

# Diffusion relaxation of solitons in finite Frenkel–Kontorova systems

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**Abstract** The notion of a soliton as a quasiparticle in the Frenkel–Kontorova system is substantiated. This allows the use of the diffusive model for the description of the processes of soliton creation and disappearance at the chain ends. The Frenkel–Kontorova model is modified through the addition of barriers with certain height and concentration to the pinning profile of the potential energy surface for the soliton motion along the chain. The ratio of the relaxation times in ideal and defective systems is estimated, and it is shown that the relaxation rate can be reduced by ten and higher orders of magnitude under quite reasonable assumptions.

## Introduction

The Frenkel–Kontorova model (elastic Hookian chain in a rigid harmonic substrate potential) [1] is widely used in the theoretical studies of the physicochemical properties of extended interacting incommensurate atomic and molecular structures (see, e.g., [2–4]).

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One of the most important results of these studies consists in the revelation of so-called solitons (stable regions of stretching or compressional deformation) in such structures. The energetics of soliton formation, the geometric parameters, and the activation energy for the soliton motion along the elastic system (pinning energy) have been found. In particular, it turned out that the pinning energy in ideal Frenkel–Kontorova models with reasonable parameters is much lower than the soliton formation energy. This, in turn, should lead to a high soliton creation and destruction (relaxation) rates at the ends of elastic subsystem and, hence, to fast establishment of thermodynamic equilibrium in the system. On the other hand, the existence of long-lived metastable states (e.g., glasses) is a well-established fact for a wide range of systems, including supramolecular ones. The question arises whether the Frenkel–Kontorova model can be modified in such a way that the relaxation time of excited states (solitons) increases by ten or higher orders of magnitude. In this communication, we propose that the pinning profile of the surface potential energy for the soliton motion along the chain be modified by introducing additional barriers. The diffusive model will be used to study the problem of influence of the additional barriers and the concentration of the relevant defects on the relaxation process.

## Statement of the problem

The energetic and geometric characteristics of the equilibrium and transition states (of the conformers or solitons) and the interaction parameters between the deformation regions were numerically obtained in

[5–8] for finite Frenkel–Kontorova systems with an arbitrary incommensurability  $\gamma = b/h$  between the interacting partners ( $b$  is the equilibrium bond length in a free elastic chain, and  $h$  is the potential period of the rigid substrate). It turned out that, for a relatively small parameter  $z \leq 0.10$ , the “exact” numerical results obtained even for the chains containing several tens of elements virtually coincide with the analytic data obtained for the infinite chains using the well-known transition procedure from discrete to continuous argument [1] ( $z = 2\pi A/(kh^2)$ , where  $A$  is the amplitude of the substrate potential and  $k$  is the bond rigidity in the chain). In our notation for the main soliton characteristics, such as the formation (creation) energy  $E^t(z, \gamma)$  from the soliton-free state ([0, 0] conformer), the maximal bond deformation  $\delta^t(z, \gamma)$  in the soliton, and the activation energy  $E_a^t(z, \gamma)$  for the soliton motion along the chain, the following expressions are obtained (the upper index  $t$  corresponds to the theoretical value):

$$E^t(z, 1) = \frac{4}{\pi} \sqrt{\frac{2z}{\pi}}$$

$$E_a^t(z, \gamma) = E^t(z, 1) = 32 \exp(-\pi^2/\sqrt{2\pi z})$$

(in units of  $kh^2/2$ ), (1)

and  $\delta^t(z, \gamma) = \delta^t(z, 1) \mp (\gamma - 1) = \sqrt{\frac{2z}{\pi}} \mp (\gamma - 1)$  (in units of  $h$ ); the sign (–) corresponds to the stretching soliton ([1, 0] conformer) and the sign (+) corresponds to the compression soliton ([0, 1] conformer).

One can readily see that

$$E^t(z, \gamma) = E^t(z, 1) \mp 2(\gamma - 1). \tag{2}$$

This follows from the fact that the soliton shape (the set of the corresponding bond lengths  $l_i$  in units of  $h$ ) and, hence, the interaction with the periodic substrate potential is independent of  $\gamma$ , while the deformational contribution to the soliton formation energy from the [0, 0] conformer with an incommensurability of  $(\gamma - 1)$  is (in units of  $kh^2/2$ ):

$$\begin{aligned} E^d(z, \gamma) &= \sum [(l_i - \gamma)^2 - (\gamma - 1)^2] \\ &= \sum (l_i - 1)(l_i - 1 - 2(\gamma - 1)) \\ &= \sum (l_i - 1)^2 - 2(\gamma - 1) \sum (l_i - 1) \\ &= E^d(z, 1) - 2(\gamma - 1)(\pm 1) \end{aligned}$$

where  $E^d(z, 1)$  is the deformational contribution taken included in  $E^t(z, 1)$  for the soliton formation energy

from the [0, 0] conformer with  $\gamma = 1$ , and  $\sum (l_i - 1) = \pm 1$  for the stretching and compression solitons, respectively. The summation goes over the region containing soliton.

Clearly, Eqs. 1 and 2 are also valid for the case of a direct numerical calculation of the  $E(z, 1)$  and  $\delta(z, 1)$  values. Besides, one should take into account that, in the case that there are no excited states in a finite-length system (at small  $z$ ), these expressions fail.

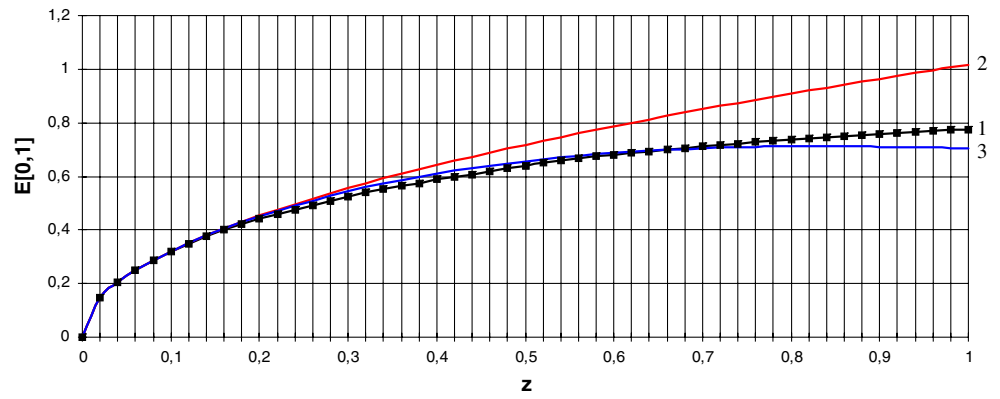
It is seen from Eq. 2 that the energy of solitonic state formation from the [0, 0] conformer becomes negative for  $z \leq z^* = \pi^3(\gamma - 1)^2/8$ . This signifies that the ground state of the system necessarily contains solitons for these  $z$  values, so that the soliton-free state ([0, 0] conformer) becomes excited state.

### Results and discussion

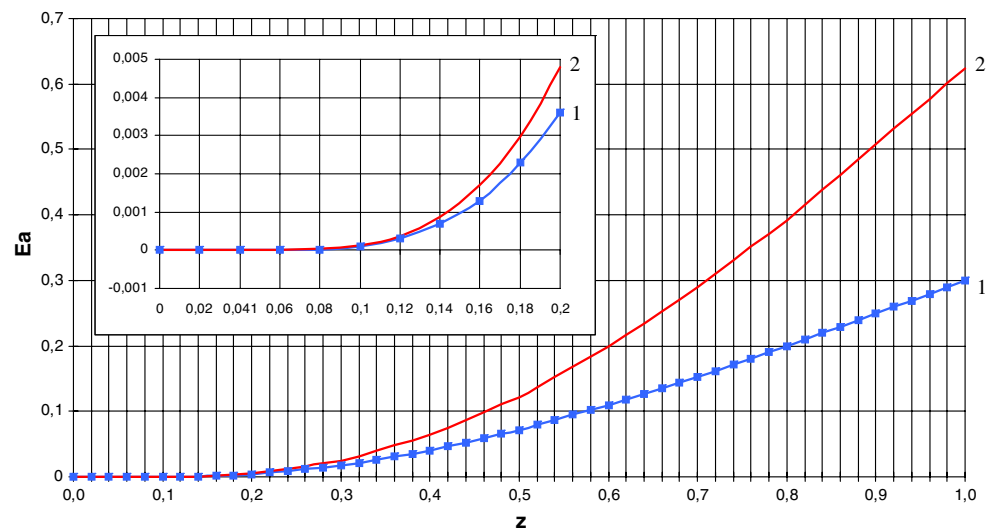
The results of numerical calculations (hereafter referred to as experimental results) of the  $E$ ,  $E_a$ , and  $\delta$  dependences on  $z$  are shown in Figs. 1, 2, 3 together with the corresponding theoretical curves. One can see from these data that the theoretical estimates virtually coincide with the experimental results at  $z < 0.1$ . However, it turned out that the maximal bond deformations in the transition and equilibrium states of the chain are, respectively, noticeably smaller and larger than the corresponding theoretical values (Fig. 3). This, likely, explains why the theoretical pinning energies at  $z > 1$  are appreciably higher than the results of numerical experiment (2). The experimental formation energies of a soliton in the equilibrium state (with allowance for pinning) virtually coincide with their theoretical values for all  $z$  (Fig. 1). However, this coincidence is a consequence of the mutual compensation of the systematically overstated theoretical formation and pinning energies, as compared to their experimental values.

The calculations also show that the center of gravity of the soliton (first moment  $M_1$  of its shape) in the equilibrium and transition states is located, respectively, in the substrate potential well and at the potential peak. The calculations of the second moments  $M_2$  of the soliton shape for these extremal points showed that, first,  $M_2 \sim z^{-1}$  and they virtually coincide (to a few % at  $z < 0.3$ ) in the equilibrium and transition states (i.e., solitons do not change their shape) and, second, the value of  $M_2$  for the stretching solitons is by a factor of  $\approx 1.23$  larger than for  $M_2$  of the compression solitons. The moments  $M_1$  and  $M_2$  were defined using the standard expressions:

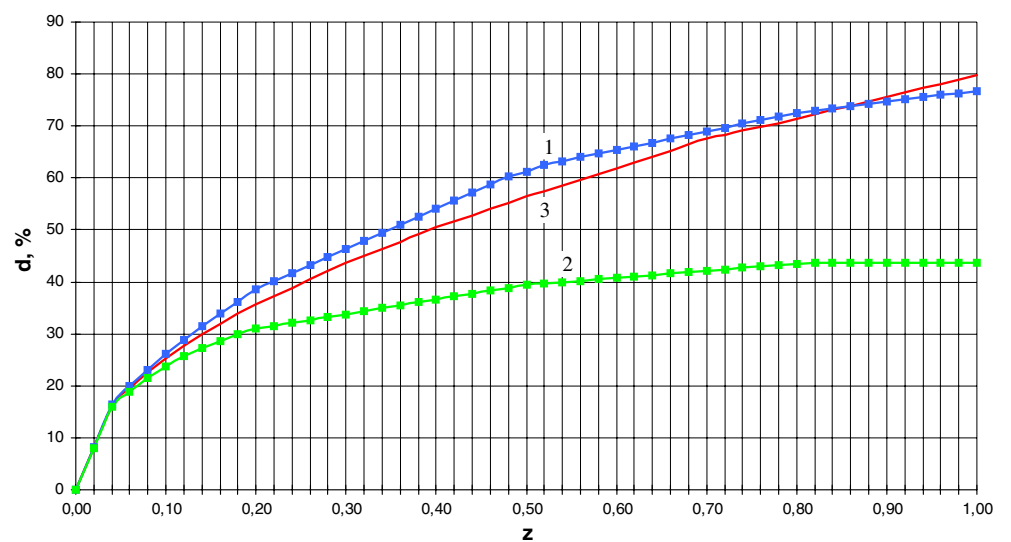
**Fig. 1** (1) Experimental and (2, 3) theoretical dependences (with and without correction for pinning, respectively) of the soliton formation energies on  $z$  (in units of  $kh^2/2$ )



**Fig. 2** (1) Experimental and (2) theoretical  $z$  dependences (in units of  $kh^2/2$ ) of the activation (pinning) energy for the soliton motion in the chain



**Fig. 3** (1, 2) Experimental (for the equilibrium and transition states, respectively) and (2) theoretical  $z$  dependences of the maximal bond deformation in the soliton (in%)



$$M_1 = \frac{\int \Delta\rho(y)y \, dy}{\int \Delta\rho(y) \, dy}; \quad M_2 = \frac{\int \Delta\rho(y)y^2 \, dy}{\int \Delta\rho(y) \, dy} - M_1^2,$$

where  $\Delta\rho(y) = \sum [\delta(y - y_i) - \delta(y - i - \frac{1}{2})]$  is the “density” difference,  $\delta(y)$  is the delta-function,  $y_i$  is the dimensionless coordinate of the  $i$ th element in the solitonic state, and  $(i + 1/2)$  is the coordinate of the  $i$ th element in the soliton-free state. The corresponding integration domain must cover the entire soliton, so that  $\int \Delta\rho(y) \, dy = \pm 1$  for the compression and stretching soliton, respectively.

Therefore, to describe the properties (including relaxational ones) of the Frenkel–Kontorova systems containing solitons, one should, first of all, determine their effective mass if they are considered as quasiparticles. Note that the creation or destruction of solitons in the chain can occur either biographically (in the course of system preparation), thermally ( $n$  the creation and recombination processes of a compression-stretching soliton pair), or at the chain ends. In the latter cases, the relaxation processes in the system can be analyzed using the diffusive model. It is natural to determine the soliton effective mass through the chain total momentum corresponding to the soliton movement with a certain effective velocity. Inasmuch as the soliton virtually does not change its shape during the process of movement, the effective velocity can be set equal to its period-averaged value, i.e., to the ratio of the substrate potential period to the time taken by the soliton center of gravity (first moment) to move this distance.

For the soliton transport over a period  $h$  of the substrate potential in time  $t$ , the soliton momentum can be written as  $p = m^*ht$ , where (by definition)  $m^* = \text{constant}$  is the soliton effective mass (averaged over the translation process). Simultaneously, all chain elements with mass  $m$  move from their initial positions  $Y_i$  to the final positions  $Y_i^*$ , and the corresponding total mean momentum (taken equal to the soliton momentum) is  $\frac{m}{t} \sum_i (Y_i^* - Y_i)$ . Thus, the soliton effective mass is  $m^* = \frac{m}{h} \sum_i (Y_i^* - Y_i)$ .

Inasmuch as  $Y_i^* = Y_{i-1} + h$  and  $Y_i = Y_{i-1} + hl_i$  for the soliton translation over the distance  $h$ , the sum  $\frac{1}{h} \sum (Y_i^* - Y_i) = \sum (1 - l_i) = \mp 1$  for the stretching and compression solitons, respectively. As a result, one has  $m^* = \mp m$ .

One can easily see that the effective mass of the stretching soliton is negative. This follows from the fact that, if this soliton moves in the positive direction, all chain elements move in the negative direction, and vice versa; for the compression soliton,

the direction of its movement coincides with that of the chain elements.

We next estimate the ratio of soliton relaxation times in the ideal and defective systems, regarding soliton as a particle with mass  $m^*$ . As a relaxation mechanism, we consider only the process of soliton disappearance at the chain ends, because it exhibits the longest-time kinetics. For simplicity, we consider the case of “strong dissolution” with only one soliton in the chain. The corresponding relaxation time can be estimated as  $\tau \sim \frac{R^2}{D}$ , where  $R$  is the chain length and  $D$  is the soliton diffusivity along the chain. Therefore,  $\frac{\tau_d}{\tau_i} \sim \frac{D_i}{D_d}$  for the chains of the same length, where the indices  $i$  and  $d$  refer to the ideal and defective system, respectively. The defects are modeled by the barriers with a height much greater than the pinning potential.

The value of  $D_i$  can simply be estimated as  $D_i \sim l_c \sqrt{\langle V^2 \rangle}$ , where  $l_c$  is the correlation length of the soliton motion (the energy of thermal motion is assumed to be greater than the pinning potential), and  $\langle V^2 \rangle$  is the mean square velocity of the soliton. The diffusion coefficient in the system with defects is estimated as  $D_d \sim l^2 W$ , where  $l$  is the mean distance between the additional barriers and  $W$  is the probability (in unit time) of barrier being overcome by the soliton.

Since the barrier height  $E_b$  is assumed to be large enough for the motion of incident soliton to be considered as ballistic (on the length on the order of  $l_c$ ), only those solitons overcome the barrier whose velocity is higher than  $V_b = \sqrt{\frac{2E_b}{|m^*|}}$ . For the Maxwellian velocity distribution, one can readily find:

$$W \sim \frac{1}{l} \sqrt{\frac{\langle V^2 \rangle}{2\pi}} \exp\left(-\frac{E_b}{kT}\right),$$

and, hence,

$$\frac{\tau_d}{\tau_i} \sim \frac{l_c}{l} \exp\left(\frac{E_b}{kT}\right). \tag{3}$$

It would appear natural that the correlation length  $l_c$  is much smaller than the distance  $l$  between the additional barriers (this is also a necessary condition for the system thermalization). Nevertheless, even for the minimal value (unity) of  $l_c$ , the exponential factor in (3) increases the relaxation time of the system in the thermodynamic equilibrium by more than 12 orders of magnitude for quite realistic values  $E_b \sim 1$  eV and  $kT \sim 0.025$  eV (room temperature) even for  $l \sim 10^5$  (almost an ideal system).

## Conclusion

Thus, the above consideration has demonstrated that the proposed modification of the Frenkel–Kontorova model provides a basic possibility of its use in studying the long-lived metastable states of the respective systems. In particular, it has been possible to explain the fact that long-lived thermodynamically equilibrium systems whose properties are determined by the preparation method and not by thermodynamics, can exist under quite reasonable assumptions (height and concentration of the additional barriers in the pinning potential).

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