(\mu_1 + \mu_2 + \mu_3) \\ b & = \cdots \\ c & = \det(T^2) = \mu_1 \mu_2 \mu_3, \end{cases},$$

where a, b, c are symmetric polynomials in t_1, t_2, t_3, hence are of the form

$$a(t_1, t_2, t_3) = A(\sigma_1, \sigma_2, \sigma_3), \qquad \begin{cases} \sigma_1 & = t_1 + t_2 + t_3 \\ \sigma_2 & = t_1 t_2 + t_2 t_3 + t_3 t_1 \\ \sigma_3 & = t_1 t_2 t_3 \end{cases}.$$

Step 2

Prove that $\sqrt{\mu_1} + \sqrt{\mu_2} + \sqrt{\mu_3}$ is a **decreasing** function of σ_3 (with fixed σ_1 and σ_2).
$\Longrightarrow$ You are left with the much easier problem

$$\inf \left\{ t_1 t_2 t_3, \quad t_1 + t_2 + t_3 = \sigma_1, \; t_1^2 + t_2^2 + t_3^3 = \sigma_1^2 - 2\sigma_2 \right\}.$$

Step 3

Find a bright, energetic and tireless PhD student (= Thaddeus Roussigné) to prove Step 2...

$$b = 2\sigma_1^4 - 12\sigma_1^2\sigma_2 + 9\sigma_2^2 + 6\sigma_1\sigma_3 \mathrm{Re}\left(Z(\mathbf{k})\right), \qquad Z(\mathbf{k}) = 3 - \mathrm{e}^{-\mathbf{i}\mathbf{k}\cdot\mathbf{b}_1} - \mathrm{e}^{-\mathbf{i}\mathbf{k}\cdot\mathbf{b}_2} - \mathrm{e}^{\mathbf{i}\mathbf{k}\cdot(\mathbf{b}_1+\mathbf{b}_2)}.$$

Symmetry breaking for $\mu < \mu_c^{(1)}$

Perform a Taylor expansion of $\underline{\mathcal{E}}(t_1, t_2, t_3)$ around (t_*, t_*, t_*), and prove that the Hessian is not positive.

No symmetry breaking for $\mu \geq \mu_c^{(2)}$

Use convexity of $x \mapsto -\sqrt{x}$, and in particular that $-\sqrt{a+b} \geq -\sqrt{a} - \frac{1}{2\sqrt{a}} b$.

Remark: The proof is not very satisfying...

- Specific to temperature $\theta = 0$;
- Specific to quadratic distortion energy;
- Only works in the thermodynamic limit (no proof for «*supercells*», or «*nano tubes*»).

Kinks in the Peierls/SSH model

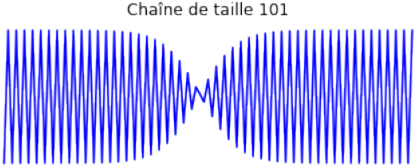
Let's go back to polyacetylene in the $\theta = 0$ case.
In the even ($L = 2N$) case, there are two minimizers $\mathbf{t}_n^{\pm} = W \pm (-1)^n \delta$.

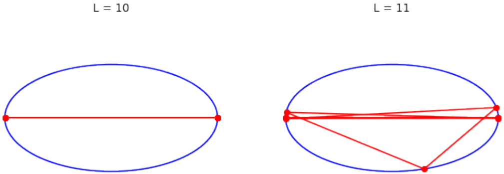
Theorem ((odd case) Garcia-Arroyo/Séré, 2011)

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 (2025))

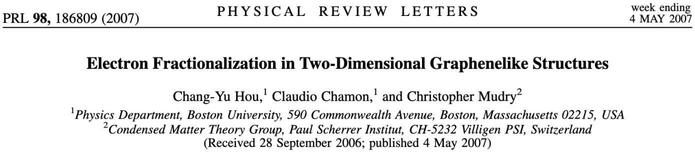
If (t_n) is any (heteroclinic) positive critical point of the infinite Peierls model, then the convergence of t_n to $t_n^\pm$ at $\pm\infty$ is exponential.

Remark: This is more difficult!

It means that the deformation is exponentially localized (and not only the edge mode).

Can we do the same with Kekulé deformed graphene?

Yes,... in some continuous limits.



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Electron Fractionalization in Two-Dimensional Graphenelike Structures

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Study the non−linear problem $\inf_{\Delta(\mathbf{x})} \left\{ -\mathrm{Tr}\left|H_\Delta^2\right| + \frac{\mu}{2}\int_{\mathbb{R}^2} |\Delta(\mathbf{x}) - 1|^2 \right\}$. with

$$H_\Delta := \begin{pmatrix} 0 & D_\Delta \\ D_\Delta^* & 0 \end{pmatrix}, \qquad D_\Delta := \begin{pmatrix} -\mathrm{i}\partial_x - \partial_y & \Delta(\mathbf{x}) \\ \overline{\Delta(\mathbf{x})} & +\mathrm{i}\partial_x - \partial_y \end{pmatrix}.$$

Remark:

The structure of H_D is very close to the *twisted bilayer graphene* one from [Bistritzer, MacDonald 2011].

Can someone explain to me what *Fractionalization* is?