Phase transition in Peierls/SSH model

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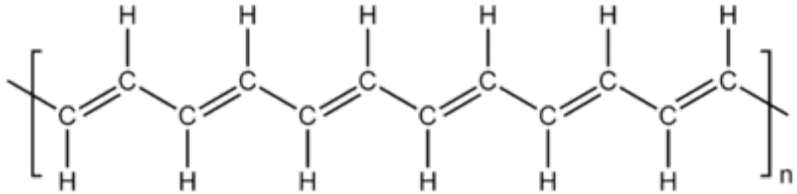
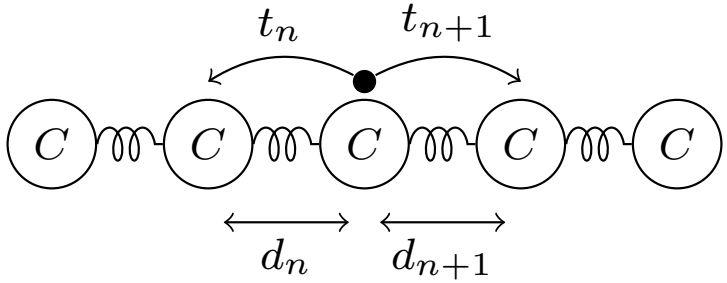
Polyacetylene



- 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).

In this talk: understand how conductivity changes with **temperature**.

Peierls model



- L Carbon *classical* atoms, linked by springs of stiffness K and rest length $d_\sharp$.
  We denote by $\{d_1, \cdots, d_L\}$ the distances between the Carbon atoms (with periodicity).
- *Quantum* non–interacting electrons in a tight–binding Hamiltonian generated by the Carbon atoms.
  We denote by γ the one-body matrix representing the electrons: $0 \leq \gamma = \gamma^* \leq 1$ (Pauli principle).

Hamiltonian

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

Peierls energy ($\sim$ 1930)

(Peierls? Hueckel? Su-Schrieffer-Heeger (SSH)?)

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

We will assume a linear relation between t_n and d_n, of the form $(t_n - t_\sharp) = -\alpha(d_n - d_\sharp)$.

Reduction of the energy

After setting $\mu := \frac{K t_\sharp}{\alpha^2}$, we end up with the rescaled energy

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

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

Lemma (Exercice 1)

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

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

Reduced energy to minimize

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

Remarks:

- There is only one parameter in the model μ (and L, but soon, we will take $L \to \infty$).
- The energy is invariant by translation.

The even case

Theorem ((even case) Kennedy/Lieb, 1987)

If $L = 2N$ is even, there are at most 2 minimizers, of the form

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

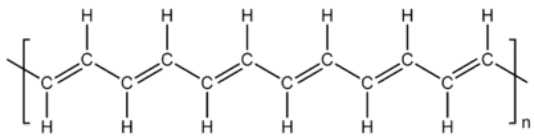
(Also true for much more complex model, such as Hubbard 1d model, see Lieb/Nachtergaele (1995)).

The corresponding Hamiltonian is of the form

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

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

Case $\delta > 0$.
There is dimerization: the translation symmetry is broken.
There are two distinct minimizers in this case.
The corresponding model is insulating.



Case $\delta = 0$.
There is a unique minimizer.
The corresponding model is metallic.

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

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

Lemma (Peierls dimerization always occur)

For all $\mu > 0$, we have $\delta > 0$.

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

We now add the 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 2)

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 concave function.
We can *copy-paste* Kennedy-Lieb's proof, and obtain

Lemma ((even case))

If $L = 2N$ is even, for all $\theta \ge 0$, there are at most 2 minimizers, of the form

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

Thermodynamic limit (with temperature)

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

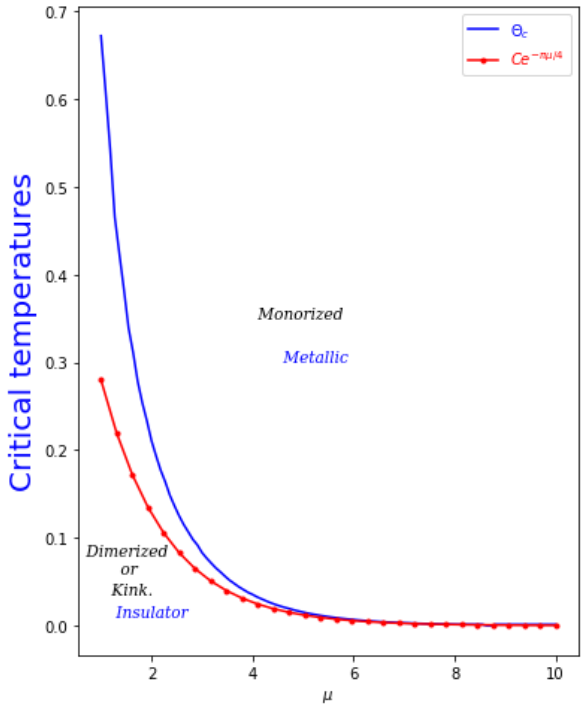
$$\underline{\mathcal{F}}(W,\delta) = \frac{\mu}{2}\left[(W-1)^2+\delta^2\right] - \frac{1}{2\pi}\int_0^{2\pi} h_\theta\left(4W^2\cos^2(s)+4\delta^2\sin^2(s)\right)\mathrm{d}s.$$

Theorem (DG, Kouandé, Séré)

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 $\theta_c(\mu) \sim_{\mu\to\infty} C\mathrm{e}^{-\frac{\pi}{4}\mu}$.



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

Idea of the proof

Well, it is a problem with two parameters (μ and θ), and two variables to optimize (W and δ)...

The Euler–Lagrange equation for (W, δ) reads (we set $h(y) := 2\log(2\cosh(\sqrt{y}))$)

$$\begin{cases} \mu(W-1) &= \dfrac{W}{\theta\pi}\displaystyle\int_0^{2\pi} h'\left(\frac{W^2}{\theta^2}\cos^2(s) + \frac{\delta^2}{\theta^2}\sin^2(s)\right)\cdot\cos^2(s)\mathrm{d}s \\ \mu\delta &= \dfrac{\delta}{\theta\pi}\displaystyle\int_0^{2\pi} h'\left(\frac{W^2}{\theta^2}\cos^2(s) + \frac{\delta^2}{\theta^2}\sin^2(s)\right)\cdot\sin^2(s)\mathrm{d}s. \end{cases}$$

- **Step 1.** The second equation always admit $\delta = 0$ as a solution $\Longrightarrow$ branch of 1–periodic solutions.
- We can select the branch of dimerized solution by dividing the second equation by δ (removing the $\delta = 0$ branch).
- **Step 2.** We can detect when this branch of dimerized solution also have $\delta = 0$ by solving the equation with $\delta = 0$.

The critical temperature θ_c is the temperature for which there exists W solution to

$$\begin{cases} \mu(W-1) &= \dfrac{W}{\theta\pi}\displaystyle\int_0^{2\pi} h'\left(\frac{W^2}{\theta^2}\cos^2(s)\right)\cdot\cos^2(s)\mathrm{d}s \\ \mu &= \dfrac{1}{\theta\pi}\displaystyle\int_0^{2\pi} h'\left(\frac{W^2}{\theta^2}\cos^2(s)\right)\cdot\sin^2(s)\mathrm{d}s. \end{cases}$$

Idea of the proof (2)

$$\begin{cases} \mu(W-1) &= \dfrac{W}{\theta\pi}\displaystyle\int_0^{2\pi} h'\left(\frac{W^2}{\theta^2}\cos^2(s)\right)\cdot\cos^2(s)\mathrm{d}s \\ \mu W &= \dfrac{W}{\theta\pi}\displaystyle\int_0^{2\pi} h'\left(\frac{W^2}{\theta^2}\cos^2(s)\right)\cdot\sin^2(s)\mathrm{d}s. \end{cases}$$

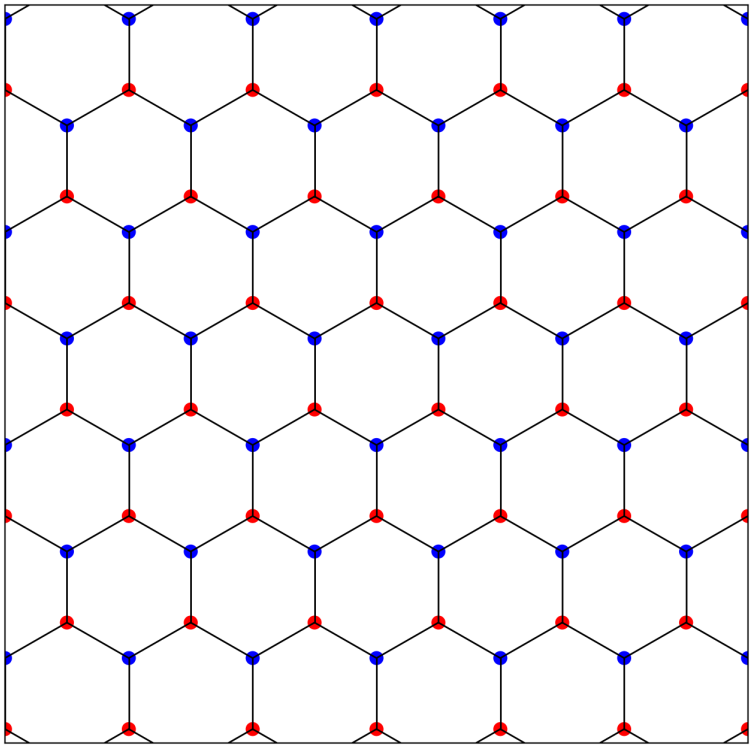
Take the difference of the two equations:

$$\mu = \frac{W}{\theta\pi}\int_0^{2\pi} h'\left(\frac{W^2}{\theta^2}\cos^2(s)\right)\cdot\left[\sin^2(s)-\cos^2(s)\right]\mathrm{d}s =: \mathcal{J}\left(\frac{W}{\theta}\right).$$

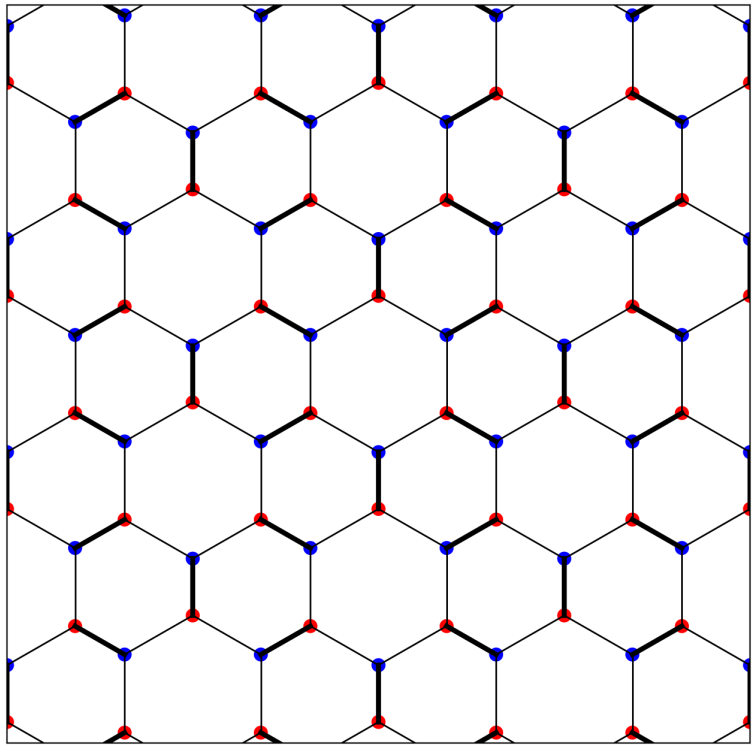
Fact: The function $x \mapsto \mathcal{J}(x)$ is increasing. So $\frac{W}{\theta} = \mathcal{J}^{-1}(\mu)$ is well-defined.
The second equation then gives the value of W (hence of $\theta = \theta_c$). □

Extension to graphene?

(current work with Thaddeus Roussigné and Éric Séré).



(a) Undistorted graphene



(b) Kekule deformation

Theorem (???)

There is a critical value μ_c so that, for $\mu < \mu_c$ graphene is Kekule distorted, while for $\mu \geq \mu_c$, it is not distorted.

Question: What is the physical value of μ?

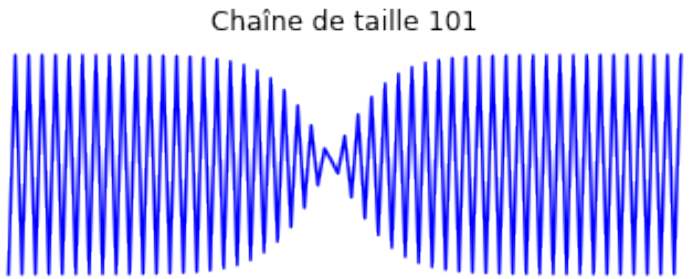
Kinks in the Peierls/SSH model

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

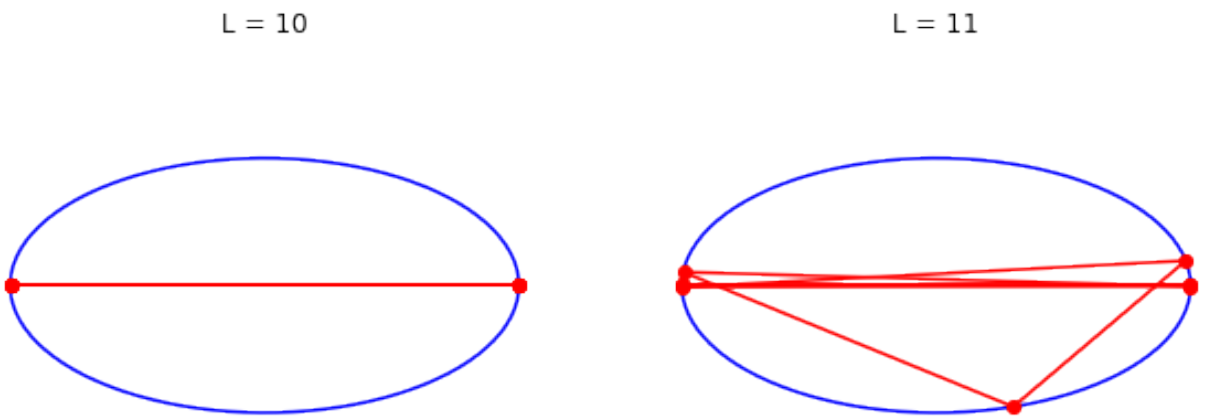
Theorem ((odd case) Garcia-Arroyo/Séré, 2011)

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
We 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.*

Critical point?

Difference energy

$$\mathcal{F}_{\mathbf{t}}(\mathbf{h}) := "\mathcal{E}(\mathbf{t}+\mathbf{h}) - \mathcal{E}(\mathbf{t})" = \frac{\mu}{2}\sum_{n\in\mathbb{Z}}(h_n + 2t_n - 2)h_n - 2\mathrm{Tr}\left[(T+H)_- - T_-\right].$$

(t_n) is a *critical point* if $\left(\nabla\mathcal{F}_{\mathbf{t}}\right)(\mathbf{0}) = 0$.

$\Longrightarrow$ Existence of N*–multi–kinks* critical points, for all N.