Thermal Solitons and Solectrons in Nonlinear Conducting Chains

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ABSTRACT: We present a model for nonlinear excitations in bio(macro)-molecules stable at room temperature and offering a possible mechanism for electron transfer over long distances (e.g., 100 Å and beyond). It is based on the excitation of generally supersonic solitons in a heated one-dimensional lattice with Morse interactions in a temperature range from low to physiological level. We study the influence of these supersonic excitations on electrons moving in the lattice. The lattice units (considered as "atoms") are treated by classical Langevin equations. The densities of the core electrons are in a first estimate represented by Gaussian densities, thus permitting to visualize lattice compressions as enhanced density regions. The evolution of excess, added free electrons is modeled in the tight-binding approximation using first Schrödinger equation and, subsequently, the assumption of local canonical equilibrium corresponding to an adiabatic approximation. The relaxation to thermal equilibrium is studied in a perturbative approach by means of the Pauli master equation. Int J Quantum Chem 110: 46–61, 2010

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1. Introduction

The exploration of the interaction between phonon-type excitations and electrons was of paramount importance for our understanding of the main mechanisms of electronic conduction in solid crystalline materials including superconductivity. In particular, we mention the "polaron" concept developed by Landau and Pekar [1–3]. On the other hand, our knowledge about the electron transfer (ET) processes in biomolecules is still far from complete as though Marcus seminal theory [4, 5] provided a most valuable breakthrough there are still open questions [6, 7]. Furthermore, biological motors often require electron transfer processes over relatively long distances with only small loss of energy [8, 9]. Davydov [10] was first to express the idea that for bio(macro)-molecules the interaction of electrons with solitonic interactions may play a role of similar importance as the earlier mentioned electron-phonon interaction in solid crystalline materials. Davydov showed that the nonlinearity induced by the electron-(acoustic) phonon interaction (polaron effect) leads to excitations which he called "electro-solitons." The latter could travel along originally harmonic lattices and assumed that they could be stable at physiological temperatures. Several authors have checked this conjecture by computer simulations. It was shown that Davydov's electro-solitons are destroyed already around 10 K lasting at most 2 ps [11–13]. However, the lack of stability of Davydov's solitons may have been due to lack of consistency in the computational scheme used with mixed quantum-classical representations (for a thorough discussion of the problem see [14]). Davydov's concept of electro-soliton is an appealing generalization of the polaron concept. Similar ideas were advanced by Fröhlich [15, 16] (for an assessment of the relationship between the two approaches see [17] and for another related work see [18]). Volkenstein [19] also advanced the idea that the displacement of an electron or electron density in a bio(macro)-molecule causes a conformational rearrangement. The electron plus the deformation of the bio(macro)-molecule was thought as similar to the polaron albeit in a nonperiodic crystalline material, and it was denoted as "conformon." Volkenstein pointed out, however, that the so-called conformon was not capable of moving at long distances without dissipation due to the inhomogeneity and aperiodicity of the system. The present article is devoted to a generalization of Landau's polaron and Davydov's electro-soliton concepts [20].

It is now well established that if the underlying lattice dynamics involves an appropriate anharmonic interaction this results in the appearance of very stable supersonic acoustic (lattice) solitons [21–27]. Furthermore, it has also been shown that the lattice solitons in a Morse chain when coupled to free, conduction electrons bring a new form of dressed electrons or electro-soliton dynamic bound states [28–36]. They have been called "solectrons" to mark the difference with Davydov's original electro-solitons. The quasi-particles which we call solectrons belong to the same family as the polarons and the electro-solitons, since they are bound states of excess electrons and lattice excitations. Let us insist upon the fact that they are essentially due to the anharmonicity of the lattice, and that their thermal stability is ensured well above 10 K up to physiological level (for a given material the actual temperature range depends on parameter values, as expected).

The rest of the article is organized as follows. After introducing the model Morse lattice (Fig. 1) [37], we develop in Section 2 a method of visualization of electron density 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 in the tight-binding approximation thus describing how lattice deformations (or relative displacements between lattice units) affect (free) electron motions and vice versa. In Section 4, we discuss the dynamics in a heat bath at finite temperature in a suitable adiabatic approximation by considering that electrons adapt instantaneously to the lattice changes. To approximately describe the relaxation to thermal equilibrium, we use in Section 5 a master equation approach following Pauli's seminal work [38–40]. We take into account the nonuniformities of the electron density and the nonuniformity of the on-site electron energy levels.

2. Dynamics of Atomic Lattice—Moving Overlap Regions as Supersonic Structures

The first step of our study is rather qualitative. Let us show that in a heated anharmonic atomic chain, the overlap regions of the wave functions form very fast moving local structures including about 10 lattice sites which are moving with supersonic velocity.

This might be a first hint on a relation to recent findings that the electronic couplings in biomolecules are determined by nonequilibrium geometries [41].

We shall consider a one-dimensional (1D) nonlinear lattice of length L with N classical particles (atoms or screened ion cores) and N noninteracting excess, added free electrons. The electrons occupy some 3D volume surrounding the 1D lattice. The electrons eventually lead 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 [7, 42–51]). For the heavy lattice atoms we consider that they obey classical Langevin dynamics, thus introducing temperature through noise [52]. In the computer simulations we shall take all lattice units with equal mass m, described by coordinates $x_n(t)$ and velocities $v_n(t)$, $n = 1,\ldots,N$, imposing periodic boundary conditions. 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

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

The subscripts locate lattice sites and the corresponding summations run from 1 to N. The mean equilibrium distance (lattice constant) between the particles in the lattice is σ ($\sigma = L/N$). With $r = x_{n+1} - x_n$ denoting the distance between nearest-neighbors the Morse potential is [37] (Fig. 1)

$$V = D\{\exp[2B(r-\sigma)] - 2\exp[-B(r-\sigma)]\}. \qquad (2)$$

B accounts for the stiffness of the lattice "springs" and D is a binding/bond breaking energy scale in the lattice. Typical parameter values for biomolecules are $\sigma \simeq 1 - 4$ Å; $D \simeq 0.05 - 0.5$ eV. This means that the oscillation frequency is in the range $1/\omega_0 \simeq 0.1 - 0.5$ ps. The stiffness of the potential is not so well known, and as typical we assume here $B \simeq 1 - 5$ Å^{-1}. The exact values of the parameters do not matter, since for consistency in the presentation we will give all results in dimensionless units which we will discuss below. A key parameter in our model is the ratio between the stiffness B and the average equilibrium distance σ between the molecules. According to our estimates this relation which determines the nonlinearity is in the range $B\sigma \simeq 1 - 20$. Here, the lower border stands for weak nonlinearity and the upper border for strong nonlinearity. In order not to overestimate the nonlinear effects, we assume that we are in the region of weak nonlinearity.

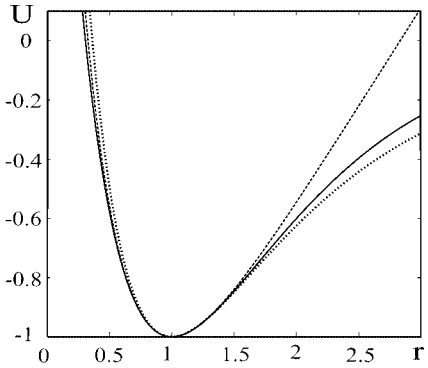

FIGURE 1. The available knowledge about depth, frequency, and stiffness of the interaction of atoms may be fitted by different potentials. Here, Toda (upper curve), Morse (middle curve), and (r^{-12}, r^{-6}) Lennard–Jones potentials suitably scaled around the minimum to have identical second and third derivatives. Relevant in our context is the repulsive part.

In principle the available knowledge about the depth of the interaction potential, the frequency of oscillations around the minimum and the stiffness of the repulsive part of the interaction of atoms may be fitted by different potentials; this is demonstrated in Figure 1. We decided to use the Morse potential, since—as far as we know—it is with respect to the repulsive forces the most realistic albeit simple potential. What is relevant in our respect is the exponential behavior of the repulsive part, and the possibility to match the stiffness (the third derivative) to available data. The attractive part of the potential, which is less realistic for the Morse model, is not of relevance in our context since solitonic excitations are determined by the repulsion between the atoms. For illustration in our computer simulations we shall use $N = 200$ and $B = 1/\sigma$. This is rather weak (small nonlinearity) but still in the range of the available data as noted earlier. With increasing values of the dimensionless parameter $(B\sigma)$ the effects described here will be even more pronounced.

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 ($n = 1, 2, .., N$) [52]

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

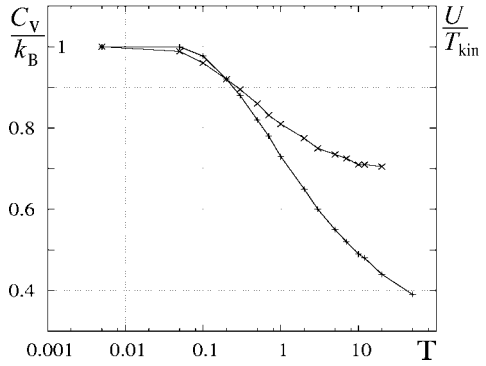

FIGURE 2. Toda–Morse lattice. Specific heat at constant volume/length (upper curve) and ratio of potential energy, U, to kinetic energy, T_{kin} (lower curve) of the anharmonic lattice (in dimensionless units according to the main text). Note that we have only the "high" temperature range. $T \simeq 0.1 - 0.5$ (even up to 1) is the soliton range. Following up in temperature there is melting (transition from solid to the hard sphere fluid: $C_v/k_B = 0.5$).

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 atoms from the heat bath. Through Einstein's relation $D_v = k_B T\gamma_0/m$, we have temperature T. The quantity σ is the length unit (though in occasions we shall use $1/B$) and the frequency of oscillations around the potential minimum ω_0^{-1} is the time unit.

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 measure the temperature T ($k_B = 8.6 \times 10^{-5}$ eV/K; $k_B T = 2D$).

The specific heat (at constant volume/length) of the atomic lattice described by the system (1) and (3) is known (Fig. 2). According to this quantity the region where nonlinearity plays significant role in our lattice is $0.75 < C_v/k_B < 0.95$. This is the multiphonon or highly deformed phonon or, better, soliton range. The corresponding temperatures in energy units are in the range $T \simeq 0.1 - 0.5$ (and even up to 1–2) or in other terms $T_{sol}^M \simeq 0.2 - 1.0D$. In electron volts (eV) 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).

We can visualize the time evolution of the lattice units and the lattice compressions and expansions, hence the solitons by representing the density of the atomic electrons. This can be achieved by considering that each lattice particle is surrounded by a Gaussian electron density (atomic density) of width $s = 0.35\sigma$. Then the total atomic electron density on the axis where the atomic centers are located is given by

$$\rho(x) = \sum_n \frac{1}{\sqrt{2\pi}s} \exp\left[-\frac{(x - x_n(t))^2}{2s^2}\right] \qquad (4)$$

where x is the coordinate on the axis and x_n the place of the atomic sites. Thus each lattice atom is like a spherical unit with continuous core electron density concentrated around its center. In regions where the atoms overlap, the density is enhanced. Note that this picture is entirely qualitative, we use it only for the purpose of visualization. This model permits identifying solitonic excitations based on the colors in a density plot. We show in Figure 3 the result of computer simulations for three temperatures $T = 0.005$ (~5 K), $T = 0.1$ (~10^2 K), and $T = 0.5$ (~5×10^2 K). The absolute temperatures given here correspond to $2D = 0.1$ eV.

The diagonal stripes correspond to regions of enhanced density (regions of overlap of the wave functions) which are running along the lattice, this is the sign of solitonic excitations. In fact the overlap regions visualized here by colors are supersonic structures which have a size of about 10 lattice units. Indeed 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 was described by Lomdahl and coworkers [11–13], 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 is for several picoseconds. Note that $T = 1$ is well above physiological temperatures. This confirms an earlier finding where at $T \simeq 300$ K stable solectrons could be identified [30, 31]. Recall that Davydov's electro-solitons and hence Lomdahl and Kerr's earlier mentioned work refer to solitons induced by the presence of originally free electrons and subsequent electron-lattice interaction (polaron-like effect). In the case we study here, the solitons are excited already before injecting electrons, and they are solely a consequence of the nonlinear lattice dynamics. What happens if excess, added free electrons are added is described in the following section.

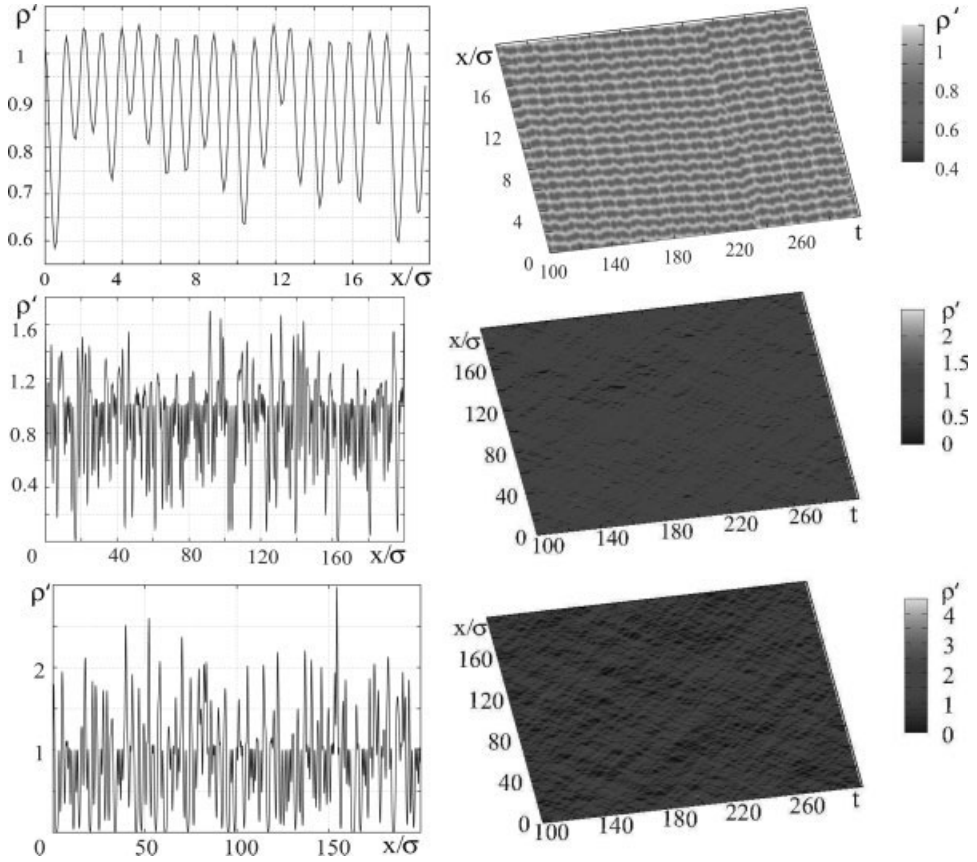

FIGURE 3. Toda–Morse lattice. Visualization of running excitations using $\rho' = \sqrt{2\pi}s\rho$, core electron density. In each case the left plot is a snapshot $\rho'(t)$, while the right plot represents trajectories $\rho'(x/\sigma, t)$ (the gray scale coding is in arbitrary units). We study three temperatures (given in units of $2D$): upper two-figures: $T = 0.005$: we see only harmonic lattice vibrations and no evidence of strong (soliton-like) excitations; center two-figures: $T = 0.1$: many density peaks show solitons (diagonal stripes). The strongest compressions move with velocity around $1.1v_{\text{sound}}$; lower two-figures: $T = 0.5$: among the many excitations appearing we observe solitons running with velocity around $1.3v_{\text{sound}}$. Parameter values: $N = 200$ and $B\sigma = 1$.

3. Electron-lattice Dynamics in Tight-Binding Approximation

Let us now study the influence of the nonlinear lattice oscillations or in other words lattice deformations on the dynamics of added, excess electrons, which are moving by hopping processes on the lattice interacting with the lattice units. The centers of the excess electrons are hopping on the 1D lattice from site to site. However to be more precise we have to realize that the electrons and their field are phenomena in the 3D-space around the lattice. In dependence on the distance from the electrons the atoms change their onsite energies, e.g. by polarization effects, and by modifying their transition probabilities. Taking only one atomic state per site in the tight-binding approximation (TBA) we can write for the excess electrons [53–55]:

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

Recall that (5) refers to initially free electrons added to the lattice atoms assumed to be located at sites "n". The Hamiltonian (5) gives a mixed quantum-classical representation of the electron dynamics using the probabilities $c_n c_n*$ of electron location at site n including classical time-dependent coordinates $x_n(t)$ of the atomic lattice sites. Purposely we shall consider the nonuniformity of the on-site energy levels (diagonal elements, V_{nn}, of the transfer matrix). Further assuming that the interactions

depend exponentially on the distance between the atoms (5) becomes

$$H_e = \sum_n \{(E_n^0 + \delta E_n)c_n^+ c_n - V_0 \exp[-\alpha(q_n - q_{n-1})](c_n^+ c_{n-1} + c_n c_{n-1}^+)\}. \quad (6)$$

Here, for convenience in notation, q_n denotes a lattice site spatial vibration (relative displacement) coordinate. This is a dimensionless coordinate (units $1/B$) defined by $x_n = n\sigma + q_n/B$. Typical parameter values are in the range $\alpha = 1 - 1.75$) [11, 13, 31]. 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). As done by Holstein and others we can assume in a first approximation that the shift is linear in the deformations [18, 47–49]

$$\delta E_n = \chi \delta x_n; \quad \delta x_n = (q_n/B), \quad (7)$$

where the "electron-phonon coupling constant," χ, estimates how much 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: $1/B$). In a real crystal this coupling between lattice deformations and electronic states, leads for high 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. Adapting these assumptions to our model we have to take into account that our model is translationally invariant and that we are considering relative lattice displacements. Accordingly, we set

$$\delta E_n \simeq \frac{\chi_1}{2}[(q_{n+1} - q_n) + (q_n - q_{n-1})], \quad (8)$$

with $\chi_1 = \chi/B$ as a new constant. Using a pseudopotential which models all electric effects including also polarization we set

$$E_n = E_n^0 - U_e \sum_{j\neq n}{}' \frac{h}{\sqrt{(x_n - x_j)^2 + h^2}}. \quad (9)$$

Here U_e is the maximal value of the shift and h is a length scale expressing the decay of the interaction strength with the distance. In the computer simulations we used mostly the parameter values $U_e = 0.1D, h = 0.3\sigma$. Further the over-dash in the sum indicates that the range is to be restricted in an appropriate way like at a distance 1.5σ from the center of the atomic core. In other words we assume that only those atoms in the neighborhood which are nearer than $3\sigma/2$ contribute to the shift of energy. We may consider the expression (9) as a semiempirical expression for the shifts albeit with two free parameters, U_e and h. In order compare with the "ansatz" (7) made by Holstein and others we consider a linearization of Eq. (9) and hence we can write

$$\delta E_n \simeq \frac{hU_e\sigma}{B(\sigma^2 + h^2)^{3/2}}[(q_{n+1} - q_n) + (q_n - q_{n-1})]. \quad (10)$$

Comparing (8) and (9) we find the relation between both models

$$\chi = U_e \frac{2\sigma h}{(\sigma^2 + h^2)^{3/2}} = \left(\frac{U_e}{\sigma}\right) \frac{2(h/\sigma)}{[1 + (h/\sigma)^2]^{3/2}}. \quad (11)$$

Then for $U_e = 0.1 - 1.0D$, $h = 0.3\sigma$, $D = 0.1$–0.5 eV, and $\sigma = 1$–5 Å we obtain $\chi = 0.001 - 0.1$ eV/Å. As the parameter values in this approach are about one or two orders of magnitude below the earlier indicated values we expect that here polaron effects are rather weak and hence the system dynamics is dominated by solitons.

The probability to find the 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

$$i\frac{dc_n}{dt} = \tau_0[E_n^0 + \delta E_n(q_{n+1}, q_{n-1})]c_n - \tau\{\exp[-\alpha(q_{n+1} - q_n)]c_{n+1} + \exp[-\alpha(q_n - q_{n-1})]c_{n-1}\}, \quad (12)$$

where E_n^0 and δE_n are dimensionless (unit: 2D); $\tau_0 = (2D/hw_0)$ and $\tau = (V_0/hw_0)$. The corresponding equations for the lattice displacements reads in this approximation

$$\frac{d^2q_n}{dt^2} = -p_n \frac{\partial \delta E_n(q_{n+1}, q_{n-1})}{\partial q_n} + \{1 - \exp[-(q_{n+1} - q_n)]\}\exp[-(q_{n+1} - q_n)] - \{1 - \exp[-(q_n - q_{n-1})]\}\exp[-(q_n - q_{n-1})] - \alpha V_0\{\exp[-\alpha(q_{n+1} - q_n)](c_{n+1}^+ c_n + c_{n+1}c_n^+) + \exp[-\alpha(q_n - q_{n-1})](c_n^+ c_{n-1} + c_n c_{n-1}^+)\}. \quad (13)$$

The problem reduces, in principle, to solving both Eqs. (12) and (13) coupled together. It is not, however, the only possible approach to our problem as we shall see below.

There are several types of of soliton-mediated electron transfer processes: (i) electron transfer (ET) from a donor to an acceptor mediated by mechanically excited lattice solitons, (ii) soliton-mediated electron transfer (ET) in a lattice in thermal equilibrium with thermally generated solitons, and (iii) electric current mediated by solitonic excitations in the presence of an external field.

Here, we study only the first two processes. Let us begin with the first problem. Let us estimate how the path of an electron may be influenced by a soliton which was generated by a perturbation in the lattice. When an excess electron is placed at a donor located at site $n = 100$ at time $t = 0$, Figure 4 shows our findings: (a) pure anharmonic lattice vibration without electron-lattice interaction ($\alpha = 0$): time evolution of one soliton, (b) free electron hence alien to lattice vibrations ($\alpha = 0$): spreading of the free electron probability density, as a natural consequence of Schrödinger equation, (c) electron-lattice interaction ($\alpha = 1{,}75$): soliton-mediated ET. The electron is dynamically bound to the soliton thus creating the traveling, generally supersonic solectron excitation. Indeed when the electron-lattice interaction is operating, we see that the electron moves with the soliton with a slightly supersonic velocity $v_{\text{el}} \sim \frac{100}{70} v_{\text{sound}}$ and is running to the right border of the square plot. Let us assume that there an acceptor is located. This means that the electron is 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 ET. In principle this effect may be used as a way to manipulate the transport of electrons between a donor and an acceptor. Clearly in our case we may have a polaron-like effect due to the electron-phonon (or soliton) interaction coupled to a genuinely added lattice solitonic effect due to the anharmonicity of the lattice vibrations. This permits soliton besides phonon-assisted hopping.

Let us summarize the findings on ET obtained so far: Electrons injected into the lattice may form very stable bound states which move with supersonic velocity along the lattice and may transfer the electron over hundreds of lattice sites. This effect points in the direction of the observation of electron transfer over long distances with only small loss of energy. The problem however remains, how stable solitons may be excited. In principle, any fast mechanical deformation or significant conformational rearrangement could be responsible for the excitation of solitons running along the lattice.

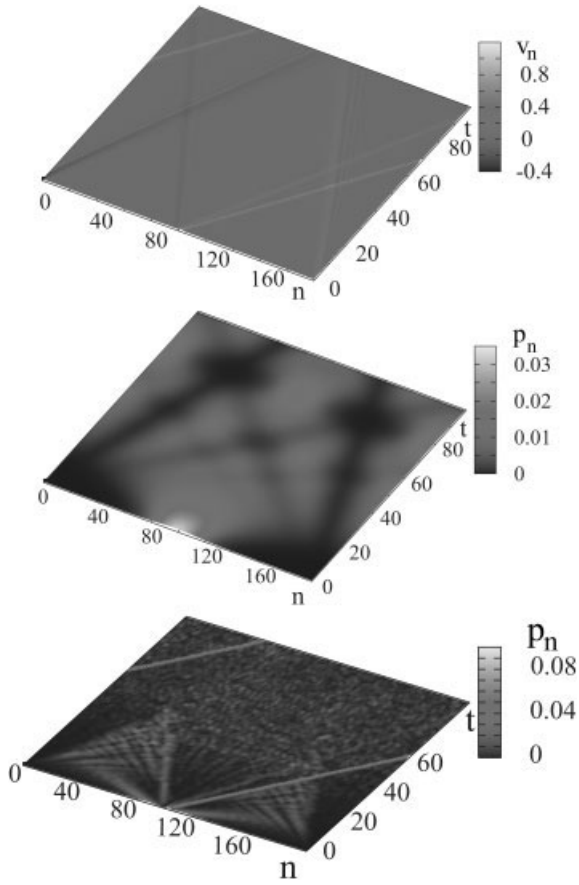

FIGURE 4. Toda–Morse lattice. Results of numerical integration of Eqs. (12) and (13). Upper figure: $\alpha = 0$, soliton alone; center figure: $\alpha = 0$, electron alone; lower figure: $\alpha = 1,75$, solectron (electron dynamically bound to the soliton). The gray scales (velocity and probability density) are in arbitrary units, just for illustration.

This however requires synchronization between the electron emission and the lattice soliton excitation. Another more physically appealing process is to look for thermally excited solitons, which are always present in the medium. This problem is investigated in the next two sections.

4. Adiabatic Approximation to the Thermal Electron Dynamics

In a heated lattice the atoms and electrons perform quite complex motions. The earlier used Schrödinger–Langevin dynamics based on the tight-binding Hamiltonian and the Langevin equations for the lattice is not so suitable for describing a heated system due to the large differences between

the electronic and the lattice relaxation times. In the following we will discuss several other approaches. In a simplest entirely classical approximation we can assume that the time evolution of the electrons is very fast defining locally a Maxwell-Boltzmann distribution. To construct this distribution we look again at the interaction between the lattice units and the surrounding excess, added free electrons. We can also assume that all lattice atoms which are near to the electron in distance 1.5σ or less contribute to the local potential $V(x)$ acting on the excess electron

$$V(x) = \sum_n V_n(x - x_n), \quad r = |x - x_n| < 1.5\sigma, \quad (14)$$

with

$$V_n(x - x_n) = -U_e \frac{h}{\sqrt{(x - x_n)^2 + h^2}}. \quad (15)$$

In accordance to Section 3 we take $U_e \simeq 0.1D$, which ensures that the electrons are only weakly bound to the atoms and may transit from one side to the other of a lattice unit. Accordingly, the electrons are able to wander through the lattice eventually creating an electric current. To place a pair of electrons between two lattice particles is in general not favorable in energetic terms, since the energy of repulsion $e^2/\epsilon_0 r$ has to be overcome; ϵ_0 denotes dielectric constant. However, the electron may attract more than two lattice atoms thus forming a deep potential hole akin to a polaron state which is a static structure corresponding to favorable energetic configurations. Here we are rather interested in the dynamic phenomena initiated by solitonic excitations in the lattice. However, we have to take into account that both of these phenomena, the local compression by a static process (polaron formation) and by a running compression (soliton excitation), are intimately connected. The choice $h \simeq 0.3\sigma$ provides shallow minima at the location of the lattice atoms with significantly deep local minima at the location of a compression. Because of the quite complex thermal motions of the atoms, we may expect a rather complex structure of the field acting on the electrons.

The potential $V(x, t)$ changes quickly and the distribution of the electrons tries to follow it as fast as possible hence electrons are "slaved" accordingly, thus permitting an adiabatic approximation. We have a situation similar to that described for free electron statistics in semiconductor theory [56]. When the electron density is sufficiently low, so that the electrons are still nondegenerated we may approximate the original Fermi–Dirac statistics by the Maxwell–Boltzmann statistics. The Boltzmann approach is often a rather good approximation which connects in a simple way the distribution with the landscapes of the local potential. Then, we take

$$n(x) = \frac{\exp[-\beta V(x)]}{\int dx' \exp[-\beta V(x')]}, \quad (16)$$

with $\beta = 1/k_B T$. Here x denotes the linear coordinate along the lattice. An example of the estimated density is shown in Figure 5 (not normalized and given in logarithmic scale). The (relatively high) peaks correspond to the enhanced probability of a soliton to meet and trap an electron. This defines the solectron, i.e., an electron "surfing" on a soliton for about 10–50 time units (i.e., a few picoseconds) then getting off it and eventually finding another soliton once more to surf-on and so on. For $T = 0.1$ we observe several rather stable running excitations (diagonal stripes) with velocity around $1.2v_{\text{sound}}$. For $T = 1$ (not shown in the figure) we have observed many weak and only a few high level excitations moving with the supersonic velocity $1.4v_{\text{sound}}$. The probabilities estimated from the Maxwell–Boltzmann distribution are strongly concentrated at the places of minima. This means that most of the electrons are concentrated near to solitonic compressions.

Let us now study the problem in a discrete quantum statistical formulation. In a first approximation we may assume the canonical equilibrium distribution

$$p_n^0 = \exp[\beta(\mu - E_n)], \quad (17)$$

where the chemical potential μ is given by the normalization. In the adiabatic approximation we assume that this distribution is attained in a very short time. The E_n are the eigenvalues of the Hamiltonian H_e. Since this eigenvalue problem with time-dependent matrix elements is very complicated, we estimate the eigenvalues by the diagonal elements of the matrix $E_n^0 + \delta E_n$. This assumption leads in linear approximation to the expression

$$p_n^0 \simeq \exp\left[-\frac{\delta E_n}{k_B T}\right] = \exp\left[-\frac{\chi(q_{n+1} - q_{n-1})}{B k_B T}\right]. \quad (18)$$

Let us now consider that one big soliton is excited in the heated system. We assume the following soliton shape

$$\exp[-3(q_n - q_{n-1}) = 1 + \beta_0 \cosh^{-1}[\kappa n - \beta_0 t]. \quad (19)$$

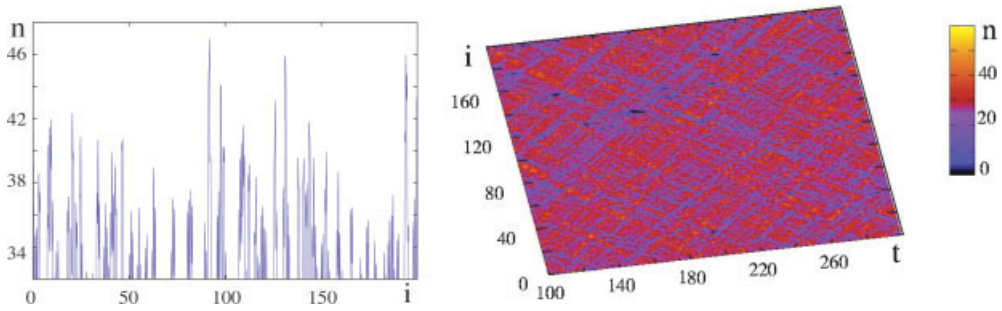

FIGURE 5. Toda–Morse lattice. Classical probability distribution of an electron in a heated anharmonic lattice in the adiabatic approximation according to local Boltzmann distribution. On the left figure a snapshot of the distribution is given for a certain time instant. On the right figure the actual time evolution of the distribution is displayed. The temperature is $T = 0.1$. Parameter values: $N = 200$, $h = 0.3, \sigma = 1$, and $B\sigma = 1$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

It seems pertinent to note that for all practical purposes a Gaussian appears as a valid approximation to (19) when using Morse or L-J potentials as shown by Rice and coworkers [22, 23]. By introducing Eq. (19) into Eq. (18) we find

$$p_n^0 \simeq [1 + \beta_0 \cosh^{-2}[\kappa n - \beta_0 t]]^{\zeta} \times [1 + \beta_0 \cosh^{-2}[\kappa(n+1) - \beta_0 t]]^{\zeta}, \quad (20)$$

where

$$\zeta = \frac{\chi}{6Bk_B T}. \quad (21)$$

We see that a solectron in a thermal medium is quite similar to a mechanically excited soliton except for some kind of twin structure and a little deformation of the shape and the amplitude, both temperature-dependent. The velocity of a solectron in a thermal medium, however, is the same as the standard soliton velocity.

Let us now proceed to a quantum statistical study of systems in thermal equilibrium. The canonical equilibrium distribution is now given by the time-dependent energy eigenvalues which lead to the expression

$$p_n^0 \simeq \exp[-c(q_{n+1}(t) - q_{n-1}(t))], \quad (22)$$

with $c = \chi / k_B T$. For systems in thermal equilibrium, the displacements have to be taken from a computer simulation of thermally excited solitons. Their distribution is a quickly changing local function of the lattice displacements. In the adiabatic approximation we assume that this distribution is attained in a very short time, as shown in Figure 6.

Instead of following just on computer simulations we may estimate the soliton frequency from the thermal statistics of the solitons in the lattice. There exists some knowledge [57–60] for Toda interactions. By using the equivalence between Toda and Morse systems (see Fig. 1) we may transfer these results at least to a good approximation to Morse systems. The calculation goes as follows: (i) we determine for single solitons with parameter κ which are described by

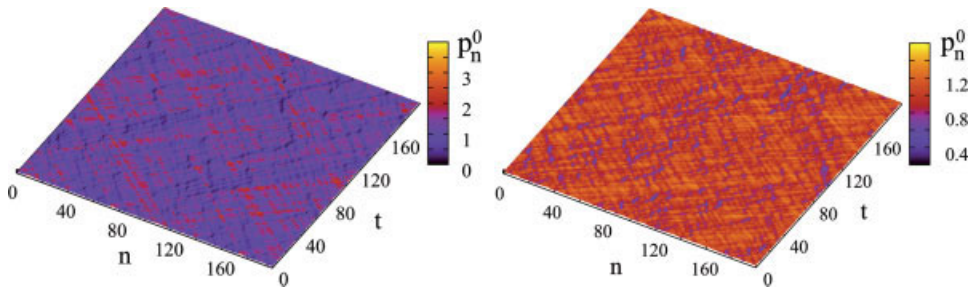

FIGURE 6. Toda–Morse lattice. Canonical probability distribution of an electron in a heated anharmonic lattice in TBA and adiabatic approximation. Left: $T = 0.1$, right: $T = 0.5$. Parameter values: $B\sigma = 1, \alpha = 1.75, V_0 = 1, \tau = 10$, and $\gamma = 0.002$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Eq. (19), as shown above. We assume that this excitation is wandering with the soliton, and (ii) we assume that the density of solitons depending on parameter κ is known. Following [59, 60] we have

$$n(\kappa, T) = \frac{4a\kappa}{\pi k_B T} \exp(-\kappa) \exp[-(E(\kappa) - 2\kappa)/k_B T], \tag{23}$$

where

$$E(\kappa) = \frac{2a}{b}[\sinh \cosh \kappa - \kappa]. \tag{24}$$

Since the occupation p_n depends on κ we get this way the electron occupation distribution. In a thermally excited system, the number of solitons depends on the initial and boundary conditions. In an infinite thermal Toda system, the number of solitons can be approximated by

$$n(T) \simeq \text{const} T^{1/3}, \tag{25}$$

a distribution assumed to be valid for Morse forces. Then the number of solitons increases with the temperature. On the other hand, their contribution to macroscopic properties, as e.g. the specific heat goes down as can be seen in Figure 2. Further the influence of solitons on the solectron formation diminishes with increasing temperature, as shown in Eq. (17). Therefore, we expect that there exists a kind of "optimal temperature" where solitons have the strongest influence on the formation of solectrons.

5. On the Relaxation to Thermal Equilibrium Using Pauli'S Master Equation

In the adiabatic approximation we assumed that the relaxation to local equilibrium is instantaneous. In reality, however, the relaxation takes a small, but finite time. In our case of 1D-TBA systems with discrete sites for the electrons, we can introduce an approximate irreversible Markov description of the relaxation following Pauli's (1928) seminal work [38]. 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 Bose–Einstein or Fermi–Dirac statistics [39, 40]. Later generalizations to canonical ensembles were connected with the development of Metropolis algorithms [61]. Applications of master equations to hopping processes in semiconductors were given by Böttger and Bryksin [54, 55] and applications to processes in biomolecules by Schlag and coworkers [50, 51]. A preliminary study of this is given in [35].

Following Pauli's approach we proceed from the Schrödinger equation (12) to a Markovian master equation for the occupation probabilities of electrons p_n in a system with the energy levels E_n:

$$\frac{dp_n}{dt} = \sum [W_{nn'} p_{n'} - W_{n'n} p_n]. \tag{26}$$

The transition probabilities derived originally by Pauli using perturbation theory for microcanonical ensembles (transitions in a narrow energy shell) read for the TBA model

$$W_0(n, n+1) = \frac{V_0}{\hbar} \exp[-2\alpha(q_{n+1} - q_n)] \times 2\pi V_0 \delta(E_n - E_{n+1}), \tag{27}$$

$$W_0(n, n-1) = \frac{V_0}{\hbar} \exp[-2\alpha(q_n - q_{n-1})] \times 2\pi V_0 \delta(E_n - E_{n-1}), \tag{28}$$

where $\delta(x)$ is Dirac's delta function. The transitions from state n to a state n', 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 thermal embedding, the situation is more complicated due to the interaction of the electrons with the lattice and the heat bath. Because of the thermal embedding, we have to go to a generalization for thermal ensembles. In such cases the transition probabilities depend on both energy levels between which the transitions occur and on the direction of the transition:

$$W(n, n+1) = \frac{V_0}{\hbar} \exp[-2\alpha(q_{n+1} - q_n)] E(n, n+1), \tag{29}$$

$$W(n, n-1) = \frac{V_0}{\hbar} \exp[-2\alpha(q_n - q_{n-1})] E(n, n-1). \tag{30}$$

The thermal factors $E(n, n')$ are not symmetrical with respect to their arguments, however there must be detailed balance

$$\frac{W(n', n)}{W(n, n')} = \exp\left[\beta\left(E_n - E'_n\right)\right]. \tag{31}$$

In other words, the relation of the thermal factors should correspond to the relation of Maxwell–Boltzmann factors. There are several possibilities to fulfill this relation [55, 62]. The simplest one is the mere Monte–Carlo procedure, where downhill transitions are weighted with $E = 1$ and uphill transitions with a factor less than unity [61]

$$E(n, n') = 1 \quad \text{if} \quad E_n < E_{n'}, \tag{32}$$

$$E(n, n') = \exp[-\beta(E_n - E_{n'})] \quad \text{if} \quad E_n > E_{n'}. \tag{33}$$

In our simulations we used this simplest approach. We underline, that this is a first approximation, and in real biomolecular systems the relaxation process is more difficult than the Monte–Carlo dynamics, which however models some of the basic features [50]. The Monte–Carlo master equation is a useful tool for computer simulations of the relaxation to thermal equilibrium distributions. For the first equilibrium Monte–Carlo study of Davydov's model see [63]. Here our approach differs from [63] in that we include anharmonic forces (Morse potential) and that we consider a nonlinear relaxation process. Since the detailed balance is obeyed, it is guaranteed that in thermal equilibrium the canonical distribution is solution of the master equation [62].

In dimensionless variables the master equation (26) for the occupation probabilities reduces to

$$\begin{aligned}\frac{dp_n}{dt} = {} & \tau\{\exp[-\alpha(q_{n+1} - q_n)]\}^2 E(n, n+1)p_{n+1} \\ & + \{\exp[-\alpha(q_n - q_{n-1})]\}E(n, n-1)p_{n-1} \\ & - \{\exp[-\alpha(q_{n+1} - q_n)]\}^2 E(n+1, n)p_n \\ & - \{\exp[-\alpha(q_n - q_{n-1})]\}^2 E(n-1, n)p_n,\end{aligned} \tag{34}$$

where $\tau = (V_0/\hbar\omega_0)$ is the adiabaticity parameter defined by the relation of the two time scales of motions. Equation (34) are used for the description of the thermal motions of the electron system as an alternative to Eqs. (12). The corresponding equations for the lattice displacements which exclude the dependence on the phases of the wave function are now

$$\begin{aligned}\frac{d^2q}{dt^2} = {} & \{1 - \exp[-(q_{n+1} - q_n)]\}\exp[-(q_{n+1} - q_n)] \\ & - \{1 - \exp[-(q_n - q_{n-1})]\}\exp[-(q_n - q_{n-1})] \\ & - 2\alpha V_0\{\exp[-\alpha(q_n - q_{n-1})]\sqrt{p_{n+1}p_n} \\ & + \exp[-\alpha(q_{n+1} - q_n)]\sqrt{p_n p_{n-1}}\},\end{aligned} \tag{35}$$

which are alternative to Eq. (13). Although the system of Eqs. (34) and (35) contains several approximations, yet it provides a rather fast and therefore useful tool for the computer simulations of the electron-lattice dynamics in thermal systems. Figure 6 illustrates results of computer simulations based on this approach. Because of the way we treat electron relaxation effects, there are differences between the methodology using the coupled Schrödinger equation and Langevin equation system (12), (13) and that using Pauli's approach albeit they are minor at least for small and for medium values of $\tau \sim 1$. For large τ , the electron relaxation in the heat bath is very fast and the distribution may be approximated by the local Maxwell-Boltzmann distribution discussed in Section 4. For $\tau \simeq 10 - 20$, the approach based on the Pauli equation (34–35) is most useful, since it provides information on deviations from the adiabatic approximation as the lattice dynamics and the electron dynamics are treated independently including their coupling. Recall that in the strict adiabatic approximation given in Section 4 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 [62]. In the 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. However, qualitatively the picture remains similar to the results obtained in section 4 as shown in Figures 7 and 8 where the solution of Eq. (34) is obtained simultaneously with that of Eq. (35).

Let us analyze now the relaxation of the distribution of injected excess electrons for several examples. In Figures 7 and 8 we show the solutions of Eqs. (34) and (35) found with two types of initial conditions for three temperatures in both cases. In the first case (Fig. 7) the initial state corresponds to an electron probability density spread over half of the

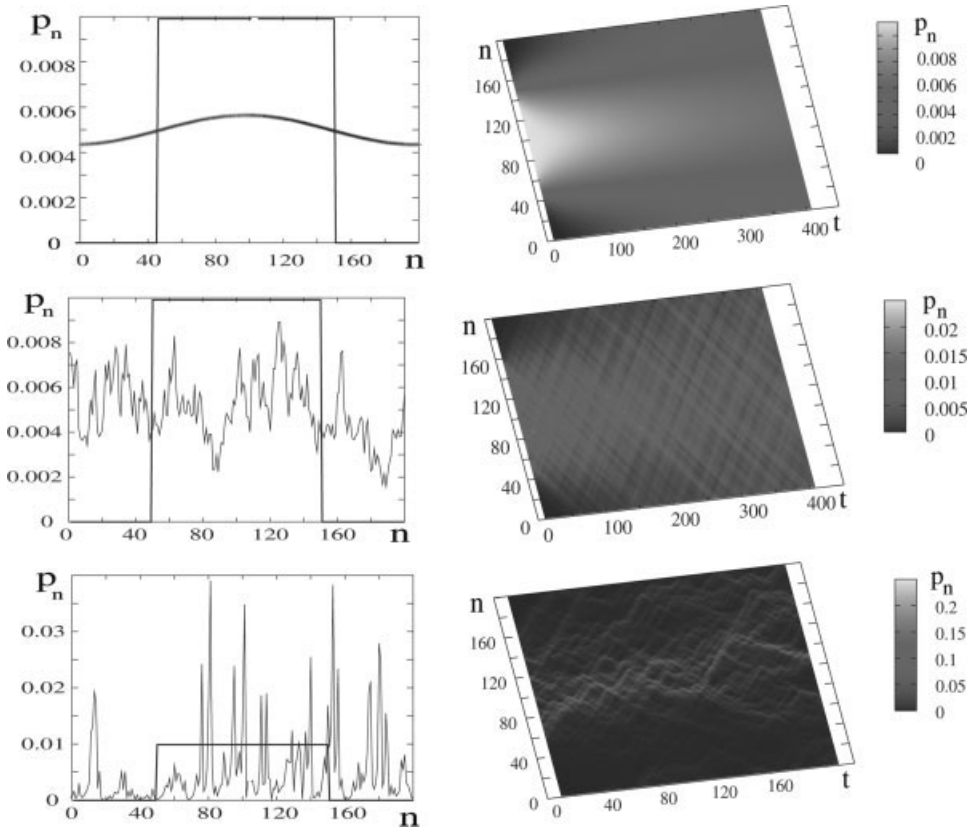

FIGURE 7. Toda–Morse lattice. Time evolution of the electron probability distribution according to Pauli's equation (34). Three temperatures (unit: 2D) are considered: upper two-figures: $T = 0$: an initially rectangular distribution tends irreversibly toward homogeneous spreading along the lattice; center two-figures: $T = 0.01$: again the initial distribution tends to be uniform along the lattice though there is electron-phonon interaction; and lower two-figures: $T = 0.5$: the initial rectangular distribution becomes localized around a few peaks thus illustrating the corresponding formation of solectrons that move with supersonic speed. Parameter values: $N = 200$, $B\sigma = 1$, $h/\sigma = 0.3$, $U_e = 0.01$, and $\tau = 1$; $\alpha = 0$, for $T = 0$, and $\alpha = 1$ for both $T = 0.01$, and $T = 0.5$.

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. 7) the opposite situation is considered. Here the electron probability density is localized in space and hence "delocalized" (spread) in the velocity space. In both cases we observe an irreversible spreading of the corresponding distribution as time proceeds for the "very cold" lattice [$T = 0$; Figs. 7(ai) and (aii), and Figs. 8(ai) and (aii)]. 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. 7(bi) and (bii); Figs. 8(bi) and (bii)]. 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 [Figs. 7(ci) and (cii)]. The latter evolve in time with the soliton motion [the solectrons are formed: Figs. 7(cii) and 8(cii)]. It can be observed that a solectron trajectory is composed of a series of trajectory fragments moving along either the right (positive velocity) or the left (negative velocity). The slope of the 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 [28, 29] as well as in the quantum mechanical study using the tight-binding model [34, 36] as e.g. splitting of the electron probability density into

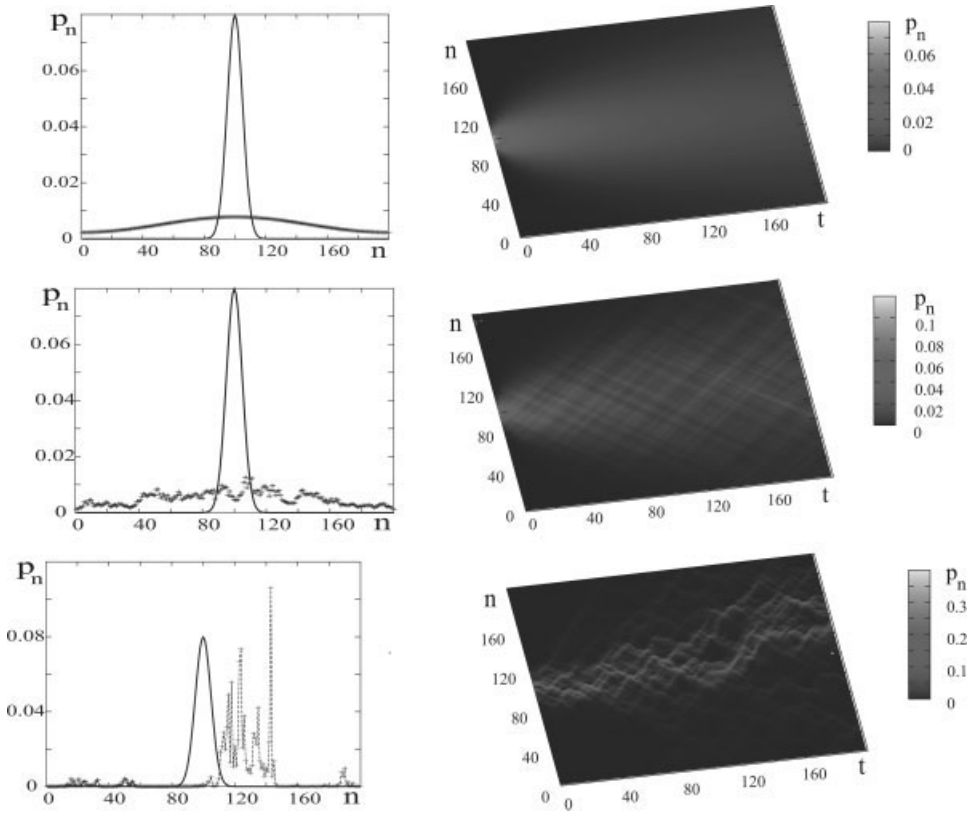

FIGURE 8. Toda–Morse-lattice. Same as in Figure 6 but using "localized" (sharper peaked than rectangular) initial distributions. Note that here time intervals are 200 time units only.

parts, merging of electron distributions, changing of host solitons (kind of promiscuity of the electron), etc. The values of the interaction parameters U_e and α cannot be fixed a priori since they depend on the particular lattice case under consideration.

6. Concluding Remarks

In anharmonic conducting lattices at temperatures high enough (including the physiological range for biomolecules, ca. 300 K), thermal solitons can be excited which lead to 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 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 electrosolitons. They also constitute a generalization of Landau's original polaron quasiparticle. Both Landau and Davydov considered only harmonic lattice vibrations.

We have shown that indeed both solitons and solectrons are stable to rather high temperatures with several picoseconds lifetimes. Our study has been based upon consideration of an anharmonic lattice (with Morse interactions) to which excess, free electrons are added. The dynamics of the lattice is classical and depending on temperature. Thermal heating excites phonons and solitons. The evolution of solitons has first been monitored by observing the evolution of the core electron density profiles surrounding the centers of the atoms originally placed at lattice sites. This is a useful alternative to the observation of just point trajectories along the purely mechanical lattice. For the excess, added free electrons we have taken two approaches: first the electrons are treated in the tight-binding approximation with evolution dictated by the Schrödinger equation. Alternatively, for heated lattices the time evolution has been described first in adiabatic approximation, by assuming that the density distribution is canonical, i.e. corresponds to local equilibrium at

any time instant. The relaxation process to the local equilibrium is then studied in a perturbative way by using a master equation approach first proposed by Pauli [38]. Our theory generalizes the master equation approach developed by Schlag and coworkers [50, 51] as we have considered the influence of a heat bath surrounding the electrons in a Monte-Carlo approximation. Since practically all proteins and biomolecules are embedded in a warm medium we wonder up to what extent our approach may be appropriate to describe electron transfer (ET) in such "molecular wires." The velocities predicted in our model computations are slightly supersonic (just for reference in DNA $v_{\text{sound}} \approx 10$ Å/ps $\simeq 1$ Km/s [42, 43]).

In conclusion we can say: (i) In a lattice with nonlinearity and excess, added free electrons dynamic bound states or quasiparticles, called here solectrons, may be generated. These rather stable bound states belong to the same family as Landau's polaron and Davydov's electro-soliton. However in our case they have a different origin, which is in the nonlinearity of the lattice, and they have a different (supersonic) speed and an enhanced stability at "high" temperatures; (ii) Mechanically excited supersonic solitons in a lattice, e.g. by sudden initial deformations or conformational structural changes, may form with excess, added free electrons solectrons that is quasiparticles which are very stable bound states and may carry charge over long distances; (iii) In a heated medium many small supersonic lattice excitations are generated forming little spots which can be able to catch the electron density. As a consequence, the electron density remains rather localized as shown in Figures 6 and 7, where we can see spots which move with supersonic velocity and have a finite life time. The dispersion is small, corresponding to an increase of the life time. However, the single, individual solectron spots are unable to carry charges over long distances, since they change stochastically their direction.

Appendix: Solitons as Matter or Charge Carriers

It is customary to denote by solitary waves certain localized (single-event) nonlinear waves of translation, i.e., waves that cause a net displacement of e.g. the liquid in the direction of the wave motion like bores in rivers. This denomination may also apply to nonlinear periodic waves or wave trains [64–67]. They were originally studied in shallow water canals, rivers, and straits though they may also appear in the open ocean [65, 68]. Surfing on a river bore or on a huge wave approaching the sea-shore is a form of wave-mediated transport. Some of those single waves or wave peaks may exhibit particle-like behavior upon collision among themselves or reflection at walls as already noted long ago by the pioneer Russell [69]. Their particle-like behavior led Zabusky and coworkers [70, 71] to introduce the concept of soliton (bores or hydraulic jumps or even kinks are also called "topological" solitons, whereas waves of "elevation" or "depression" are denoted as non-topological solitons—aka "bright" and "dark" solitons, respectively—in condensed matter physics). They dealt with the dynamics of one-dimensional (1D) anharmonic lattices and their (quasi)continuum approximation [72], provided by the Boussinesq–Korteweg–de Vries equation [73, 74]. Their work built upon seminal research done by Fermi and coworkers [75–77] who tried to understand equipartition in a lattice by adding anharmonic forces. They used 1D lattices with 16, 32, and 64 units interacting with "springs" obeying x^2 and x^3 forces and another described by a nonlinear but "piecewise linear" function. The force proportional to displacement follows Hooke's law and defines the realm of linear oscillations, harmonic in Fourier space and phonons in the quantum mechanics realm [3, 53]. Also worth recalling are the significant achievements of Visscher and collaborators using the Lennard–Jones potential [78] who, while trying to understand heat transfer, explored the role of anharmonicity and of impurities (doping a given lattice with different masses, thus generating isotopically disordered lattices). We also wish to highlight the work done by Toda on the lattice (he invented) with a peculiar exponential interaction that due to its integrability permitted obtaining exact explicit analytical solutions [21, 79]. The Toda interaction yields the hard rod impulsive force in one limit (the fluid-like or "molten" phase) while in another limit it becomes a harmonic oscillator (the lattice crystal-like solid phase). Through a suitable Taylor expansion it provides the above-mentioned anharmonic forces beyond Hooke's law. Rice and coworkers [22, 23] explored soliton features in 1D lattices with Toda, Morse and L-J potentials including the standard (12-6) case and the (32-6) so-called standard-screw potential. More recently, Heeger and coworkers have used (topological) solitons to explain the electric conductivity of polymers [80] though in this case solitons come from the degeneracy of the ground state and not from an originally underlying lattice anharmonicity in

trans-polyacetylene the case most studied by those authors. Finally, let us mention that Del Rio et al. [81] have shown that in driven-dissipative lattices solitonic traveling periodic waves [82] can act as dynamical ratchets (as in Brownian ratchets and molecular motors) and hence can transport matter or charge due to the asymmetry of the wave peaks and not of the underlying potential.

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