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A quantized SSH model: Equilibrium and stretching

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Abstract. We present a one-mode quantized version of the semiclassical Su–Schrieffer–Heeger model, relevant for the study of conjugated polymers. The model is soluble. We give its equilibrium states at all temperatures and prove the existence of kink–antikink solutions. We impose stretching constraints in order to make the model boundary condition invariant. A uniform stretching of the lattice is considered. A formula for a temperature-dependent sound velocity is derived. The influence on the critical temperature and on the dimerization is rigorously derived.

1. Introduction

Conjugated polymer chains have been modelled by theories for one-dimensional metals. The succession of single and double bindings between the carbon atoms of the polymer is a consequence of the fact that the dimerization of the lattice lowers the electron energy at the Fermi level. This is a Peierls instability. The semiclassical Su–Schrieffer–Heeger (SSH) model [1–3] has been proved to be a good theoretical model for understanding conjugated polymers. The π -electrons are itinerant and hop on the chain and are coupled to the ionic motions, contributing to the effective elastic energy of the chain, which is modelled by a classical displacement field. The hopping amplitude of the π -electrons is a function of the displacements and this leads to an interaction between the classical and the quantum degrees of freedom. For a review of this model, see [4]. The success of the model is based on the persistence of the kink–antikink ground states. With rigorous results, it is proved [5, 6] that at half-filling, the ground-state configuration of the displacements is either homogeneous or that it has period two as predicted by the Peierls–Fröhlich (PF) instability. We are interested in a full quantum version of the model, i.e. a version in which the lattice vibrations are also quantized. It is expected, but there is no proof, that the Peierls instability persists when the quantum fluctuations of the positions of the atoms are taken into account [7] for the full quantized version of the SSH model.

In this paper we do not address this difficult problem, but a more modest one. The PF instability was initiated by Mattis and Langer [8]. They argued that the one-mode model interaction of electrons and lattice vibrations should be exactly soluble. The mathematical basis for the PF instability in this model is given in [9]. Therefore we consider the one-mode SSH model (see section 2) which can be found out of the full quantized SSH model by restricting the interaction to the resonant mode $q = \pm 2k_F$, k_F is the Fermi level wavevector, which is shown to be the responsible term for the PF-phase transition [9]. We call our model the Mattis–Langer SSH model or the one-mode quantized SSH model.

First we construct explicitly the equilibrium states of this model and prove that the PF phase transition persists. The proof is based on the analysis of the relevant self-consistency equation which is derived on the basis of correlation inequalities.

When quantizing the semi-classical SSH model a boundary term appears, which is linear in the total stretching of the chain and hence introduces the problem of boundary conditions. Since we are mainly interested in the bulk properties of the system, we introduce to the model Hamiltonian a term linear in the stretching with a multiplicative constant, which we choose in such a way that the supplementary boundary disappears. In doing so we are inspired by the work of Vos *et al* [10, 11]. In section 3 we compute this constant, known as the stretching coefficient γ . It not only depends on the temperature, but also on the quantum-mechanical order parameter, known as the dimerization amplitude. As in the semiclassical SSH, the effect of the boundary term on the system is a contraction of the chain.

In section 4 we discuss how to implement a uniform stretching in our model and what its effect on the phase transition is, namely on the critical temperature and on the order parameter. As a consequence of a screening effect, by the presence of the electrons, the sound velocity of the polyacetylene polymer decreases. For the ground state of the semiclassical SSH model, a formula has already been derived in [11]. We derive a quantum model for our formula which is valid for all temperatures. Moreover, in our computation we keep track of the fact that the order parameter does depend on the stretching coefficient. In the ground-state limit ($T \rightarrow 0$) we obtain an expression similar to the one in [11].

2. Model

First let us repeat the SSH model that is used to describe the physics of conjugated polymer transpolyacetylene $(\text{CH})_N$, on the basis of the one-dimensional tight-binding Hamiltonian. One considers N material points of a linear lattice

$$\Lambda = [a, 2a, \dots, Na]$$

where a is the lattice distance or the uniform spacing between adjacent CH groups. The first Brillouin zone is $\Lambda_1^* = \{k : e^{ikNa} = 1 \text{ or } k = \frac{2\pi n}{Na}, n = 0, \pm 1, \dots, \pm \frac{N}{2}\}$. The semiclassical SSH Hamiltonian is

$$H_\Lambda = H_{\Lambda,el} + H_{\Lambda,\ell}$$

where the π -electron–lattice coupling is

$$H_{\Lambda,el} = - \sum_{x \in \Lambda} (t - \alpha(q(x+a) - q(x)))(a^\dagger(x)a(x+a) + \text{h.c.}).$$

$a^\dagger(x)$ are the electron creation and annihilation operators, t the bare hopping constant for the electrons and α the coupling constant of the electron–lattice interaction; the lattice part of the Hamiltonian is

$$H_{\Lambda,\ell} = \frac{K}{2} \sum_{x \in \Lambda} (q(x+a) - q(x))^2 + \frac{1}{2M} \sum_{x \in \Lambda} p(x)^2 - \gamma \sum_{x \in \Lambda} (q(x+a) - q(x)).$$

M is the mass of the CH group, K the harmonic force constant for bond length deviations from the equal spacing and γ is the stretching force on a finite chain. The last term is introduced [10–13] in the Hamiltonian in order to counterbalance the compression of the total length of the lattice which is a consequence of the electron–lattice interaction.

The first step is to quantize the lattice vibrations, i.e. to consider $q(x)$ and $p(x)$ as operators satisfying the commutation relations

$$[q(x), p(y)] = i\delta_{x,y} \quad x, y \in \Lambda.$$

If we introduce the Fourier-transforms, Q_k, P_k :

$$q(x) = \frac{1}{\sqrt{N}} \sum_{k \in \Lambda_1^*} e^{ikx} Q_k \quad p(x) = \frac{1}{\sqrt{N}} \sum_{k \in \Lambda_1} e^{ikx} P_k$$

then the lattice part $H_{\Lambda, \ell}$ becomes

$$H_{\Lambda, r} = \frac{P_0^2}{2M} + \frac{1}{2N} \sum_{\substack{k \in \Lambda_1^* \\ k \neq 0}} P_k P_{-k} + \frac{K}{2} \sum_{\substack{k \in \Lambda_1^* \\ k \neq 0}} Q_k Q_{-k} 2(1 - \cos ka) \\ - \frac{K}{2N} \left(\sum_{\substack{k \in \Lambda_1^* \\ k \neq 0}} Q_k (e^{ika} - 1) \right)^2 - \frac{\gamma}{\sqrt{N}} \sum_{\substack{k \in \Lambda_1^* \\ k \neq 0}} Q_k (1 - e^{ika}).$$

In the following we disregard the kinetic energy of the centre of mass. Introducing the creation and annihilation operators for $k \neq 0$ of the phonons,

$$b_{k, \Lambda} = \frac{1}{\sqrt{2M\Omega_k}} (M\Omega_k Q_k + iP_{-k}) \quad b_{k, \Lambda}^* = (b_{k, \Lambda})^*$$

and the phonon spectrum,

$$\Omega_k = \left(\frac{2K}{M} (1 - \cos ka) \right)^{1/2}$$

one obtains

$$H_{\Lambda, \ell} = \sum_{k \in \Lambda_1^*} \Omega_k \left(b_{k, \Lambda}^* b_{k, \Lambda} + \frac{1}{2} \right) - \frac{K}{4M\Omega} (d_{\Lambda} + d_{\Lambda}^*)^2 - \Gamma (d_{\Lambda} + d_{\Lambda}^*) \quad (1)$$

where

$$d_{\Lambda} = \frac{1}{\sqrt{N}} \sum_{k \in \Lambda_1^*} b_{k, \Lambda} (1 - e^{-ika}) \left(\frac{\Omega}{\Omega_k} \right)^{1/2} \\ \Omega = \Omega_q \quad q = \frac{\pi}{a} \quad \Gamma = \frac{\gamma}{(2M\Omega)^{1/2}}.$$

The irrelevant constant $\sum_k \frac{\Omega_k}{2}$ in (1) is again disregarded.

As far as the electron–lattice part $H_{\Lambda, e\ell}$ of the Hamiltonian is concerned, we also transform it to momentum space. The electron creation and annihilation operators are

$$a(x) = \frac{1}{\sqrt{N}} \sum_{k \in \Lambda_1^*} e^{ikx} a_k \quad \text{and} \quad a_k^* = (a_k)^*.$$

The hopping term becomes

$$-t \sum_{x \in \Lambda} a^*(x) a(x+a) + \text{h.c.} \\ = - \sum_{k \in \Lambda_1^*} 2t (\cos ka) a_k^* a_k + \frac{t}{N} \sum_{kk' \in \Lambda_1^*} (e^{ik'a} a_k^* a_{k'} + \text{h.c.})$$

and the electron–phonon interaction:

$$\alpha \sum_{x \in \Lambda} (q(x+a) - q(x)) (a^*(x) a(x) + \text{h.c.}) \\ = \frac{\lambda}{\sqrt{N}} \sum_{k, k' \in \Lambda_1^*} \left(b_{k, \Lambda} (e^{ika} - 1) \left(\frac{\Omega}{\Omega_k} \right)^{1/2} + \text{h.c.} \right) \left(e^{ik'a} a_{k'+k}^* a_{k'} + \text{h.c.} \right)$$

$$+ \frac{\lambda}{N} (d_{\Lambda} + d_{\Lambda}^*) \sum_{k, k' \in \Lambda_1^*} \left(e^{ik'a} a_k^* a_{k'} + \text{h.c.} \right)$$

where

$$\lambda = \frac{\alpha}{(2M\Omega)^{1/2}}.$$

Collecting the previous calculations and leaving out the non-extensive contributions from the potential term and the hopping term, one obtains the fully quantized form of the SSH model:

$$\begin{aligned} H_{\Lambda} = & - \sum_{k \in \Lambda_1^*} 2t (\cos ka) a_k^* a_k + \sum_{k \in \Lambda_1^*} \Omega_k b_{k, \Lambda}^* b_{k, \Lambda} \\ & + \frac{\lambda}{\sqrt{N}} \sum_{k, k'} \left(e^{ik'a} a_{k'+k}^* a_{k'} + \text{h.c.} \right) \left(b_{k, \Lambda} (e^{ika} - 1) \left(\frac{\Omega}{\Omega_k} \right)^{1/2} + \text{h.c.} \right) \\ & + \left(\frac{\lambda}{N} \sum_{k, k'} \left(e^{ik'a} a_k^* a_{k'} + \text{h.c.} \right) - \Gamma \right) (d_{\Lambda} + d_{\Lambda}^*). \end{aligned} \quad (2)$$

Quantizing the lattice vibrations, the interaction in $H_{\Lambda, el}$ yields a supplementary boundary term

$$\frac{\lambda}{N} \sum_{k, k'} \left(e^{ik'a} a_k^* a_{k'} + \text{h.c.} \right) (d_{\Lambda} + d_{\Lambda}^*).$$

This term depends on the boundary conditions and even disappears for periodic boundary conditions. However, with the aim of making the model and system boundary condition invariant, this term was introduced. The constant γ will be chosen in such a way that the last term of (2) has a zero expectation value in the equilibrium states of the system. We remark that this term has no contribution to the energy density, and therefore only enters if one considers finite-size effects.

In the next section we shall also consider the effects of a uniform stretching of the chain. Therefore we keep the $\Gamma = \gamma/(2M\Omega)^{1/2}$ term along at this moment. In this case the value of γ will affect the sound velocity in the chain.

The model (2) is not an exactly soluble model, owing to the presence of electron–phonon couplings in the interaction for all modes. Inspired by the Mattis–Langer model [8] and also by [9], where it is rigorously shown that the mode $k = \frac{\pi}{a}$ is solely responsible for the occurrence of the Peierls transition, we initially propose to study the one-mode case, which we obtain from the interaction in (2) by leaving out all interactions with $k \neq \frac{\pi}{a}$. In a natural way, we also have to leave out the corresponding terms in the boundary contribution term. All of this leads to the consideration of the following one-mode quantized SSH model

$$\begin{aligned} H_{\Lambda} = & 2t \sum_{k \in \Lambda_1^*} (\cos ka) a_k^* a_k + \sum_{k \in \Lambda_1^*} \Omega_k b_{k, \Lambda}^* b_{k, \Lambda} - \frac{2\lambda}{\sqrt{N}} \sum_{k \in \Lambda_1^*} \left(e^{ika} a_{k+q}^* a_k + \text{h.c.} \right) (b_{\Lambda} + b_{\Lambda}^*) \\ & + \left(\frac{\lambda}{N} \sum_{k \in \Lambda_1^*} 2(\cos ka) a_k^* a_k - \Gamma \right) (d_{\Lambda} + d_{\Lambda}^*) \end{aligned} \quad (3)$$

where $q = \frac{\pi}{a}$ and $b_{\Lambda} = b_{q, \Lambda}$. This is the model which we shall study further and which is a Mattis–Langer version of the quantized semiclassical SSH model. One realizes that treating this version of the model is only a first step in the study of the fully quantized SSH model. However, one guesses that the physics one-mode version yields a good idea of the physical properties described by the fully quantized model.

3. Equilibrium states and Peierls transition

First we characterize the equilibrium states in the thermodynamic limit. There are many ways of doing that. We follow the method used in [9] which is based on correlation inequalities. It is advantageous for us here in the sense that one can see that the equilibrium states are determined by the commutator with the Hamiltonian.

Any equilibrium state at inverse temperature, denoted by ω_β in the thermodynamic limit ($\Lambda \rightarrow \mathbb{Z}$), for a system given by the local Hamiltonians H_Λ is a solution of the correlation inequalities given by [14]:

$$\lim_{\Lambda \rightarrow \mathbb{Z}} \beta \omega_\beta(A^*[H_\Lambda, A]) \leq \omega_\beta(A^*A) \ln \frac{\omega_\beta(A^*A)}{\omega_\beta(AA^*)} \quad (4)$$

for all local observables A . This characterization holds, of course, also for finite-volume Gibbs states.

For our purposes, it is important to specify the structure of the local algebra of observables. Let $\mathcal{H} = \ell^2(\mathbb{Z}_a)$ and $\mathcal{A}_\pm \equiv \mathcal{A}_\pm(\mathcal{H})$ the $CAR(+)$, respectively the $CCR(-)$ algebras for the one-particle space \mathcal{H} ; these are the electron and phonon observables. We also use the obvious notations $\mathcal{A}_\pm^\Lambda = \mathcal{A}_\pm(\ell^2(\Lambda))$ for the observables confined to the finite-volume Λ . The algebra of observables for our total system is then given by the tensor product:

$$\mathcal{A} = \mathcal{A}_+ \otimes \mathcal{A}_-$$

and

$$\mathcal{A}_\Lambda = \mathcal{A}_+^\Lambda \otimes \mathcal{A}_-^\Lambda.$$

The algebra of all local observables is given by $\bigcup_{\Lambda} \mathcal{A}_\Lambda$.

Up to an isomorphism the CAR fermion algebra \mathcal{A}_+ has the structure

$$\mathcal{A}_+ = \otimes_{n \in \mathbb{Z}_a} \mathcal{A}_+(\mathbb{C}) = \otimes_{n \in \mathbb{Z}_{2a}} \mathcal{A}_+(\mathbb{C}^2).$$

Because of this representation and because the operator b_Λ is \mathbb{Z}_{2a} -permutation invariant, one can use the result of [15] and write the equilibrium state ω_β , the solution of (4), as an integral over equilibrium product states on the product algebra $\mathcal{A} = \mathcal{A}_+ \otimes \mathcal{A}_-$:

$$\omega_\beta = \int \mu(d\tau) \eta_{\beta,\tau}^+ \otimes \eta_{\beta,\tau}^-$$

where $\eta_{\beta,\tau}^\pm$ are extremal \mathbb{Z}_{2a} -permutation invariant states on \mathcal{A}_\pm . This means that we can limit our search for equilibrium states to the search for the states $\eta_{\beta,\tau}^\pm$. We drop the label τ for convenience.

Furthermore, as ω_β is the limit ($\Lambda \rightarrow \mathbb{Z}$) state of the Gibbs states ω_β^Λ , also the $\eta_{\beta,\tau}^\pm$ are limit states of finite volume states for effective Hamiltonians defined by:

$$\begin{aligned} \lim_{\Lambda} (\eta_{\beta,\tau}^+ \otimes \eta_{\beta,\tau}^-)(X^*[H_\Lambda, X]) &= \lim_{\Lambda} (\eta_{\beta,\tau}^{+,\Lambda} \otimes \eta_{\beta,\tau}^{-,\Lambda})(X^*[H_\Lambda, X]) \\ &= \lim_{\Lambda} \eta_{\beta,\tau}^{+,\Lambda}(X^*[H_{+,\Lambda}^{\text{eff}}, X]) \end{aligned}$$

for all $X \in \mathcal{A}_+$ and analogously for $H_{-,\Lambda}^{\text{eff}}$. One can easily find the effective Hamiltonians:

$$H_\Lambda^{\text{eff}} = H_{+,\Lambda}^{\text{eff}} + H_{-,\Lambda}^{\text{eff}} \quad (5)$$

where

$$H_{+\Lambda}^{\text{eff}} = \sum_k -2 \left(t - \frac{\lambda L_\Lambda}{N} \right) (\cos ka) a_k^* a_k - 2\lambda \sigma_\Lambda \sum_k (e^{ika} a_{k+q}^* a_k + \text{h.c.})$$

$$H_{-\Lambda}^{\text{eff}} = \sum_k \Omega_k b_{k,\Lambda}^* b_{k,\Lambda} - 2\lambda \chi_\Lambda (b_\Lambda + b_\Lambda^*) + \left(\frac{\lambda}{N} \sum_k (2 \cos ka) \rho_\Lambda(k) - \Gamma \right) (d_\Lambda + d_\Lambda^*)$$

where

$$\sigma_\Lambda = \eta_\beta^- \left(\frac{b_\Lambda + b_\Lambda^*}{\sqrt{N}} \right)$$

$$L_\Lambda = \eta_\beta^- (d_\Lambda + d_\Lambda^*)$$

$$\chi_\Lambda = \eta_\beta^+ \left(\frac{1}{\sqrt{N}} \sum_k (e^{ika} a_{k+q}^* a_k + \text{h.c.}) \right)$$

$$\rho_\Lambda(k) = \eta_\beta^+ (a_k^* a_k).$$

Time invariance of the equilibrium state $\eta_\beta = \eta_\beta^+ \otimes \eta_\beta^-$ yields for each finite volume in particular

$$\eta_\beta^{+,\Lambda} \otimes \eta_\beta^{-,\Lambda} ([H_\Lambda^{\text{eff}}, b_\Lambda]) = 0$$

which gives the following consistency equation between the electron and the phonon subsystem

$$\Omega \sigma_\Lambda = 4\lambda \frac{\chi_\Lambda}{\sqrt{N}} + \mathcal{O} \left(\frac{1}{N} \right). \quad (6)$$

The systems H_Λ (3) and H_Λ^{eff} (5) have the same expectation values in the thermodynamic limit for all quasilocal observables. Therefore the η_β^\pm are the equilibrium states for the effective Hamiltonians H_\pm^{eff} . Since the latter ones are at most quadratic in the creation and annihilation operators the states η_β^\pm are completely known, i.e. all expectation values or correlations are computable. Therefore the model H_Λ (3) is sometimes known as soluble. However, the states η_β^+ and η_β^- are coupled to each other by the consistency equation (6). Already on the basis of the symmetry properties of these states the thermodynamic limit ($\Lambda \rightarrow \mathbb{Z}$) of equation (6) is guaranteed. A standard and easy but tedious computation yields the following explicit form of the equation in the thermodynamic limit

$$\frac{\pi \Omega}{16\lambda^2 a} \sigma = \sigma \mathcal{G}(\beta, \sigma) \quad (7)$$

where

$$\mathcal{G}(\beta, \sigma) = \int_{-\frac{\pi}{2a}}^{\frac{\pi}{2a}} dk \sin^2 ka \frac{\tanh \frac{\beta E(k, \sigma)}{2}}{E(k, \sigma)}$$

$$E(k, \sigma) = (\varepsilon(k)^2 + \varphi(k, \sigma)^2)^{1/2} \text{sign } \varepsilon(k)$$

$$\varepsilon(k) = -2t \cos ka$$

$$\varphi(k, \sigma) = 4\lambda \sigma \sin ka.$$

We remark that $E(k, \sigma)$ is the spectrum of the electronic excitations which is obtained by diagonalizing the Hamiltonian $H_{+,\Lambda}^{\text{eff}}$. We are now ready to formulate the proof of the existence of the Peierls phase transition.

Theorem 3.1. There exists a critical temperature T_c such that:

- (i) for $T > T_c$, the unique solution of (7) is $\sigma = 0$;
- (ii) for $T < T_c$, equation (7) has the solutions $\sigma = 0$ and $\sigma = \sigma_0 \neq 0$, where σ_0 satisfies

$$\mathcal{G}(\beta, \sigma_0) = \frac{\pi\Omega}{16\lambda^2 a}.$$

If $\sigma_0 > 0$, then the electronic spectrum $E(k, \sigma_0)$ has a gap at $k = \frac{\pi}{2a}$:

$$\lim_{k \rightarrow \pm \frac{\pi}{2a}} E(k, \sigma_0) = \pm 4\lambda\sigma_0.$$

Proof. Clearly $\sigma = 0$ is always a solution of equation (7). For $\sigma \neq 0$ (7) becomes

$$\frac{\pi\Omega}{16\lambda^2 a} = \mathcal{G}(\beta, \sigma).$$

If σ tends to zero, then $\mathcal{G}(\beta, \sigma)$ tends to $\mathcal{G}(\beta, 0)$, which diverges for large β . Indeed the integrand of $\mathcal{G}(\beta, 0)$ (see (7)) has non-integrable singularities at the edges of the integration interval. Hence there exists a β_c or T_c such that

$$\mathcal{G}(\beta_c, 0) = \frac{\pi\Omega}{16\lambda^2 a}.$$

On the other hand $\sigma \rightarrow \mathcal{G}(\beta, \sigma)$ is monotonically decreasing to zero. Hence for $T < T_c$, there exists a value σ_0 such that

$$\mathcal{G}(\beta, \sigma_0) = \frac{\pi\Omega}{16\lambda^2 a} \quad \sigma_0 = \sigma_0(T).$$

This proves the existence of a second order phase transition at T_c . The rest of the theorem is straightforward. \square

The phase transition is seen by the creation of the gap in the electronic spectrum. It is also seen in the phonon properties of the model. These must be derived from the boson term, H_-^{eff} , of the effective Hamiltonian. At $T = T_c$ the phonon state obtains a change from \mathbb{Z}_a for $T \geq T_c$, to \mathbb{Z}_{2a} translation symmetry for $T < T_c$, i.e. one obtains a structural phase transition at T_c . Indeed consider the position operator

$$q(x) = \frac{1}{\sqrt{N}} \sum_{k \in \Lambda_1^*} e^{ikx} Q_k = \frac{1}{\sqrt{N}} \sum_{k \in \Lambda_1^*} e^{ikx} \frac{b_{k,\Lambda} + b_{-k,\Lambda}^*}{\sqrt{2M\Omega_k}}.$$

By reusing the diagonalized form of H_+^{eff} , one finds:

$$\eta_\beta^-(q(x)) = \begin{cases} \frac{e^{iqx}}{\sqrt{2M\Omega}} \sigma_0 & \text{for } T < T_c \\ 0 & \text{for } T \geq T_c. \end{cases} \quad (8)$$

In this derivation we also used that for $k \neq q = \frac{\pi}{a}$:

$$\lim_{\Lambda} \eta_\beta^-(\sqrt{N} b_{k,\Lambda}) = 0 \quad (9)$$

which we discuss at the end of this section. Result (8) means that one obtains boson condensation in the $k = q$ phonon mode. For our model it means that there exists a critical temperature T_c such that, for $T < T_c$, the polymer transpolyacetylene is dimerized. The dimerization amplitude is given by

$$u = \frac{|\sigma_0|}{\sqrt{2M\Omega}}$$

which is proportional to the order parameter.

Now we are also able to compute explicitly the total stretching of the chain. It is given by

$$L = \lim_{\Lambda} L_{\Lambda} = \lim_{\Lambda} \eta_{\beta}^{-} (d_{\Lambda} + d_{\Lambda}^*).$$

We remark that:

$$\frac{d_{\Lambda} + d_{\Lambda}^*}{\sqrt{2M\Omega}} = q(N) - q(1).$$

One computes

$$L = 2\sigma + \frac{8}{\Omega} \left(\Gamma - \frac{\lambda a}{\pi} \int_{-\frac{\pi}{a}}^{\frac{\pi}{a}} dk \rho_{\beta}(k, \sigma) \cos ka \right) \quad (10)$$

where

$$\rho_{\beta}(k, \sigma) = \lim_{\Lambda} \eta_{\beta}^{+} (a_k^* a_k) = \frac{1}{2} - \varepsilon(k) \frac{\tanh \frac{\beta E(k, \sigma)}{2}}{2E(k, \sigma)}.$$

The first contribution in L is directly related to the phase transition order parameter. The second contribution comes from the compensating Γ -force term in the Hamiltonian. The third term in (10) is exactly the amount of contraction of the chain. In order to make our model boundary condition invariant we define Γ as follows

$$\frac{\gamma}{(2M\Omega)^{1/2}} = \Gamma = \Gamma(\beta, \sigma) = \frac{\lambda a}{\pi} \int_{-\frac{\pi}{a}}^{\frac{\pi}{a}} dk \rho_{\beta}(k, \sigma) \cos ka. \quad (11)$$

This means that the stretching force is temperature and order parameter dependent. In the literature [12] one finds often the value $\Gamma = \frac{4\lambda}{\pi}$. However, this value was derived before, although only in the case of the ground state ($T = 0$) and without dimerization ($\sigma = 0$). If we compute (11) in this case, one obtains $\Gamma = \frac{2\lambda}{\pi}$, i.e. a factor of 2 difference. This difference is a simple consequence of the fact that we did not take into account the spin of the electrons, yielding a doubling of the density $\rho_{\beta}(k, \sigma)$. In other words, formula (11) gives a correct generalization of the value of the stretching force, extended to finite temperatures and dependent on the order parameter in a one-mode quantized SSH model. It is consistent with what can be found in the literature.

Finally, we remark that (9) follows straightforwardly from (11) and the fact that Γ is finite.

4. Uniform stretching

The content of this section is very much inspired by the work of Vos *et al* [10, 11] in which they consider the ground state of the semi classical SSH model. We apply their ideas to our one-mode quantum SSH model and consider the influence of a uniform stretching of the chain on the critical temperature, and the order parameter at all temperatures. We also discuss its influence on the sound velocity.

A uniform stretching is a mode ($k = 0$)-phenomenon for a lattice with spacing parameter a . As is conceived in [10, 11], we describe it by performing a transformation:

$$q(x + a) - q(x) \rightarrow q(x + a) - q(x) + \delta$$

in the original Hamiltonian (see section 2); δ is the stretching parameter, measuring the amount of uniform stretching.

The effect of this transformation in the Hamiltonian results in a substitution of the hopping parameter t into $t - \alpha\delta$, in adding an elastic term $NK\delta^2/2$ and in subtracting a stretching term $N\gamma\delta$. We forget about all changes to a lower N -order in the Hamiltonian.

Initially it is clear that this modification of the model Hamiltonian does not affect the solvability of the model as explained in section 3. Mathematically the effect on the Peierls transformation amounts solely to the substitution of the hopping parameter t by $t - \alpha t$. In the following we study some effects of this uniform stretching.

4.1. Influence on critical temperature

The critical temperature, $T_c(\delta)$, is now implicitly defined by the following equation (see theorem 3.1)

$$\mathcal{G}(\beta_c(\delta), \delta) = \frac{\pi \Omega}{16\lambda^2 a} \tag{12}$$

where

$$\mathcal{G}(\beta_c(\delta), \delta) = \int_{-\frac{\pi}{a}}^{\frac{\pi}{a}} dk \sin^2 ka \frac{\tanh \frac{\beta_c(\delta)E(k,\delta)}{2}}{E(k, \delta)}$$

$$E(k, \delta) = -2(t - \alpha\delta) \cos ka.$$

We remark that the critical temperature T_c (or β_c) depends on the parameter δ . In the function $\mathcal{G}(\beta_c(\delta), \delta)$, for notational convenience we do not note the dependence on the order parameter, which is equal to zero at T_c . We look for the behaviour of $T_c(\delta)$ as a function of δ in the neighbourhood of $\delta = 0$. For $\frac{\alpha\delta}{t} \ll 1$, one has

$$\beta_c(\delta) \approx \beta_c(0) + \beta'_c(0) \frac{\alpha\delta}{t}.$$

We compute $\beta'_c(0)$ from (12):

$$\beta'_c(0) = - \frac{\left. \frac{\partial \mathcal{G}(\beta_c(\delta), \delta)}{\partial \delta} \right|_{\delta=0}}{\left. \frac{\partial \mathcal{G}(\beta_c(\delta), \delta)}{\partial \beta_c(\delta)} \right|_{\delta=0}} = \frac{\frac{\beta_c(0)}{2} \int_{-\frac{\pi}{2a}}^{\frac{\pi}{2a}} dk \sin^2 ka \left(\frac{1}{\cosh^2 x} - \frac{\tanh x}{x} \right) \Big|_{x=\frac{\beta_c(0)E(k,0)}{2}}}{\int_{-\frac{\pi}{2a}}^{\frac{\pi}{2a}} dk \frac{\sin^2 ka}{2 \cosh^2 \frac{\beta_c(0)E(k,0)}{2}}}.$$

As $\beta_c(0) > 0$, the sign of $\beta'_c(0)$ is determined by the sign of the function

$$x \rightarrow f(x) = \frac{\tanh x}{x} - \frac{1}{\cosh^2 x} \quad x \in \mathbb{R}.$$

However, $f(x) \geq 0$ is equivalent to

$$\frac{\sinh x \cosh x}{x} \geq 1$$

and in turn, to

$$\frac{\sinh 2x}{2x} \geq 1.$$

It follows that $\beta'_c(0) < 0$, hence we have the following.

Theorem 4.1. At $\delta = 0$, the critical temperature T_c is an increasing function of the uniform stretching parameter.

From a physical point of view, it is rather clear that an increasing uniform stretching is like making the hopping probability smaller while the electron-phonon interaction remains

unchanged. The net result is like enhancing the interaction and hence makes the phase transition more probable. This is expressed by an increasing critical temperature. The same phenomenon can be seen if one notes the influence of the stretching on the order parameter at constant temperature.

4.2. Influence on order parameter

On the basis of theorem 3.1, for $\beta > \beta_c$, the order parameter $\sigma(\delta)$, as a function of δ is determined by the equation:

$$\mathcal{G}(\beta, \delta, \sigma(\delta)) = \frac{\pi \Omega}{16\lambda^2 a} \quad (13)$$

where

$$\mathcal{G}(\beta, \delta, \sigma(\delta)) = \int_{-\frac{\pi}{2a}}^{\frac{\pi}{2a}} dk \sin^2 ka \frac{\tanh \frac{\beta E(k, \delta, \sigma(\delta))}{2}}{E(k, \delta, \sigma(\delta))}$$

$$E(k, \delta, \sigma(\delta)) = [4(t - \alpha\delta)^2 \cos^2 ka + 16\lambda^2 \sigma^2(\delta) \sin^2 ka]^{1/2} \text{sign}[-2(t - \alpha\delta) \cos ka].$$

For $\frac{\alpha\delta}{t} \ll 1$, one can again consider

$$\sigma(\delta) \approx \sigma(0) + \sigma'(0) \frac{\alpha\delta}{t}.$$

We compute $\sigma'(0)$ from (13):

$$\sigma'(0) = \left. \frac{d\sigma(\delta)}{d\delta} \right|_{\delta=0} = - \frac{\left. \frac{\partial \mathcal{G}(\beta, \delta, \sigma(\delta))}{\partial \delta} \right|_{\delta=0}}{\left. \frac{\partial \mathcal{G}(\beta, \delta, \sigma(\delta))}{\partial \sigma(\delta)} \right|_{\delta=0}} = \frac{\int_{-\frac{\pi}{2a}}^{\frac{\pi}{2a}} dk \left(\frac{t \sin ka \cos ka}{E(k, 0, \sigma(0))} \right)^2 I(\beta, k, \sigma(0))}{\int_{-\frac{\pi}{2a}}^{\frac{\pi}{2a}} dk \sigma(0) \left(\frac{2\lambda \sin^2 ka}{E(k, 0, \sigma(0))} \right)^2 I(\beta, k, \sigma(0))}$$

where

$$I(\beta, k, \sigma(0)) = f(x) = \frac{\tanh x}{x} - \frac{1}{\cosh^2 x} \geq 0$$

$$x = \frac{\beta E(k, 0, \sigma(0))}{2}.$$

Hence, one has:

$$\sigma(\delta) \approx \sigma(0) \left(1 + \frac{1}{\sigma^2(0)} \Delta \right) \quad \text{with } \Delta > 0.$$

We have proved the following.

Theorem 4.2. Up to the first-order in the stretching parameter, the absolute value of the order parameter increases.

4.3. Sound velocity

The sound velocity in conjugated polymers decreases because of the screening effect which is itself a consequence of the presence of the electrons [16]. In [10, 11], Vos *et al* derived a rigorous formula for the sound velocity, applicable in the semiclassical SSH model, where the lattice vibrations are considered as classical variables. Their arguments are based on classical hydrodynamics. In principle our model (3) is fully quantum mechanical, and there do not exist quantum-hydrodynamical equations. We now face a basic problem, which is

not as easy to overcome. Therefore we hope that the starting point definition of the sound velocity given by [10]:

$$c = \frac{a}{\sqrt{M}} \sqrt{\frac{d^2 \varepsilon}{d\delta^2}} \tag{14}$$

is also a good enough approximation for the quantum case. In (14) $M = a\rho$, the mass, ρ the density, and ε the energy per lattice cell. The derivatives with respect to δ have to be evaluated at equilibrium, i.e. at $\delta = 0$.

In our case the energy density ε is given by

$$\varepsilon = \lim_{\Lambda} (\eta_{\beta}^+ \otimes \eta_{\beta}^-) \left(\frac{H_{\Lambda}}{N} \right)$$

where H_{Λ} is given by the one-mode quantized SSH model. It has the form

$$\varepsilon = \varepsilon_+ + \varepsilon_- + \frac{K\delta^2}{2} - \gamma\delta \tag{15}$$

where

$$\varepsilon_{\pm} = \lim_{\Lambda} \eta_{\beta}^{\pm} \left(\frac{H_{\pm, \Lambda}^{\text{eff}}}{N} \right).$$

Using the explicit diagonalization of H_{\pm}^{eff} , and the self-consistency equation (7) one obtains explicitly:

$$\begin{aligned} \varepsilon_+ &= -\frac{a}{2\pi} \int_{-\frac{\pi}{2a}}^{\frac{\pi}{2a}} dk E(k, \delta, \sigma) \tanh \frac{\beta E(k, \delta, \sigma)}{2} \\ \varepsilon_- &= \frac{a}{2\pi} \int_{-\frac{\pi}{a}}^{\frac{\pi}{a}} dk \frac{\Omega_k}{1 + e^{\beta \Omega_k}} + \frac{\Omega \sigma^2}{4}. \end{aligned}$$

We also recall (11) and the relation

$$\Gamma = \frac{\gamma}{(2M\Omega)^{1/2}}.$$

Therefore γ in (15) depends on σ , but also on δ :

$$\gamma(\delta, \sigma) = \frac{\alpha a}{\pi} \int_{-\frac{\pi}{2a}}^{\frac{\pi}{2a}} dk 2(t - \alpha\delta) \cos^2 ka \frac{\tanh \frac{\beta E(k, \delta, \sigma)}{2}}{E(k, \delta, \sigma)}.$$

Collecting all this in formula (15), one obtains explicitly the energy density ε as a function of δ :

$$\varepsilon = \varepsilon(\delta, \sigma(\delta)). \tag{16}$$

Consequently from (14) we have a formula for the sound velocity, which generalizes the one in [10], and can be written as:

$$c = \frac{a}{\sqrt{M}} \left[\varepsilon_{\delta\delta} + 2\varepsilon_{\sigma\delta} \frac{d\sigma}{d\delta} + \varepsilon_{\sigma\sigma} \left(\frac{d\sigma}{d\delta} \right)^2 + \varepsilon_{\sigma} \frac{d^2\sigma}{d\delta^2} \right]^{1/2} \tag{17}$$

where we used the notation

$$\varepsilon_{xy} = \frac{\partial^2 \varepsilon}{\partial x \partial y}$$

with x, y equal to δ and/or σ .

A rather elegant form for the sound velocity can be found as follows. From the self-consistency equation (13) one computes $\frac{d\sigma}{d\delta}$ in terms of the derivatives of the function \mathcal{G} :

$$\mathcal{G}_\delta + \mathcal{G}_\sigma \frac{d\sigma}{d\delta} = 0.$$

One more derivative yields $\frac{d^2\sigma}{d\delta^2}$:

$$\mathcal{G}_{\delta\delta} + 2\mathcal{G}_{\sigma\delta} \frac{d\sigma}{d\delta} + \mathcal{G}_{\sigma\sigma} \left(\frac{d\sigma}{d\delta}\right)^2 + \mathcal{G}_\delta \frac{d^2\sigma}{d\delta^2} = 0$$

and the sound velocity (17) can be written in the following compact form

$$c = c_0 \left(\frac{\theta_{\delta\delta} + 2\theta_{\sigma\delta} \frac{d\sigma}{d\delta} + \theta_{\sigma\sigma} \left(\frac{d\sigma}{d\delta}\right)^2}{K \mathcal{G}_\sigma} \right)^{1/2} \quad (18)$$

where $c_0 = a\sqrt{\frac{K}{M}}$ is the bare sound velocity and

$$\theta_{xy} = \varepsilon_{xy} \mathcal{G}_\sigma - \mathcal{G}_{xy} \varepsilon_\sigma.$$

Expression (18) is somewhat complicated because of the presence of the integrals, which should be approached numerically.

An interesting aspect of (18) is that the formula is valid for all temperatures, in particular it allows the possibility of studying the sound velocity in the neighbourhood of the critical temperature. However, as the formula is rather complicated, for the moment we leave this analysis for another occasion at which we also intend to study the quantum fluctuations in the critical region. Instead we limit ourselves here to looking at the ground-state limit ($T \rightarrow 0$) of (18) and its comparison with the ground-state result of [10, 11].

Taking the ground-state limit $\beta \rightarrow \infty$, it is, first of all, interesting to remark that

$$\varepsilon_\sigma = 0 \quad \text{and} \quad \varepsilon_{\sigma\sigma} > 0$$

in full correspondence with the variational principle. One also checks that

$$\frac{d\sigma}{d\delta} = -\frac{\varepsilon_{\sigma\delta}}{2\varepsilon_{\sigma\sigma}} \quad (19)$$

yielding for (17) in the ground state, the following formula

$$c = c_0 \left(\frac{\varepsilon_{\delta\delta}}{K} - \frac{3}{4K} \frac{\varepsilon_{\sigma\delta}^2}{\varepsilon_{\sigma\sigma}} \right)^{1/2} \quad (20)$$

which, up to a factor of $\frac{3}{4}$, does coincide with the expression for the sound velocity in [10, 11] for the SSH model. The origin of the discrepancy lies in the fact that we have taken into account the σ -dependence of the counterterm factor γ , based on formula (11). Indeed if one omits this dependence, then one obtains:

$$\frac{d\sigma}{d\delta} = -\frac{\varepsilon_{\sigma\delta}}{\varepsilon_{\sigma\sigma}} \quad (21)$$

instead of relation (20). If one uses (21) one obtains straightforwardly the formula

$$c = c_0 \left(\frac{\varepsilon_{\delta\delta}}{K} - \frac{\varepsilon_{\sigma\delta}^2}{K \varepsilon_{\sigma\sigma}} \right)^{1/2}$$

which is the result of [10, 11]. This remark stresses another aspect of the content of our formula (18), compared with what is known in the literature.

As a conclusion of the computation of the sound velocity in the one-mode quantum SSH model, one should make it clear that we started from formula (14), which is based on classical hydrodynamics. A genuine quantum base for it is lacking. Quantum hydrodynamics is inexistent in the sense that very little has been done at *ab initio* derivations of the hydrodynamical equations for quantum systems. The situation is not clear as to what extent quantum effects are relevant and on which hydrodynamic level they are important.

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