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Local electron distributions and diffusion in anharmonic lattices mediated by thermally excited solitons

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Abstract. We study the excitation of solitons in lattices with Morse interactions in a wide temperature range and their influence on (free) electrons moving in the lattice. The lattice units (considered as "atoms" or "screened ion cores") are treated by classical Langevin equations. For visualizations the densities of the core (valence) electrons are in a first estimate represented by Gaussian densities, thus permitting to visualize lattice compressions. The evolution of the (free) electrons is modelled in the tight binding approximation first using Schrödinger equation and, subsequently, a stochastic description of the evolution as a Markov process. We investigate electron transfer assisted by solitons and solitonic influences on macroscopic transport in particular on diffusion. Then we consider the electron-lattice interaction and obtain numerical solutions of the simultaneously evolving Langevin and Pauli master equations. We show that the proposed mechanism of riding on thermal solitons is relatively fast (of the order of the sound velocity).

PACS. 63.20.Ry Anharmonic lattice modes – 05.60.-k Transport processes – 05.45.Yv Solitons – 71.38.-k Polarons and electron-phonon interactions

1 Introduction

Davydov and collaborators [1–3] investigated the interaction of electrons with the dynamical excitations in lattices. It was shown that due to the nonlinearity induced by the electron-(acoustic) phonon interaction (polaron or electron self-trapping effect) soliton-like excitations which he called "electro-solitons" may travel along dynamically *harmonic* lattices. Davydov predicted that these excitations could be stable at finite temperatures and could persist even at physiological temperatures. Several authors have checked this conjecture and have found on the basis of simulations that Davydov's electro-solitons are destroyed already around 10 K lasting at most 2 ps [4–6]. However – as far as we know – the controversy about the thermal stability of Davydov's solitons is not closed. For example, it is not excluded, that the deficiencies of mixed quantum-classical representations are responsable for some of the instabilities seen in simulations of the Davydov electro-solitons (for a thorough discussion of the problem see [7]).

Heeger, Schrieffer and collaborators have used (topological) solitons to explain the electric conductivity of polymers like in trans-polyacetilene the case most studied by those authors [8]. In this case solitons come from the degeneracy of the ground state and not from an originally underlying dynamic anharmonicity.

It is now well established that if the underlying lattice dynamics involves *anharmonic* interaction, this results in the appearance of very stable *supersonic* acoustic solitons like in a Toda and other nonlinear lattices [9–17,19,20]. We follow here this idea and make use of the Morse potential (akin to the Lennard-Jones potential and to the Toda repulsive interaction) together with the electron-lattice interaction. As shown in Figure 1, these potentials can be scaled around the minimum in such a way, that the first three derivatives are identical, what guarantees a close relationship of their nonlinear (supersonic) excitations. These excitations bring a new form of dressed electrons or compound (electro-soliton)-lattice soliton dynamic bound states. They have been called "solectrons" to mark the difference with Davydov's original electro-solitons. Then we show that due to the added lattice *anharmonicity* and the excitation of lattice solitons the thermal stability of solectrons is ensured well above 10 K.

After introducing the model lattice problem in Section 2, we develop a method of visualization of the nonuniformities, which allows us to estimate the region of solitonic excitations as well as their life times. Section 3 deals with the electron-lattice interaction thus describing how lattice deformations (or relative displacements between

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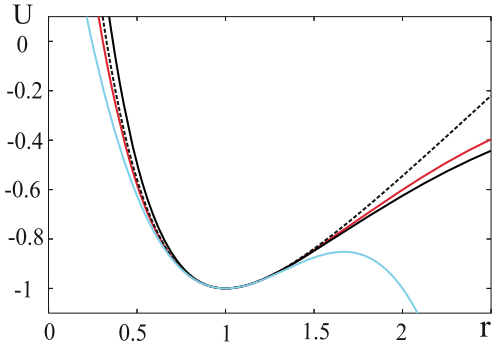

Fig. 1. (Color online) Interaction along lattice (top-down display): Toda (upper dashed curve), Morse (2nd from above), Lennard-Jones (3rd from above), and Fermi-Pasta-Ulam (FPU-3, lowest full line) potentials suitably scaled around a common minimum to have identical second and third derivatives.

lattice units) affect (free) electron motions and vice versa. In Section 4, we introduce a (Pauli) master equation approach to follow the coupled electron-lattice evolution, a subject which is further explored in depth by considering various temperatures in Section 5. We then discuss the evolution of solectrons. This is done with no adiabatic approximation to the electron evolution hence considering simultaneously the time evolution of both electrons and lattice units. Then we obtain a clear picture of the classical and the quantum-mechanical approaches to the electron-lattice coupled evolution. Section 6 deals with features of soliton-mediated diffusion. There we also comment on soliton-assisted electron transfer (ET) along the lattice. We compare the main results obtained in this work with earlier findings [21–26]. Finally we discuss possible applications of the mechanism of riding on thermal solitons to problems of long-range electron transfer through bonds in donor-bridge-acceptor complexes [27]. This is a problem of high interest for many biological processes and possibly also for molecular-scale electronic devices [27–32]. We will show that the mechanism of riding on thermal solitons might be relatively fast in comparison to other ET mechanisms. The existence of thermal solitons in nonlinear lattices is well studied in many independent investigations [9,10,33].

2 Thermal solitons in nonlinear lattices

We shall consider 1D anharmonic lattices with embedded electrons eventually leading to donor-acceptor ET or electric current in the presence of an external field (a wealth of information about both items in biomolecules and the diversity of approaches taken can be found in the references [27–32,34–36]). The system consists of N classical particles (atoms or screened ion cores) and N non-interacting free electrons with periodic boundary conditions on a lattice of length L. The electrons occupy some 3D volume surrounding the 1D lattice. For the *heavy* lattice particles we assume that they obey classical Langevin dynamics, with a phenomenological damping γ_0 and some external source of (Gaussian white) noise thus introducing temperature. In the numerical simulations we shall consider the lattice units all with equal mass m, described by coordinates $x_n(t)$ and velocities $v_n(t)$, $j = 1, \ldots, N$. The Hamiltonian consists of the classical lattice component H_a, and the contribution of the electrons H_e, which includes the interactions with the lattice deformations. Focusing on the lattice part we set

$$H_a = \frac{m}{2}\sum_n v_n^2 + \frac{1}{2}\sum_{n,j} U(x_n,\, x_j). \tag{1}$$

The subscripts locate lattice sites and the corresponding summations run from 1 to N. Let us assume that the mean equilibrium distance (lattice constant) between the particles in the lattice is σ ($\sigma = L/N$). We shall assume that the lattice particles repel each other by exponential repulsive forces and attract each other by weak dispersion forces with a potential which depends on the relative distance $r = x_{n+1} - x_n$ between nearest-neighbors only. We will approximate the potential by the earlier mentioned Morse function (Fig. 1)

$$U(r) = D\left\{\exp[2B(r-\sigma)] - 2\exp[-B(r-\sigma)]\right\}. \tag{2}$$

For illustration in our computer simulations we shall use $N = 200$ and $B = 1/\sigma$. Then in the presence of random forces (hence non zero temperature) and also external forces, H, the evolution of lattice particles is described by Langevin equations ($n = 1, 2, ..., N$)

$$\frac{d}{dt}v_n + \frac{1}{m}\frac{\partial H}{\partial x_n} = -\gamma_0 v_n + \sqrt{2D_v}\,\xi_n(t). \tag{3}$$

As earlier announced, the stochastic forces $\sqrt{2D_v}\,\xi_n(t)$ model a surrounding heat bath (Gaussian white noise). The parameter γ_0 describes the common standard friction frequency acting on the lattice units or atoms from the surrounding heat bath. The validity of an Einstein relation is assumed $D_v = k_B T\gamma_0/m$, where T denotes temperature. We shall use $1/B$ as the length unit which is most appropriate for Toda and Morse potentials with respect to the scaling properties [22,23,33], the alternative choice of σ as the length unit is less useful. Further we use the frequency of oscillations around the potential minimum ω_0^{-1} as the time unit. Typical parameter values for biomolecules are $\sigma \simeq 1{-}5$ Å; $B \simeq 1{-}5$ Å^{-1}; $D \simeq 0.05{-}0.5$ eV [27–32,34–36]. This means that $B\sigma \simeq 1{-}25$ and $1/\omega_0 \simeq 0.1{-}0.5$ ps. As the energy unit we shall use $2D = m\omega_0^2\sigma^2/(B\sigma)^2$, that with $B\sigma = 1$ reduces to $m\omega_0^2\sigma^2$, traditionally used by most authors. This energy will be used also as the unit to scale the temperature T ($k_B = 8.6 \times 10^{-5}$ eV/K).

The specific heat (at constant volume/length) of system (1) and (3) is known (Fig. 2). In first, linear approximation the specific heat of a Morse lattice is given by

$$\frac{c_v}{k_B T} = 1 - \frac{3}{8D}k_B T + O(T^2). \tag{4}$$

According to our estimates the region where nonlinearity plays significant role in our lattice is $0.75 < C_v/k_B < 0.95$.

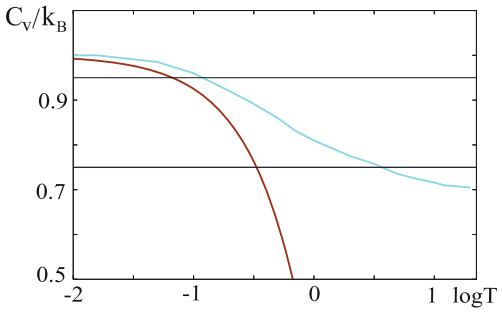

Fig. 2. (Color online) Morse lattice. Specific heat at constant volume/length (upper curve according to computer simulations) and first-order approximation of the anharmonic lattice as a function of the temperature (lower curve – linear in T approximation). The two horizontal lines $C_v/k_B = 0.95$ and 0.75 define the interval where nonlinear effects begin and where our model breaks down, respectively.

This is the multiphonon range (past the Dulong-Petit plateau) on the way to melting in the system. The corresponding temperatures in our energy units are in the range $T \simeq 0.1{-}0.5$ (and even up to 1–2). Introducing the binding strength of the Morse lattice, we foresee that solitonic effects are to be expected in the range $T_{sol}^{M} \simeq 0.2{-}1.0D$. In electron-volts this would be the range $T_{sol}^{M} \simeq 0.01{-}0.1$ eV. For biological macromolecules this estimated range of temperatures includes the range of physiological temperatures (about 300 K).

The time evolution of the lattice units is represented by the density of the (*valence*) electrons which are moving tight to the ion cores by a Gaussian distribution (atomic electronic density) of width $s = 0.35\sigma$. Our method shows in fact the overlap of the wave functions of the core electrons of the atoms. Thus each lattice atom is represented like a soft (Gaussian) sphere with continuous density concentrated around its center. In regions where the atoms overlap, the density is enhanced. This permits identifying solitonic excitations based on the colors in a density plot. An example is shown in Figure 3 for the temperature $T = 0.5$ ($\sim 10^3$ K).

The diagonal stripes correspond to regions of enhanced density which are running along the lattice which is the sign of solitonic excitations. Checking the slope we see that the excitations which survive more than 10 time units move with *supersonic* velocity. The pictures shown are quite similar to what has been described by Lomdahl and Kerr [5,6] with a life time of at most 2 ps which are stable only up to 10 K. Ours, however, live about 10–50 time units that more than several picoseconds. Besides they survive even at $T > 0.5$ which is well above physiological temperature. This confirms an earlier finding were at $T \simeq$ 300 K stable solectrons could be identified [21,22].

3 Electron-lattice dynamics and soliton-mediated effects

Assuming that there is only one atomic state per ion we get for the electrons the following simplified form of the

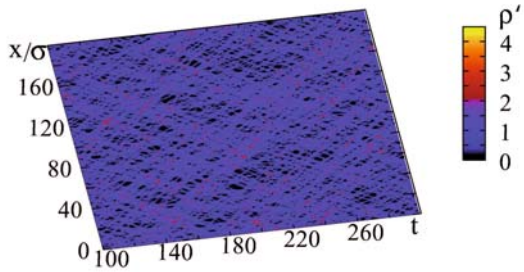

Fig. 3. (Color online) Morse lattice. Visualization of a running solitonic excitation for the temperature $T = 0.5$ ($\simeq 10^2$ K) due to the overlap of the atomic cores. They appear as diagonal stripes, which move with velocity about $1.3v_{sound}$. Parameter values: $N = 200$ and $B\sigma = 1$.

Hamiltonian within the tight-binding approximation

$$H_e = \sum_n \left[E_n(..., x_{n-1}, x_n, x_{n+1}, ...)c_n^+ c_n - V_{n,n-1}(x_n, x_{n-1})(c_n^+ c_{n-1} + c_{n-1}^+ c_n)\right]. \quad (5)$$

Recall that (5) refers to initially *free* electrons added to the lattice atoms (or screened ion cores) assumed to be located at sites "n". We take into account non-uniformity of the on-site energy levels E_n. Further assuming that the interactions depend exponentially on the distance between the ions (5) can be written as

$$H_e = \sum_n \left[(E_n^0 + \delta E_n)c_n^+ c_n - V_{n,n-1}(c_n^+ c_{n-1} + c_n c_{n-1}^+)\right], \quad (6)$$

with

$$V_{n,n-1} = V_0 \exp[-\alpha(q_n - q_{n-1})]. \quad (7)$$

Here, for convenience in notation, q_n denotes a lattice site spatial vibration (relative displacement) coordinate defined by $x_n = n\sigma + q_n/B$. There is the problem that for some values of the deviations (and typical parameter values, $\alpha = 1{-}1.75$) the exponents may take on very large values. To cope with this difficulty for large deviations we may alternatively use exponential functions with saturation. Two important parameters are related to the classical oscillation frequency ω_0 and the frequency of quantum hopping processes of the electron $\omega_{el} \sim V_0/\hbar$. We define

$$\tau = \frac{V_0}{\hbar\omega_0} = \frac{\omega_{el}}{\omega_0}, \qquad \tau_0 = \frac{2D}{\hbar\omega_0}. \quad (8)$$

In the following we assume that the relation between the quantum frequency and the frequency of the classical oscillations (adiabaticity parameter) is at least of the order of ten. The term E_n^0 denotes on-site energy levels of the unperturbed lattice and δE_n is the perturbation due to the lattice vibrations (harmonic as well as anharmonic modes may contribute). The simplest assumption is a linear dependence on the deviations

$$\delta E_n = \chi(q_n/B), \quad (9)$$

where the "electron-phonon coupling constant", χ, indicates that the on-site energy level E_n, i.e. the local site energy, depends on the displacement of the oscillator site; q_n is dimensionless (unit: $1/B$). As shown e.g. in [34–36], this coupling between lattice deformations and electronic states, leads for large enough values of the parameter χ to the formation of *polarons*. In view of the above given parameter values, the value of the coupling constant is in the range $\chi \simeq 0.1{-}2$ eV/Å. We have to take into account that our model is translationally invariant and we are considering relative lattice displacements. Accordingly, we set

$$\delta E_n \simeq \frac{\chi_1}{2}\left[(q_{n+1}-q_n)+(q_n-q_{n-1})\right], \tag{10}$$

with $\chi_1 = \chi/B$ as a new constant. This model may be used to consider small polarons [7,34–36].

Using a pseudopotential which accounts for all electric effects of larger range including polarization we can write [17,18]

$$V(x_n) = V_0 - V_e \sum_{j\neq n}{}' \frac{h}{\sqrt{(x_n-x_j)^2+h^2}}, \tag{11}$$

where the over-dash in the sum indicates that it is to be restricted in an appropriate way introducing screening effects. In our calculations we cutted the sum at a distance 1.5σ from the center of the ion core (screening distance). In other words we include all terms corresponding to lattice units which are nearer than $3\sigma/2$. This potential (11) comes from plasma theory (electrons interacting with ion cores) [18]. Here our physical picture is based on electrons embedded into a lattice of *neutral* atoms. Let us assume that the electron is located at the site "n" where it is in a bound state E_n^0. This energy is in part due to the polarization of the atoms at the other sites j located at x_j. For the polarization energy we use the standard "ansatz"

$$V(x_n) = V_0 - V_e \sum_{j\neq n}{}' \frac{r_0^4}{[(x_n-x_j)^2+r_0^2]^2}. \tag{12}$$

Here r_0 is a characteristic distance and U_e the polarization energy. In order to be in quadratic order consistent with (11) we make the choice $r_0 = 2h$. Any displacement of the other atoms changes the polarization energy. For example the displacement of the right neighbor to $x_{n+1} = (n+1)\sigma + q_{n+1}/B$ changes the polarization energy electron-atom by the amount

$$\delta V(x_n) = -V_e \frac{16h^4}{[4h^2+(\sigma+q_{n+1}/B)^2]^2}. \tag{13}$$

We assume in this approach that the energy levels are shifted like the energies created by the pseudopotentials acting on the nth electron from the side of the neighboring atoms. In order to compare this approach with the linear shifts used in the literature, we consider also the linear (small polaron) approximations to equations (11) and (12). The pseudopotential approach gives in linear approximation

$$\delta E_n \simeq V_e \frac{h\sigma}{B(\sigma^2+h^2)^{3/2}}\left[(q_{n+1}-q_n)+(q_n-q_{n-1})\right], \tag{14}$$

and in the polarization approach gives in linear form

$$\delta E_n \simeq V_e \frac{64h^4\sigma}{B(\sigma^2+4h^2)^3}\left[(q_{n+1}-q_n)+(q_n-q_{n-1})\right]. \tag{15}$$

Comparing (10) and (14) we find in the pseudopotential approach

$$\chi_1 = V_e \frac{2\sigma h}{B(\sigma^2+h^2)^{3/2}}, \tag{16}$$

and comparing (10) and (15) we find in the polarization approach

$$\chi_1 = V_e \frac{128\sigma h^4}{B(\sigma^2+4h^2)^3}. \tag{17}$$

Recall that $\chi = B\chi_1$. Then for $V_e = 0.01D$, $h = 0.3\sigma$, in the framework of the pseudopotential model the shift constant $\chi = 0.004D$ and for the polarization model $\chi \simeq 0.003D$. Assuming $D = 1$ eV, and $\sigma = 2$ Å we obtain $\chi = 0.002{-}0.003$ eV/Å. These calculations correspond to the parameter values: $\chi = 0.005D$, $h = 0.3$, $U_e = 0.01$. In some calculations (Sect. 4) to illustrate of the effects we use a shift factor which is ten times higher, namely $\chi = 0.05D$. Since the parameter value for χ_1 used in this work is about one or two orders of magnitude below the values used in [34–36] we expect that here polaron effects (self-trapping as a consequence of electron-lattice coupling) are rather weak and hence the system dynamics is dominated by solitons.

The probability to find an electron at the lattice site or atom located at x_n, i.e. the occupation number p_n, is $p_n = c_n c_n^*$. Solving the Schrödinger equation for the components of the wave function c_n we get

$$\begin{aligned} i\dot{c}_n &= \tau \sum_m E_{n,m}c_m = \tau_0[E_n^0 + \delta E_n(q_k)]c_n \\ &-\tau\left\{\exp[-\alpha(q_{n+1}-q_n)]c_{n+1} + \exp[-\alpha(q_n-q_{n-1})]c_{n-1}\right\}, \end{aligned} \tag{18}$$

where an over-dot denotes time derivative; $q_k = (q_1,...,q_n,...)$ E_n^0 and δE_n are dimensionless (unit: 2D). The corresponding equations for the lattice displacements reads in this approximation

$$\begin{aligned} \ddot{q}_n = &-p_n \frac{\partial \delta E_n(q_k)}{\partial q_n} \\ &+\{1-\exp[-(q_{n+1}-q_n)]\}\exp[-(q_{n+1}-q_n)] \\ &-\{1-\exp[-(q_n-q_{n-1})]\}\exp[-(q_n-q_{n-1})] \\ &-\alpha V_0\left\{\exp[-\alpha(q_{n+1}-q_n)](c_{n+1}^+c_n + c_{n+1}c_n^+)\right. \\ &\left.+\exp[-\alpha(q_n-q_{n-1})](c_n^+c_{n-1}+c_{n-1}^+c_n)\right\}. \end{aligned} \tag{19}$$

The problem reduces, in principle, to solving coupled together both equations (18) and (19). First we heat the system to a given temperature ($T = 0.1$, 0.5 in the example shown in Fig. 4). Then we switch-off the heat bath and

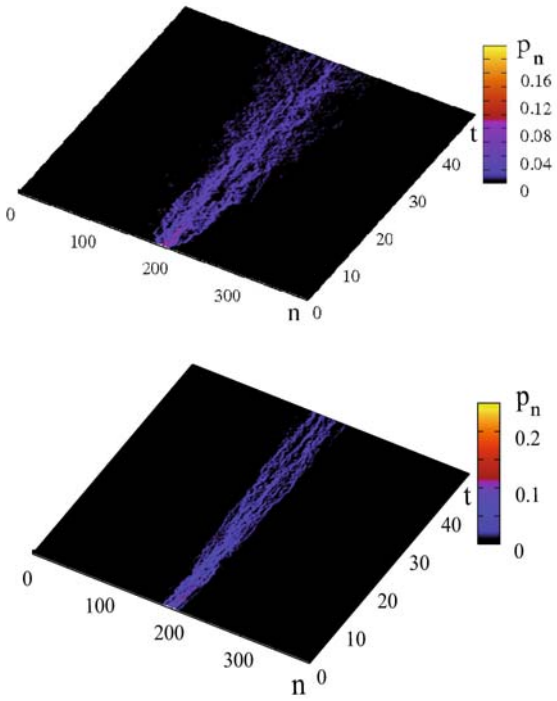

Fig. 4. (Color online) Morse lattice. Example of the spreading of the electron density and the mean square displacement for the temperatures $T = 0.1$ (above), and $T = 0.5$ (below) from simulations with the TBA-Schrödinger equation. The initial density condition is delta-like, concentrated around the center. Parameter values: $N = 400$, $B\sigma = 1$, $\alpha = 1.75$, $\chi_1/2D = 0.1$, and $\tau = 10$.

solve the coupled system of lattice and electron equations, in our example for delta-like initial electron densities.

The stochastic simulations show that the spreading of the electron density is a complex diffusion-like process. Evidently the thermal solitons create a kind of diffusive channel which stabilizes the electrons. We will study this in more details further below. However, before we will develop an alternative way of doing computer simulations.

4 Electron dynamics on thermal lattices based on master equations

So far our analysis has been based on the Schrödinger equation for the free electrons (in the tight binding approximation) coupled to the Langevin equation for the classical lattice particles. This tacitly assumes the existence of a heat bath in which the lattice particles are embedded. In principle this picture provides a complete description of the coupled lattice-electron dynamics. The irreversibility is guaranteed by the friction-noise terms in the Langevin-equations (3). We may describe this way also irreversible solitonic excitations at finite temperature. However, a serious problem connected with this approach is the very long relaxation times of the electrons due to the large separation between the time scales of the electrons and the lattice particles. A second serious problem is intrinsic to the mixed quantum-classical representations. Of course the Langevin-equations for the classical particles and the TBA-equations for the electrons are internally consistent, however the feedback between electrons and lattice particles may violate the rules of quantum mechanics [7,37]. This leads to some difficulties with respect to general principles and also with respect to computer simulations. In the standard theory of electronic transport this problem is solved by Boltzmann-type descriptions or by Fokker-Planck-type equations, which introduce an irreversible behavior in a consistent way [37,38]. The main problem is here to give a correct description of the coupling to the heat bath. In our case of the 1D-tight binding systems, the situation is somehow simpler due to the discrete character of the electronic states, which allows a description by discrete Markov chain equations [37,39–45]. The Markov approach to electron dynamics goes back to Pauli's (1928) seminal work [46]. Pauli started from the Schrödinger equation and derived by perturbation theory a Markov chain description and an expression for the transition probabilities. He introduced an irreversible master equation expressing the balance between the transitions in an ensemble. Pauli's equation is valid for a *microcanonical* ensemble and neglects symmetry effects. Further extensions took into account the symmetry of the wave functions and offered a description compatible with the statistics of Bose-Einstein or Fermi-Dirac [47]. Later generalizations were done by Van Hove and others [48] as well as with the development of Metropolis algorithms for *canonical* ensembles [49]. Applications to hopping conduction in solids were given by several authors [39–43]. The first applications of the master equation formalism to electron transfer in macromolecules seem due to Schlag and collaborators [44,45]. With respect to general aspects we mention also recent developments based on path-integral Monte-Carlo algorithms [50,51].

The ingredients of our model are:

(i) quantum electrons located in discrete states, which are coupled to a heat bath and to a classical lattice;
(ii) classical lattice units coupled to the heat bath and to the quantum electrons;
(iii) the heat bath.

Simplifying this situation we assume that the thermal electrons allow a Markov description. We support this conjecture by moving from the *reversible* Schrödinger equation for the tight-binding model to an *irreversible* Pauli master equation description. Following Pauli's method we introduce a master equation for the occupation probabilities of electrons p_n in a system with the energy levels E_n:

$$\frac{dp_n}{dt} = \sum \left[W_{nn'} p_{n'} - W_{n'n} p_n \right] . \tag{20}$$

The transition probabilities were derived by Pauli using perturbation theory for *microcanonical* ensembles (transitions in a narrow energy shell). Applications of this formalism to our Schrödinger equation (18) confronts us with the question of applicability of the perturbation approach to our basic TBA-equation. Note that the diagonal part

of equation (18) is – in dependence on the deformations – not always small relative to the off-diagonal elements. We disregard here this problem and assume that there exists an appropriate unitary transformation which makes the off-diagonal elements sufficiently small to satisfy the conditions of the perturbation approach. However at present we do not have a general solution to this problem. For example, evidently processes of tunnelling between wells cannot be modelled within a stochastic approach. Within Pauli's stochastic model the transition probabilities for the tight-binding model read

$$W_0(n,n') = \frac{V_0}{\hbar}\exp\left[-2\alpha|q_{n'}-q_n|\right]2\pi V_0\delta\left(E_n-E_{n'}\right), \tag{21}$$

where $n' = n\pm 1$ and $\delta(x)$ is Dirac's delta distribution. The transitions from state n to a state n' at one of the nearest-neighbor sites should correspond to the same energy level (or to a level within a narrow shell). In the case of a dissipative embedding, the situation is more complicated due to the interaction of the electrons with the dissipative heat bath. Schlag and collaborators [44,45] use a special dissipative mechanism with a damping constant γ which leads to the transition probabilities

$$W_1(n,n') = \frac{V_0^2}{\hbar^2}\exp\left[-2\alpha|q_n-q_{n'}|\right]\frac{\gamma}{\gamma^2+[(E_n-E_{n'})/\hbar]^2}. \tag{22}$$

Instead of a delta-like shell we have now a Lorentz profile around it. In the limit $\gamma\to 0$ these expressions tend to the Pauli formula with a delta-factor. Temperature effects are however not included. When the electrons are embedded into a heat bath together with the thermal lattice particles, we have to go to a generalization for thermal ensembles. In such cases the transition probabilities depend in a non-symmetric way on the energy levels $E_n, E_{n'}$ between which the transitions occur:

$$W(n,n') = \frac{V_0}{\hbar}\exp\left[-2\alpha|q_n-q_{n'})\right]E(n,n',\beta). \tag{23}$$

The temperature-dependent thermal factors $E(n,n',\beta)$ is not symmetric with respect to the arguments but they are subject to the condition of detailed balance

$$\frac{W(n',n)}{W(n,n')} = \exp\left[\beta(E_n-E_{n'})\right]. \tag{24}$$

In other words, the relation of the thermal factors should correspond to the relation of Boltzmann factors. The property (24) suggests the symmetry

$$E(n,n') = \exp\left[-\frac{\beta}{2}\left(E_n-E_{n'}\right)\right]F(n,n'), \tag{25}$$

$$F(n,n') = F(E_n-E_{n'}), \tag{26}$$

where $F(n,n')$ is an even function. There are several variants for this even function $F(x)$ given in the literature. Assuming that the heat bath is a carrier of phonons which drive transitions by a one-photon mechanism, Bonch-Bruevich and coworkers derived the following expression [39–41]

$$F(n,n') = \sinh^{-1}\left(\frac{\beta}{2}|E_n-E_{n'}|\right). \tag{27}$$

A different approach to hopping systems was obtained by starting from the von Neumann equation for the density matrix by Böttger and Bryksin [42,43].

We will use here a more simple phenomenological ansatz which is based on the well-known Monte-Carlo procedure. In this approach the downhill transitions are weighted with $E = 1$ and uphill transitions with a factor less than unity [51],

$$E(n,n') = 1 \quad \text{if} \quad E_n < E_{n'}, \tag{28}$$

$$E(n,n') = \exp\left[-\beta(E_n-E_{n'})\right] \quad \text{if} \quad E_n > E_{n'}. \tag{29}$$

This corresponds to the F-function.

$$F(n,n') = \exp\left[-\frac{\beta}{2}|E_n-E_n'|\right]. \tag{30}$$

The Monte Carlo procedure and the corresponding master equation is a useful tool for computer simulations of electron hopping processes. Since the detailed balance is obeyed, it is guaranteed that in thermal equilibrium the canonical distribution is solution of the master equation [52].

In order to simplify our computer simulations we used so far only the Monte Carlo procedure. More refined algorithms are left to future studies. Within the Monte Carlo algorithm the master equation for the occupation probabilities reads in dimensionless variables (20)

$$\begin{aligned}\frac{1}{\tau}\frac{dp_n}{dt} = {} & \exp\left[-2\alpha q_{n+1,n}-\frac{\beta}{2}E_{n,n+1}-\frac{\beta}{2}|E_{n,n+1}|\right]p_{n+1}\\ & +\exp\left[-2\alpha q_{n,n-1}-\frac{\beta}{2}E_{n,n-1}-\frac{\beta}{2}|E_{n,n-1}|\right]p_{n-1}\\ & -\exp\left[-2\alpha q_{n+1,n}-\frac{\beta}{2}E_{n+1,n}-\frac{\beta}{2}|E_{n+1,n}|\right]p_n\\ & -\exp\left[-2\alpha q_{n,n-1}-\frac{\beta}{2}E_{n-1,n}-\frac{\beta}{2}|E_{n-1,n}|\right]p_n,\end{aligned} \tag{31}$$

where $q_{n,n'} = q_n - q_{n'}$, $E_{n,n'} = E_n - E_{n'}$ and $\tau = (V_0/\hbar\omega_0)$ is the adiabaticity parameter or ratio between the two time scales of motions. Equations (31) are used for the description of the thermal motions of the electron system as an alternative to equations (18). The corresponding equations for the lattice particles which exclude the dependence on the phases of the wave function are now

$$\begin{aligned}\ddot{q}_n = {} & \{1-\exp[-q_{n+1,n}]\}\exp[-q_{n+1,n}]\\ & -\{1-\exp[-q_{n,n-1}]\}\exp[-q_{n,n-1}]\\ & -2\alpha V_0\left\{\exp[-\alpha q_{n,n-1}]\sqrt{p_{n-1}p_n}\right.\\ & \left.+\exp[-\alpha q_{n+1,n}]\sqrt{p_np_{n+1}}\right\}-p_n\frac{\partial\delta E_n}{\partial q_n},\end{aligned} \tag{32}$$

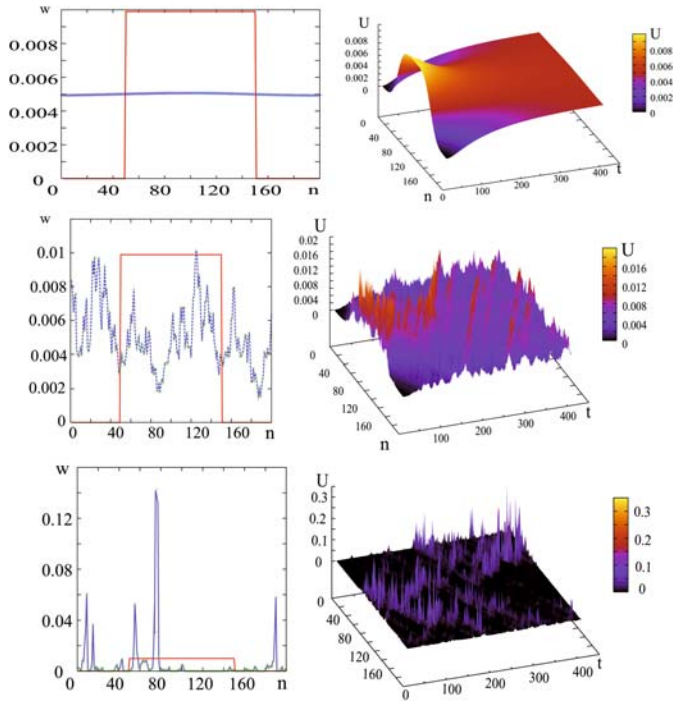

Fig. 5. (Color online) Morse lattice. Time evolution of the electron probability distribution according to Pauli's equation. Three temperatures are considered: upper set: $T = 0$: an initially rectangular distribution tends irreversibly towards homogeneous spreading along the lattice; center set: $T = 0.01$: again the initial distribution tends to be uniform along the lattice though there is electron-phonon interaction; and lower set: $T = 0.5$: the initial rectangular distribution becomes localized around a few peaks thus illustrating the corresponding local formation of solectrons. Parameter values $N = 200$, $\alpha = 0.5$ and $\tau = 10$.

which are alternative to equations (19). The system of equations (31)–(32) contains several approximations, in particular the perturbation approximation. However it provides a rather fast and therefore useful tool for the computer simulations of the electron-lattice dynamics in thermal systems. Figure 5 illustrates results based on this approach. Due to the way we treat the electron dynamics there are differences between the methodology using the coupled Schrödinger equation and Langevin equation system (18), (19) and that using Pauli's approach albeit they are minor differences. An advantage of the Pauli approach is, that it can be generalized to include the influence of spin and symmetry effects which were neglected so far in our theory and in the computer simulations.

5 Stochastic dynamics of the thermal electron-lattice excitations

The master equation (31) models the electron dynamics as a stochastic process. The electron is hopping from site to site and the function $p_n(t)$ gives the probability to find the electron at the time t at the location n. The coefficients of the master equation are time-dependent through the lattice deformations $q_k(t)$ thus leading to a mixed classical-stochastic description. The present description is closely related to the adiabatic approximation. This approach assumes in the case of low temperatures [23] that the electron system is at any time in the local ground state of the classical subsystem and assumes for the case of higher temperatures that a local canonical distribution around the ground state is realized [25,26]. The canonical distribution is here defined as

$$p_n(t) = Z^{-1} \exp\left[-\beta E_n(t)\right], \tag{33}$$

where the $E_n(t)$ are the eigenvalues of H_e, in other words the eigenvalues of the matrix E_{nm} for a given lattice configuration at time t. Since this is a very difficult task, approximations are required. As earlier noted, due to the way we treat the relaxation effects there are differences between the methodology using the adiabatic assumption and that using Pauli's approach albeit they are minor differences at least for small values of adiabaticity $\tau \sim 1$. For large τ, the electron relaxation in the heat bath is very fast and the distribution may be approximated by a local Boltzmann-Maxwell or Fermi-Dirac distribution. For values of the τ-parameter, say for $\tau \simeq 10{-}20$, the approach based on the Pauli equations (31, 32) is most useful, since it provides information on deviations from the adiabatic approximation. The Pauli method (31, 32) goes beyond the adiabatic approximation since both the lattice dynamics and the electron dynamics are treated including their coupling. Recall that in a strict adiabatic approximation one assumes that the electrons adapt "instantaneously" to any change in the lattice. In other words one assumes that the electrons follow in a very fast way to the new lattice configuration and may be described at any time by the canonical distribution [52]. In the new approach based on Pauli's method we take into account that the electrons need time to follow the lattice motions what leads to certain delay in their response and to some deviations from the stationary solution. Qualitatively however the picture remains similar to the results obtained in Section 4.

In Figures 5 and 6 the solution of equation (20) is obtained simultaneously with that of equation (32). In difference to some earlier work [25,26] we used here a moderate value of the relaxation parameter $\tau = 10$ which makes the relaxation much faster. According to the estimates given by Hennig et al. [22,23] this parameter is in the range $\tau = 10{-}30$. The other parameter values used in the simulations are: $N = 200$, $B\sigma = 1$, $\chi_1 = 0.005D$, $\alpha = 0$ for $T = 0$, and $\alpha = 1$ for $T > 0$. The solutions were found with two types of initial conditions for three temperatures in both cases. In the first case (Fig. 5) the initial state corresponds to an electron probability density spread over almost the entire lattice length (note the homogeneous, constant distribution between sites 50 and 150), for which the velocity is "localized" accordingly (Heisenberg rule). In the second case (Fig. 6) the opposite situation is considered. Here the electron probability density is localized in space and hence "delocalized" (spread) in the velocity

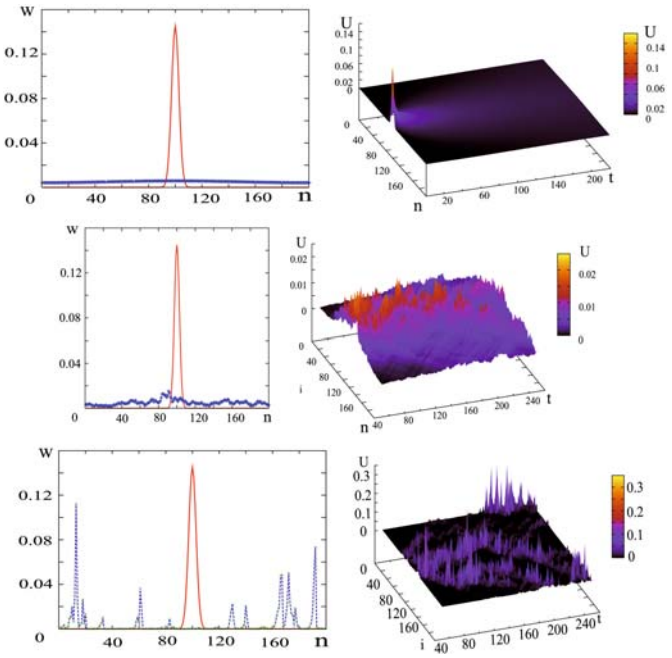

Fig. 6. (Color online) Morse lattice. Same as in Figure 5 (with the same parameter values) but using "localized" (delta-like) initial distributions. Note that here time intervals are 200 time units only.

space. In both cases we observe an irreversible spreading of the corresponding distribution as time proceeds for the "very cold" lattice ($T = 0$; Figs. 5 and 6). Both the initial and "final" distributions (after a time lapse of 400 or 200 units) are displayed (upper plots). Below we can see the time evolution of the distributions. If the lattice is heated to the temperature corresponding to the usual phonon range ($T = 0.01$) in both cases we continue observing a similar irreversible spreading of distributions along the lattice (Figs. 5 and 6). As the temperature is increased ($T = 0.5$) we start observing the role of anharmonicity: solitons become excited that "localize" the electron probability density, not forming a single peak but rather several relative maxima at each time instant (Fig. 5). The latter evolve in time with the soliton motion (the solectrons are formed: Figs. 5 and 6). It can be observed that a solectron trajectory is formed of a series of trajectory fragments moving along either to the right (positive velocity) or to the left (negative velocity). The slope of each trajectory defines the actual soliton (and solectron) velocity. This is to be expected as there is no external electric field. This apparent symmetry would be broken by such a field whatever the value of its strength could be.

Noteworthy is that several of the effects described above have been seen already using only classical theory [16,17,19,20] as well as in the quantum mechanical study using the tight-binding model [21–24] as e.g. splitting of the electron probability density into parts, merging of electron distributions, changing of host solitons, etc.

6 Soliton-mediated diffusion processes

Looking at Figures 5 and 6 we see a spreading of the electron density, which is diffusion-like in both of our simulation approaches (Schrödinger as well as stochastic approach). Of course on the basis of a few stochastic simulations we cannot make a final estimate of the temperature-dependence of the diffusion coefficient. However, it appears that the thermal solitons seem to create a diffusive channel which stabilize the electrons. The diffusive picture is obtained by coarse-graining of the stochastic picture. Instead of sites as the elements of the description we go to "soliton spots" spanning over about ten sites. The electron is now hopping between these "soliton spots", which are moving with supersonic velocity.

The question of whether the observed phenomena really belong to a proper diffusion process is not a trivial task. Let us first look at the case $T = 0$. Then the process is described at least in the continuous limit by a nonlinear Schrödinger equation. For a linear lattice this equation was investigated long ago by Brizhik and Davydov [2]. They could prove that this nonlinear Schrödinger equation describes an evolution of the electron density which is quite complex. There is a strong dependence on the initial density distribution and in some cases a fractal-like splitting of the density is observed. Similar investigations for a class of nonlinear lattices were carried out by Zolotaryuk, Spatschek and Savin [15]. For this reason we cannot expect that our processes are diffusion-like at all temperatures. At least in the low-temperature range there should be effects of the type described by the above mentioned authors. However, with increasing temperature, the thermal effects would tend to smooth more and more any fractal-like effects and the electron density should evolve diffusion-like with hopping between the soliton spots which move supersonically.

The diffusion coefficient may be estimated on the basis of the Einstein relation for the mean square displacement. For the one-dimensional case the mean square displacement is connected with time and effective diffusion constant by the relation

$$\langle(\delta n)^2\rangle_t = 2D_{\mathit{eff}}t. \tag{34}$$

Here $n(t)$ is the position (the site) for an electron which starts at n_0 at $t = 0$. The average is to be done as follows. First, the quantum-mechanical average is to be taken

$$\langle(\delta n)^2\rangle_t = \sum_n (n - n_0)^2 c_n(t)c_n^*(t). \tag{35}$$

However this is not enough as we still have to average over many realizations of the classical lattice dynamics. Accordingly, we define a function of time

$$d(t) = \langle(\delta n)^2\rangle_t = \frac{1}{K}\sum_{i=1}^{K}\sum_n (n - n_0)^2 c_n^i(t)c_n^{i*}(t). \tag{36}$$

This corresponds to the average over a large number K of realizations i. As we see from the examples, the individual trajectories of the electrons remain in certain conical

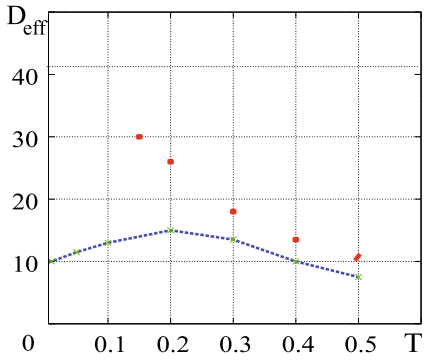

Fig. 7. (Color online) Estimate of the diffusion constant as a function of temperature. The curve was obtained by simulations with the Master equation in combination with the Langevin equation ($\alpha = 1, \chi_1 = 0.1$). The points outside the main curve were obtained with the Langevin-Schrödinger-TBA-model ($\alpha = 1.75$, $\chi_1 = 0$). Other parameter values: $N = 200$, $B\sigma = 1$.

region. In other words the electron density remains rather concentrated in certain angle, which is described roughly by a Gaussian distribution of diffusion type

$$P(n,t) = \text{const.}\frac{1}{\sqrt{4\pi D_{\mathit{eff}} t}} \exp\left[-\frac{-(n-n_0)^2}{4D_{\mathit{eff}} t}\right]. \quad (37)$$

We calculated the mean square displacement for several temperatures and represented the diffusion function $d(t)$ from simulations as shown in Figure 6 by a linear fit. For $T < 0.1$ not good approximation by a straight line can be achieved. The shape of the curves $d(t)$ for $T < 0.1$ does not correspond to a linear behavior, this is just what we expect. For $0.1 < T < 0.5$ we see however a nice quasi-linear shape for all t. On the basis of several sets of computer simulations with the master equation we obtain the curve shown in Figure 7. The values of D_{eff} below $T \simeq 0.1$ have to be considered as extrapolations based on a fit to the piecewise linear region. The curve in Figure 7 corresponds to extensive simulations with the master equation model. The effective diffusion shows a maximum around $T \simeq 0.4$. This observed maximum is compatible with some predictions given in earlier work based on a different semiclassical model [17,18]. The prediction based on the semiclassical model was that solitonic excitations are expected to significantly enhance diffusivity first, then reaching a maximum and then going to a decrease [16–18]. The maximum was expected at temperatures where the specific heat has a turning point that means at around $T \simeq 0.1{-}0.5$.

For comparison we did also some simulations on the basis of the Langevin-equation coupled to the TBA-Schrödinger equation. The results for several temperatures are demonstrated in Figure 4 by points. Here we observe a continuous decrease of $D_{\mathit{eff}}(T)$ with T which is similar to a hyperbola. The diffusion constant as a function of temperature was estimated for the Schrödinger-TBA-model with the parameters ($\alpha = 1.75, \chi_1 = 0$, $N = 200$, $B\sigma = 1$).

From the physical point of view the most interesting result is the decrease of the effective diffusivity with the temperature. We believe that the pole near $T = 0$ may be an artefact due to the problems of consistency between the TBA-Schrödinger equation and the classical Langevin equation. Beyond the maximum the two descriptions are more or less compatible, taking into account the different value of the α-parameter.

The problems we are discussing here may be of interest for investigations of single electron transfer (ET) along the lattice from a *donor* to an *acceptor*. As we have seen, the path of an electron may be influenced by a soliton. When an added, excess electron is placed in the lattice together with a soliton emitted at same time in same place, the electron may be dynamically bound to the soliton thus creating the solectron excitation [22,23,25]. As we have shown in such a case the electron may move with the soliton with a slightly supersonic velocity $v_{el} > v_{sound}$. In certain cases the electron may even be guided by the soliton from *donor* to *acceptor*. In reality the electron cannot ride on just a single soliton from donor to acceptor. Several solitons should be involved in transport. Therefore the above given soliton velocity is an upper bound for the transfer. As we have shown here, thermal solitons, which have random motion directions and path lengths originate quite different effect and may even slow down the speed of electrons. In principle these effects may be used as a way to manipulate the transport of electrons between donor and acceptor [27]. Although aiming at a different model approach ours here is a generalization of the phonon-assisted hopping process earlier studied by several authors [28–32,34–36]. Clearly in our case we may have a polaronic (self-trapping) effect due to the electron-phonon (or soliton) interaction. However due to our choice of parameter values for the electron-lattice coupling which is in the weak coupling range, a different effect due to genuine lattice solitons plays the major role. The electrons are coupled to a genuinely added lattice solitons due to the anharmonicity of the lattice vibrations. Hence we have not just phonon-assisted hopping but rather soliton-assisted hopping. One may describe this mechanism also as "riding" on thermal solitons. By returning from equation (34) to dimensionsional units as Angström and seconds we find with $D_{\mathit{eff}} \simeq 15$ for the squared length crossed by riding on thermal solitons in time t the estimate

$$l^2(t)[\text{Å}] \simeq 160 \times 10^{12} t[\text{s}]. \quad (38)$$

Correspondingly we find for the log of the reciprocal time often used in experimental work on the ET donor-acceptor [27] the relation

$$\lg \frac{1}{t[\text{s}]} \simeq 14.2 - 2\lg(l(t)[\text{Å}]). \quad (39)$$

Except for small distances our estimated reciprocal time is clearly above the estimate for the data [27] which we fitted by

$$\lg \frac{1}{t[\text{s}]} \simeq 12 - 0.4 l(t)[\text{Å}]. \quad (40)$$

This way we may conclude that our ET mechanism is rather fast and evidently is not identical with the actual

mechanism of ET on a bridge between donor and acceptor. The reason is that the actual mechanism is controlled by relatively slow tunneling processes which are not included so far in our simulations. The question about the interference of the slow tunneling processes with the fast soliton-riding processes remains open so far. May be the study of this problem could be of interest for further applications to ET problems.

7 Concluding remarks

In nonlinear conducting lattices at temperatures high enough (including the physiological range), thermal solitons can be excited which lead to transient strong local lattice compressions. This deforms the potential landscape in which the electrons are moving. The electrons tend to be trapped in the regions of maximal density of lattice points created by the local compressions and then forced to move dynamically bound to the solitons. These excitations have been called solectrons to mark the difference with Davydov's electro-solitons.

We have shown that under appropriate conditions the electrons are rather concentrated in clusters (traps) near to solitonic compressions. The electrons are attracted to the local compressions what justifies the concept of solectrons. In 1D-systems the clusters are always disconnected. Electricity may be carried only by moving clusters. Therefore we cannot expect that a 1D-system goes under the influence of solitonic compressions to highly conducting states. However we may expect that this situation changes drastically in 2D- or quasi-2D systems. In 1D the local compressions are soliton-like. In 2D-systems the excitations are similar with respect to the local density and local energy, however they are different with respect to the mathematical representations, they are no more cnoidal waves. As shown by Astakhova and Vinogradov, a continuous description of these excitations is possible by some generalization of the Kadomtsev-Petviashvili equation [53]. What is only relevant in our context is the local density enhancement and the corresponding local potential wells. Then with increasing density of the solitonic droplets, percolation becomes possible, a question to be discussed elsewhere. We have shown that indeed both solitons and solectrons are stable to rather high temperatures lasting for several picoseconds. This result extends earlier results obtained for Davydov electro-solitons that were shown to be stable only up to at most 10 K. Indeed the anharmonicity stabilizes the electron-soliton bound states. We have shown that the electron is basically hopping from solectronic trap to solectronic trap, in a coarse-grained description this evolution is at higher temperatures diffusion-like.

Our study has been based upon consideration of an anharmonic lattice (with Morse interactions) to which free electrons are added. The dynamics of the lattice is classical and depending on temperature. Thermal heating excites phonons and solitons. For the conduction electrons we have taken two approaches: first the electrons are treated in the tight binding approximation with evolution dictated by a Schrödinger equation. Alternatively for thermal systems, the time evolution has been described first by coarse-graining in a stochastic picture using a master equation approach following a seminal work by Pauli [46,47]. Our theory generalizes a master equation approach developed by Schlag et al. [44,45] as we have considered the influence of a heat bath surrounding the electrons. In an intermediate range of temperature these thermal systems may be described also after a second coarse-graining by diffusion equations. Since practically all proteins and biomolecules are embedded in a thermal medium we wonder up to what extent our approach may be appropriate to describe special electron transfer processes (ET) in such "molecular wires".

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