Peierls instability and heteroclinic connections in polyacetylene chains

Éric Séré

sere@ceremade.dauphine.fr

(CEREMADE, Université Paris-Dauphine PSL, France)

joint works with M. Garcia Arroyo, D. Gontier, A. Kouande

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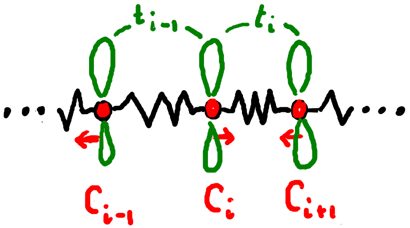
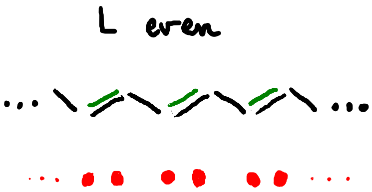
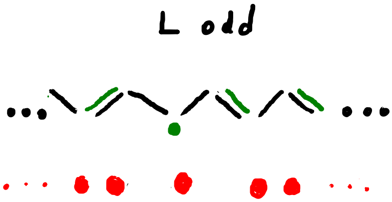
Discrete model of polyacetylene (Su-Schrieffer-Heeger '79)

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:

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

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 distorsion energy $\frac{\mu}{2}\sum_{i=1}^{L}(t_i - 1)^2 \quad (\mu > 0)$.

Total energy of the chain:

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

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 for L even

Theorem (Kennedy-Lieb, PRL 1987)

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

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

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 $\delta > 0$ (instability of the monorized state) was predicted by Frölich '54 and Peierls '55. Kivelson-Heim '82 showed that for N even, one always has $\delta_N > 0$. But for N odd and small, one may have $\delta_N = 0$.

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

Predicted by Su-Schrieffer-Heeger '79 who proposed the profile $t_i^\infty = W + (-1)^i \delta \tanh(i/\ell)$ as variational approximation.

Theorem (Garcia Arroyo-S., hal-00769075)

For $L = 2N+1$, let $\boldsymbol{t}^{(N)}$ be a minimizer of $\mathcal{E}^{(L)}$. When $N \to \infty$, up to extraction and space translation $i \mapsto i + \tau_N$, one has the pointwise convergence $t_i^{(N)} \to t_i^\infty$ ($\forall i$), where $\boldsymbol{t}^\infty = (t_i^\infty)_{i \in \mathbb{Z}}$ satisfies

$$\sum_{i<0} (t_i^\infty - W + (-1)^i \delta)^2 + \sum_{i>0} (t_i^\infty - W - (-1)^i \delta)^2 < \infty$$

$$\textit{and} \quad t_i^\infty = 1 + \frac{4}{\mu} \gamma(\boldsymbol{t}^\infty)_{i,i+1}\,, \quad \gamma(\boldsymbol{t}^\infty) := \mathbb{1}_{(-\infty,0)}(T^\infty)\,,$$

$$\textit{with} \quad (T^\infty \psi)_i = t_{i-1}^\infty \psi_{i-1} + t_i^\infty \psi_{i+1}\,, \quad \forall \psi \in \ell^2(\mathbb{Z}, \mathbb{C})\,.$$

The configuration $\boldsymbol{t}^\infty$ is a solution of the self-consistent equations interpolating between the dimerized states: $\lim_{i \to \pm\infty} (t_i^\infty - t_i^\pm) = 0$.

Spectral gap (L infinite)

• When $t_i^\pm = W \pm (-1)^i \delta$ 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 $\delta > 0$. The lower band is occupied, the upper band is empty (insulator).

• The gap closes when $\delta = 0$ (metal).

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

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

and 0 is an eigenvalue of multiplicity one. The corresponding eigenvector decreases exponentially as $|i| \to \infty$.

Exponential localization

Theorem (Gontier-Kouande-S., in preparation)

Let $\boldsymbol{t} = (t_i)_{i\in\mathbb{Z}}$ *be such that for some* $s \in \{-1, 1\}$,

$$\sum_{i<0}(t_i - W - s(-1)^i\delta)^2 + \sum_{i>0}(t_i - W - (-1)^i\delta)^2 < \infty\,.$$

With $(T\psi)_i = t_{i-1}\psi_{i-1} + t_i\psi_{i+1}$ *and* $\gamma(\boldsymbol{t}) := \mathbb{1}_{(-\infty,0)}(T)$, *assume that*

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

Then there is $\rho > 0$ *depending only on* μ *and* C *depending on* $\boldsymbol{t}$ *such that*

$$|t_{-i} - W - s(-1)^i\delta| + |t_i - W - (-1)^i\delta| \le Ce^{-\rho i}\,, \quad \forall i > 0\,.$$

Exponential localization was already known for the TLM continuum model of polyacetylene (Takayama, Lin-Liu, Maki '80) which has explicit solutions.

L even at a positive temperature θ

Let $S(x) := x \ln(x) + (1-x)\ln(1-x)$ be the fermionic entropy function.

Our goal now is to minimize the free energy

$$\mathcal{F}^{(2N)}_{\mathrm{full},\theta}(\boldsymbol{t},\gamma) := \frac{\mu}{2}\sum_{i=1}^{2N}(t_i-1)^2 + 2\left\{\mathrm{Tr}\left(T\gamma\right) + \theta \mathrm{Tr}\left(S(\gamma)\right)\right\}$$

under the constraints $\gamma = \gamma^*$, $0 \leq \gamma \leq 1$.

Minimizing $\mathcal{F}^{(2N)}_{\mathrm{full},\theta}$ in the variable γ one gets

$$\boxed{\mathcal{F}^{(2N)}_{\theta}(\boldsymbol{t}) := \frac{\mu}{2}\sum_{i=1}^{2N}(t_i-1)^2 - \mathrm{Tr}\left(h_\theta(T^2)\right)}$$

with

$$h_\theta(x) := 2\theta \ln\left(2\cosh\left(\frac{\sqrt{x}}{2\theta}\right)\right) \underset{\theta\to 0}{\longrightarrow} \sqrt{x}.$$

Peierls metal-insulator transition for L even

Theorem (Gontier-Kouande-S., Ann. Henri Poincaré 2023)

For any $L = 2N$, with N an integer and $N \geq 2$, there exists a critical temperature $\theta_c^{(L)} := \theta_c^{(L)}(\mu) \geq 0$ such that:

- *for $\theta \geq \theta_c^{(L)}$, the minimizer of $\mathcal{F}_\theta^{(L)}$ is unique and 1-periodic;*
- *for $\theta \in (0, \theta_c^{(L)})$, there are exactly two minimizers $\boldsymbol{t}^\pm$, which are dimerized, of the form $t_i^\pm = W_N(\mu,\theta) \pm (-1)^i \delta_N(\mu,\theta)$.*

In addition,

1. *If $L \equiv 0 \mod 4$, this critical temperature is positive ($\theta_c^{(L)}(\mu) > 0$ for all $\mu > 0$).*
2. *If $L \equiv 2 \mod 4$, there is $\mu_c := \mu_c(L) > 0$ such that for $\mu \leq \mu_c$, $\theta_c^{(L)}$ is positive ($\theta_c^{(L)} > 0$), whereas for $\mu > \mu_c$, $\theta_c^{(L)} = 0$. Moreover as a function of L we have $\mu_c(L) \sim \frac{2}{\pi} \ln(L)$ at $+\infty$.*

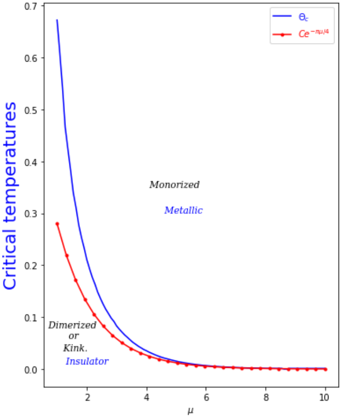
Peierls metal-insulator transition for $L = \infty$

Theorem (Gontier-Kouande-S., Ann. Henri Poincaré 2023)

For $L = 2N$, as $N \to \infty$, $W_N(\mu, \theta)$, $\delta_N(\mu, \theta)$ converge to positive limits $W(\mu, \theta) > \delta(\mu, \theta)$ and the critical temperature $\theta_c^{(L)}(\mu)$ converges to a positive limit $\theta_c(\mu)$.

• *In the large μ limit, $\theta_c(\mu) \sim C \exp\left(-\frac{\pi}{4}\mu\right)$, with $C \approx 0.61385$.*
• *For μ fixed, in the regime $0 < \theta_c - \theta << 1$ there is $K > 0$ such that $\delta(\theta) = K\sqrt{\theta_c - \theta} + o\left(\sqrt{\theta_c - \theta}\right)$.*

Peierls metal-insulator transition for $L = \infty$ (numerics)



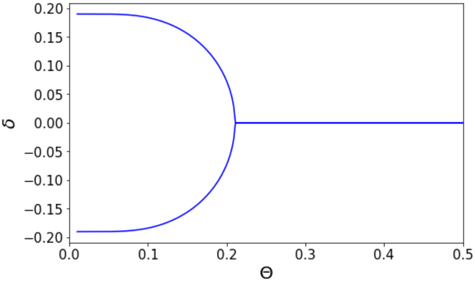


Figure: (Left) the critical temperature $\mu \mapsto \theta_c(\mu)$ and its asymptotic $Ce^{-\frac{\pi}{4}\mu}$. (Right) The bifurcation of δ in the thermodynamic model. We took $\mu = 2$, and the critical temperature is found to be $\theta_c = 0.2112$.

A fundamental convexity tool

The following result is well-known:

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.

Convexity in action

In their proof, Kennedy-Lieb take $I = \mathbb{R}_+$ and $\varphi(x) = -\sqrt{x}$. This allows them to write

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

with $< T^2 >:= \frac{1}{2N}\sum_{k=1}^{2N} \Theta_k T^2 \Theta_k^{-1}$, $\Theta_k = \Theta_1^k$ and

$$\Theta_1 := \begin{pmatrix} 0 & 1 & 0 & \cdots & 0 \\ 0 & 0 & 1 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \cdots & 1 \\ 1 & 0 & 0 & \cdots & 0 \end{pmatrix}$$

is the shift of one unit.

Three parameters

It turns out that $< T^2 >= 2y^2 + z\Omega$ with

$$y^2 = \frac{1}{2N}\sum_{i=1}^{2N} t_i^2\,, \quad z = \frac{1}{2N}\sum_{i=1}^{2N} t_i t_{i+1} \quad \text{and} \quad \Omega_{ij} = \delta_{|i-j|\in\{2,2N-2\}}.$$

As a consequence, with $x = \frac{1}{2N}\sum_{i=1}^{2N} t_i$ we get $\mathcal{E}^{(L)}(\mathbf{t}) \geq e_L(x, y^2, z)$, where

$$e_L(x, y^2, z) := \frac{\mu L}{2}(y^2 - 2x + 1) - \mathrm{Tr}\left(\sqrt{2y^2 + z\Omega}\right).$$

Then Kennedy-Lieb show that e_L has a unique minimizer, which indeed corresponds to a dimerized state or its translation of one unit.

A refinement

Taking $I = [0,1]$ and $\varphi(x) = -\sqrt{x} - x^2/8$, Kennedy-Lieb obtain the refined inequality

$$\mathcal{E}^{(L)}(\mathbf{t}) \geq e_L(x, y^2, z) + \frac{\mathrm{Tr}\left((T^2 - < T^2 >)^2\right)}{8\|T\|^3}$$

and this allows them to prove that all minimizers are 2-periodic.

A priori bounds

The refined inequality is also used in our works on heteroclinic configurations:

• For $L = 2N + 1$, combined with an a priori estimate on $\mathcal{E}^{(L)}(\mathbf{t}^{(N)})$, it gives a bound of the form $\sum_{i=1}^{N} \rho_i^{(N)} \leq C$ with

$$\rho_i^{(N)} := \left(t_i^{(N)} + t_{i+1}^{(N)} - 2W\right)^2 + \left(t_i^{(N)} t_{i+1}^{(N)} - W^2 + \delta^2\right)^2 .$$

Note that ρ_i is small when the pair $\{t_i^{(N)}, t_{i+1}^{(N)}\}$ is close to the pair $\{W - \delta, W + \delta\}$. The bound allows to prove that $\boldsymbol{t}^\infty$ connects the two dimerized states.

• To prove the exponential localization one needs to know that the Hessian of $\mathcal{E}^{(L)}$ at $\boldsymbol{t}^+$ is positive definite, with uniform bound on its inverse. The refined inequality provides this bound (after some work).

Positive temperatures

For $\theta > 0$ and $L = 2N$, we take $I = \mathbb{R}_+$ and $\varphi = -h_\theta$. Then we are reduced to a minimization problem in $\mathbb{R}^3$ and we easily show that the minimizers of the free energy are either monorized or dimerized and that the corresponding couple (W, δ) is unique.

To prove our results on the phase transition, we study in detail the system of two Euler-Lagrange equations satisfied by W, δ. For $L \to \infty$ we find that the critical temperature $\theta_c(\mu)$ is such that the following two equations of unknown W have a common solution:

$$\begin{cases} \mu(W-1) & = \dfrac{4}{\pi}\displaystyle\int_0^{\pi/2} \tanh\left(\dfrac{W\cos(s)}{\theta}\right)\cos(s)s \\ \mu W & = \dfrac{4}{\pi}\displaystyle\int_0^{\pi/2} \tanh\left(\dfrac{W\cos(s)}{\theta}\right)\dfrac{\sin^2(s)}{\cos(s)}s. \end{cases}$$

Perpectives

• The relations between the discrete SSH model and the continuous TLM model (equivalent to Gross-Neveu) remain unclear. The two models should have the same behaviour in the regime $\mu >> 1$, but in the limit $\mu \to \infty$ they both become degenerate.

• There should be solutions of multi-soliton type. A strategy could be to prove their existence in the regime $\mu >> 1$.

• For $L = 2N + 1 \to \infty$ and $0 < \theta < \theta_c(\mu)$ one expects the convergence of the minimizers to a heteroclinic connection.

• What can be said if the interaction between electrons is taken into account?

• We have assumed that the carbon atoms are static. What can be said if this constraint is removed?

THANK YOU !