Journal of Experimental and Theoretical Physics, Vol. 93, No. 4, 2001, pp. 895–902.
Translated from Zhurnal Éksperimental'noĭ i Teoreticheskoĭ Fiziki, Vol. 120, No. 4, 2001, pp. 1027–1036.
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MISCELLANEOUS

On the Applicability of the Frenkel–Kontorova Model to Describing the Dynamics of Vacancies in a Polymeric Crystal Chain

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Received April 10, 2001

Abstract—The necessary conditions of the applicability of the Frenkel–Kontorova one-dimensional model [the approximation of immobile neighboring chains plus sine-Gordon (continual) equation for nonlinear dynamics of the chain under consideration] to describing the dynamics of vacancies in a polymeric crystal chain are determined. It is shown that these conditions are satisfied for polyethylene crystals. The physical mechanism of model applicability limitations is established. © *2001 MAIK "Nauka/Interperiodica".*

1. INTRODUCTION: ONE-DIMENSIONAL MODELS FOR DESCRIBING NONLINEAR DYNAMICS IN THREE-DIMENSIONAL SYSTEMS

One of the most important achievements of nonlinear physics is the possibility of describing localized waves that propagate at a constant velocity, that is, solitons or soliton-like excitations. Such waves are often observed in physical systems, but they are seldom truly one-dimensional. These are either waves in filamentary systems (a magnetic flux quantum in a long and narrow Josephson contact, a solitary surface wave in a shallow and narrow channel with water, or an optical pulse of a picosecond width in a thin optical fiber waveguide made of a nonlinear material) or plane waves (a turning wave in a uniaxial ferromagnet with anisotropy of the type of an easy magnetization plane, ion–sound waves in a homogeneous collisionless nonisothermal plasma and magnetoacoustic waves in a cold plasma placed into a magnetic field, or an optical pulse in a nonlinear medium). In this context, examples of quasi-one-dimensional waves virtually localized along a line and propagating in a three-dimensional (3D) medium like truly one-dimensional excitations are very interesting. For instance, a soliton of stretches in a polymeric crystal (that is, a chain unit vacancy without rupture of internal bonds localized in a small chain portion) is a quasi-one-dimensional soliton.

Solutions corresponding to nontopological solitons in multidimensional systems such as Langmuir (electron) waves in a cold plasma are often unstable with respect to the wave collapse, although sometimes, new stable solitons localized in all directions appear, for instance, as magnetoacoustic waves in a cold 2D plasma. The problem of taking into account the 3D character of real physical objects for topological solitons, which are solutions to equations of the sine-Gordon type, is qualitatively different in nature. The turning region in a one-dimensional ferromagnet with anisotropy of the type of an easy magnetization plane, an edge dislocation in a low-molecular-weight crystal, or a chain unit vacancy in a polymeric crystal chain should exist as static objects (structural defects) in the 3D as well as in one-dimensional case. In a 3D system, only the type of their dynamic behavior may change from soliton-like (motion at a constant velocity in a cold crystal) to pinning because of a lowering of the upper bound of the spectrum of velocities.

In this work, we study the conditions of the applicability of the one-dimensional Frenkel–Kontorova model to analyzing nonlinear dynamics of a topological localized soliton-like excitation in a 3D system for the example of a vacancy in a polymeric crystal chain. We also consider the physical mechanisms responsible for changes in dynamic behavior of structural defects described above.

2. POINT STRUCTURAL DEFECTS IN POLYMERIC CRYSTAL CHAINS

The energy characteristics and the type of the dynamics of structural defects determine the relaxation properties and the special features of phase transitions in crystals. For this reason and in view of the availability of polymers with high crystallinity degrees, many studies of point and line structural defects in crystals formed by chain molecules have appeared during recent years.

Because of strong anisotropy and hierarchy of interactions (intrachain covalent chemical bonds are several orders of magnitude more rigid than interchain van der Waals bonds), vacancies with rupture of intrachain covalent bonds are virtually immobile. Such crystals can, however, contain other, specially polymeric, point defects caused by chain deformations rather that the rupture of intrachain bonds. These defects may be localized on a small chain portion, for instance, a chain can contain a chain unit vacancy or (a plane zigzag chain) a point defect of rotation through 180° accompanied by chain elongation or contraction by half the chain period to preserve crystallographic order outside the defect region.

The idea that polymeric crystal chains can contain torsional defects with elongation was originally advanced in [1, 2] in relation to dielectric α-relaxation in weakly oxidized polyethylene; the exact form of this defect was established in [3]. The model including Brownian movement of such a defect along the chain as a relaxation mechanism (see review [4] and two series of works, [2, 5] and [6]) allowed some special features of the process to be explained, namely, its occurrence in the crystalline fraction, anisotropy with respect to the direction of the applied field vector, the local character of the mechanism, the presence of the α-peak in dielectric relaxation of polyethylene and isotactic polypropylene and its absence for syndiotactic polypropylene and isotactic polystyrene [7]. Since then, the dynamics of structural defects of this type in polymeric crystals have been studied fairly extensively [3, 6–10].

Movement of a point structural defect along a chain in a polymeric crystal is usually treated in the quasi-one-dimensional approximation of immobile neighboring chains and is described in terms of topological soliton-like excitations in the continual approximation as a nonlinear wave which freely propagates at a constant subsonic velocity along the chain and changes the state of the chain after its passage.

Calculations of the characteristics of solitons even in the approximation of immobile neighboring chains requires knowledge of the form of the interatomic interaction potential and its parameters, which cannot be obtained from experimental data, but which to a substantial degree determine the type of behavior of defects. The idea that expanding the interchain potential in a polymeric crystal into the Fourier series can be performed analytically by considering the potential of a linear chain of atoms and summing their contributions by the Poisson summation rule was long ago advanced by McCullough [11]. This approach was used to estimate the temperature dependence of shear moduli in paraffins [12] and to calculate crystal potential energy minima corresponding to the monoclinic and orthorhombic polyethylene polymorphs [13]. The potential of a linear chain of atoms was calculated not only for Lennard-Jones-type interatomic interactions but also for slowly decreasing Coulomb interactions (see review [14]). More recently [15], this method was used to determine the form of the interatomic potential in polyethylene.

In all these works, the periodic potential of a linear chain of atoms was truncated after the first harmonic of the obtained Fourier expansion, $A_0 + A_1\cos(2\pi z/c)$, where c is the distance between chain atoms. The correctness of this approximation was checked by trial calculations of the amplitude of the next harmonic. Physical criteria of the applicability of such an approximation (the sine-Gordon equation for describing nonlinear chain dynamics) to various real crystals were not, however, formulated.

On the other hand, it is not quite clear whether or not the environment of a chain can be considered immobile in analyzing the dynamics of chain point defects. Molecular dynamics simulations show [16, 17] that mobility of neighboring chains can have a noticeable effect on the dynamics of defects. In several works (e.g., see [18]), mobility of neighboring chains was taken into account by phenomenologically introduced terms which, in the limit of stationary neighboring chains, corresponded to the approximation of the first harmonic in the Fourier expansion, but the physical meaning of these terms was not discussed.

In this work, we make an attempt to fill up the two gaps specified above and determine the limits of the applicability of the Frenkel–Kontorova one-dimensional model (the approximation of immobile neighboring chains plus the sine-Gordon equation for the nonlinear dynamics of the chain under consideration) to describing the dynamics of vacancies in a polymeric crystal chain (Sections 4 and 3, respectively). An example of a real polymeric crystal which satisfies these criteria and to which the Frenkel–Kontorova one-dimensional model is applicable is described in Section 5.

3. A PERIODIC POTENTIAL OF A LINEAR CHAIN OF ATOMS

Consider potential $W(c, b, z)$ created on axis z by a linear chain of rigidly fixed atoms situated parallel to this axis at distance b; c is the interatomic distance (Fig. 1). The analysis will be performed specifically for van der Waals interactions between a "test" atom and every other chain atom,

$$U_{LJ}(r) = U_0 u(r) = U_0\left(\frac{r_0}{r}\right)^6\left[\left(\frac{r_0}{r}\right)^6 - 2\right].$$

Here, U_0 is the potential energy minimum and r_0 is the point at which this minimum is attained. The summation over all atoms yields

$$W(c, b, z) = \sum_{l=-\infty}^{\infty} U_{LJ}\left(\sqrt{b^2 + \left(\frac{c}{2} + lc - z\right)^2}\right). \qquad (1)$$

If the equilibrium position of the test atom at the $z = 0$ point is largely determined by interactions with its two nearest neighbors (atoms with numbers 0 and –1), the "local" case, then

$$\varepsilon_U \equiv \left|\frac{U_{LJ}(l=1)}{U_{LJ}(l=0)}\right| \ll 1.$$

Let us introduce the $y = b/r_0$ dimensionless variable and the $\delta = c/2r_0$ parameter and write the terms of (1) in an explicit form. In "local" equilibrium, when $y^2 + \delta^2 \approx 1$, the ε_U value only depends on parameter δ. Physically meaningful are δ values in the (0, 1) interval. At a constant c parameter, the optimal b distance from the neighboring chain tends to infinity when $\delta \longrightarrow 0$ and to zero when $\delta \longrightarrow 1$.

Selecting $\varepsilon_U = 0.03$ as a boundary of the local case, we find that the potential of the atom at $z = 0$ is in reality only determined by two nearest atoms from the neighboring chain if $\delta > \sqrt{3/8} \approx 0.61$.

Otherwise (when the contributions of the other atoms are large), sum (1) can be calculated by the Poisson summation formula,

$$\sum_{n=-\infty}^{\infty} F(nh) = \int_{-\infty}^{\infty} \frac{d\zeta}{h} F(\zeta) \sum_{m=-\infty}^{\infty} \exp\left(2i\pi m\frac{\zeta}{h}\right).$$

Then,

$$\begin{aligned} W(c, b, z) &= \int_{-\infty}^{\infty} \frac{dx}{c} U_{LJ}(\sqrt{b^2+x^2}) \\ &\times \left[1 - 2\cos\left(\frac{2\pi}{c}x\right)\cos\left(\frac{2\pi}{c}z\right)\right. \\ &+ 2\cos\left(\frac{2\pi}{c}2x\right)\cos\left(\frac{2\pi}{c}2z\right) \\ &\left.- 2\cos\left(\frac{2\pi}{c}3x\right)\cos\left(\frac{2\pi}{c}3z\right) + \ldots\right]. \end{aligned} \quad (2)$$

All these integrals are easily found by the theory of residues, and the expansion of the $W(\delta, y, z)$ potential periodic along z into a Fourier series takes the form

$$\begin{aligned} W(\delta, y, z) &= \frac{3\pi}{8\delta}U_0\left[W_0(y) + f(\delta, y)\cos\left(\frac{2\pi}{c}z\right)\right. \\ &\left.- f\left(\frac{\delta}{2}, y\right)\cos\left(\frac{2\pi}{c}2z\right) + f\left(\frac{\delta}{3}, y\right)\cos\left(\frac{2\pi}{c}3z\right) - \ldots\right]. \end{aligned} \quad (3)$$

Here, the main contribution to the potential only depends on the interchain distance and is independent of either z or δ,

$$W_0(y) = \frac{1}{y^5}\left(\frac{21}{64}\frac{1}{y^6} - 1\right).$$

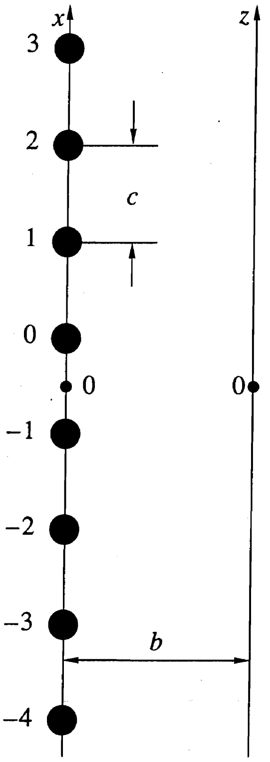

Fig. 1. Linear chain of atoms with fixed positions along the x axis. Each atom interacts with the test atom situated on the z axis according to the Lennard-Jones potential. The total potential energy of the test atom is found as a function of chain period c, distance between axes b, and test atom position z.

The amplitudes of the harmonics are given by the $f(\delta, y)$ function,

$$f(\delta, y) = -\frac{2}{3}\exp\left(-\pi\frac{y}{\delta}\right)\frac{1}{y^5}\left(\frac{Q_5(\pi y/\delta)}{8y^6 \times 5!} - Q_2\left(\pi\frac{y}{\delta}\right)\right),$$

$$Q_5(p) = p^5 + 15p^4 + 105p^3 + 420p^2 + 945p + 945,$$

$$Q_2(p) = p^2 + 3p + 3.$$

The condition of the applicability of expansion (3) is the smallness of the ratio of the first harmonic amplitude to the main term. This condition determines the boundary of the "collective" case: the requirement $|f(\delta, y_0)/W_0(y_0)| < 0.1$, where y_0 is the position of the $W_0(y)$ function minimum, is equivalent to the condition $\delta < 0.41$. The amplitude of every next harmonic is then much less than that of the preceding harmonic because of the exponential dependence of the f function on the harmonic number. Even at $\delta = 0.41$, the amplitude of the second harmonic is 100 times lower than that of the first one. If we retain the first harmonic in the expansion (this is necessary to obtain the dependence of the chain potential on z), the weaker condition $|f(\delta/2, y_0)/f(\delta, y_0)| < 0.1$ extends the boundary of the collective case to $\delta = 0.55$.

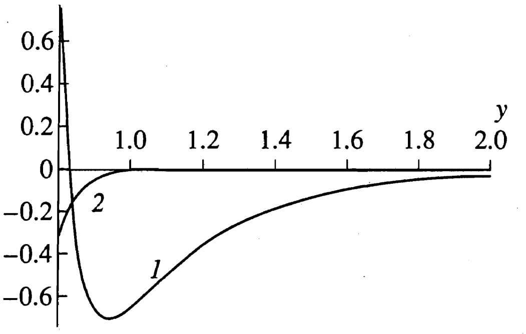

Fig. 2. Main contribution W_0 (curve *1*) to the potential of a linear chain of atoms (Fig. 1) and the $f(\delta = 0.3, y)$ amplitude (curve *2*) of the first harmonic along z as functions of dimensionless distance $y = b/r_0$ (r_0 is the equilibrium Lennard-Jones interatomic potential distance) between axes x and z.

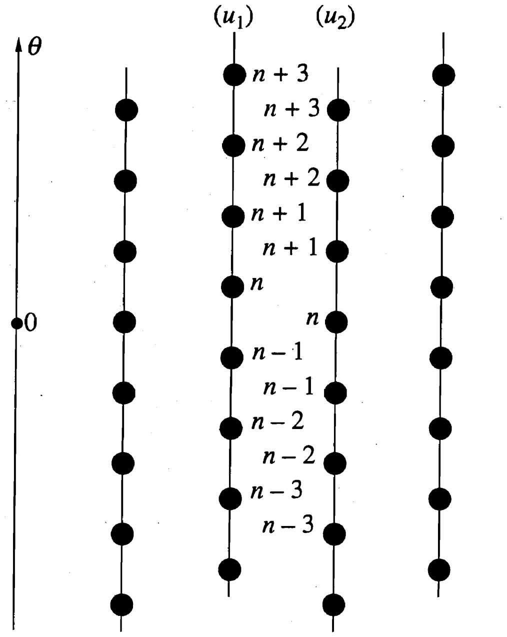

Fig. 3. Equilibrium two-dimensional crystal formed by linear chains.

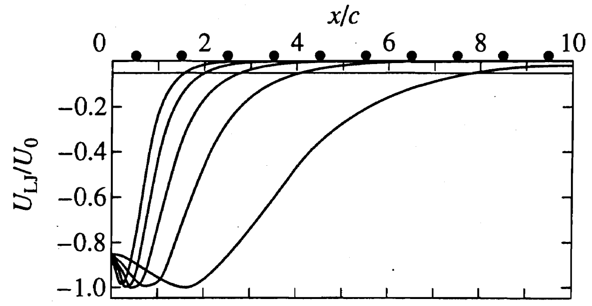

Fig. 4. Potential created by one chain atom situated at point x (Fig. 1) at the position of the test atom situated at $z = 0$ on the z axis as a function of dimensionless distance x/c (c is the chain period). At the selected $b = r_0y_0$ interchain distance, the main contribution of the whole chain to the potential is minimum. Curves for different δ parameter values are plotted, from left to right: $\delta = 0.5$, 0.4, 0.3, 0.2, and 0.1. Solid circles along the x/c axis are real atomic positions on the axis. The horizontal line corresponds to the −0.05 level.

We see that, in the collective case, the z dependence of the potential generated on the axis of a linear chain of atoms is largely determined by one harmonic. This distinguishes the collective case from the local case, in which the periodic substrate is created by flat wells with narrow barriers in between. It follows that the boundary of the collective case is also the boundary of the applicability of the sine-Gordon equation to describing the nonlinear dynamics of a chain in a polymeric crystal.

Understanding the type of the polymeric crystal under study is necessary for correctly estimating the type of mobility of point defects in its chains. It is known [19] that, if barriers are narrow, a much larger interchain rigidity is required for kinks to move along chains without pinning than when there is a single harmonic.

The $W_0(y)$ and $f(\delta = 0.3, y)$ functions are plotted in Fig. 2. The $W_0(y)$ function attains a minimum at

$$y = y_0 = \left(\frac{21}{64}\times\frac{11}{5}\right)^{1/6} \approx 0.94713161\ldots.$$

The $f(\delta = 0.3, y)$ function is negative at reasonable y values (it takes on exceedingly small positive values of the order of 10^{-6} at $y > 1.4$). This means that, if we wish to construct a two-dimensional crystal of linear chains, we must displace atoms of every next chain by half the period with respect to atoms of the preceding chain (Fig. 3).

Let us estimate the number of particles that make a noticeable (for instance, larger than 5% of U_0) contribution to the potential in the collective case. At $z = 0$ and $b = y_0r_0$, the potential created by a chain atom at point x (Fig. 1) is given by

$$\frac{U_{LJ}\left(\sqrt{(r_0y_0)^2 + x^2}\right)}{U_0} = \frac{1}{y_0^6}\left[1 + \left(\frac{x}{c}\frac{2\delta}{y_0}\right)^2\right]^{-3}$$
$$\times\left\{\left[1 + \left(\frac{x}{c}\frac{2\delta}{y_0}\right)^2\right]^{-3}\frac{1}{y_0^6} - 2\right\}.$$

The plots of this function obtained at various δ values are given in Fig. 4. As expected, four particles make noticeable contribution to the potential ($N_s = 4$) if $\delta \sim$ 0.4–0.5. The data on the other δ values are given in the table.

Let us estimate the ratio between the amplitude of the first harmonic in (3) to the lowest Lennard-Jones interatomic potential energy at various δ. These ratios, $(3\pi/8\delta)|f(\delta, y_0)|$, are also given in the table. We see that, even at the boundary ($\delta = 0.5$), the amplitude of the substrate is smaller than $0.25U_0$, whereas at arbitrary $\delta >$ 0.61 (the local case), half the difference of potential hump and well energies exceeds $4.7U_0$.

This is an important difference between the local and collective cases. The width of a topological kink is

Dependence of the N_s number of atoms actually forming potential at the $z = 0$ point (Fig. 1) and the amplitude of the first harmonic of this potential on δ

δ	0.1	0.2	0.3	0.4	0.5
N_s	8×2	4×2	3×2	2×2	2×2
$\frac{3\pi}{8\delta}\lvert f(\delta, y_0)\rvert$	7×10^{-8}	4.45×10^{-3}	7.33×10^{-2}	0.191	0.239

proportional to the square root of the ratio between intrachain and substrate rigidities. At a large substrate amplitude (even if the substrate is sinusoidal), substantial intrachain rigidity is required for kinks to remain fairly broad and experience no deceleration caused by emission of energy into chain phonon modes [20].

It follows that the transition from the collective to the local case causes an increase in the amplitude of the linear chain potential and changes its form from purely sinusoidal to broad wells separated by narrow barriers. This corresponds to the transition from the soliton type of mobility of point defects to emission of phonons by defects (and the corresponding lowering of the upper spectrum bound) and, eventually, to purely diffusive mobility type with pinning.

4. TAKING INTO ACCOUNT MOBILITY OF NEIGHBORING CHAINS. INTERCHAIN INTERACTION POTENTIAL

The interaction energy between two chains whose atoms are displaced by $(u_1)_n$ and $(u_2)_n$ from their equilibrium positions shown in Fig. 3 is usually written in the form [18]

$$W(u_1, u_2) = \varepsilon_0 \int_{-\infty}^{\infty} \frac{du}{c} \times \left\{ -\alpha\left[1 - \cos\left(\frac{2\pi}{c}(u_1 - u_2)\right)\right] + \beta \frac{\partial u_1}{\partial y}\frac{\partial u_2}{\partial y} \right\}. \tag{4}$$

Setting u_2 equal to zero, we obtain the sine-Gordon equation for the nonlinear dynamics of the first chain, u_1. The criterion of the applicability of this equation was discussed in Section 3. Let us add interaction energy (4) to the Hamiltonian

$$H_0 = \varepsilon_0 \int_{-\infty}^{\infty} \frac{dy}{c} \left\{ \frac{1}{2}\left(\frac{\partial u_1}{\partial t}\right)^2 + \frac{1}{2}\left(\frac{\partial u_1}{\partial y}\right)^2 + \left[1 - \cos\left(\frac{2\pi}{c}u_1\right)\right] + \frac{1}{2}\left(\frac{\partial u_2}{\partial t}\right)^2 + \frac{1}{2}\left(\frac{\partial u_2}{\partial y}\right)^2 + \left[1 - \cos\left(\frac{2\pi}{c}u_2\right)\right] \right\} \tag{5}$$

and consider the dynamics of a kink in chain u_1. Assuming that $\alpha \ll 1$ and $\beta \ll 1$, one can find [18] within the framework of the perturbation theory that interaction (4) between chain u_1 and mobile chain u_2 changes the shape of the kink and causes the appearance of a perturbation in chain u_2 which moves together with the kink. The amplitude of this perturbation is proportional to $\alpha + \beta/(1 - v^2)$, where v is the velocity of the kink in units of v_s, the sound velocity of an isolated chain. The amplitude increases infinitely as the velocity of the kink approaches the v_s value, which shows that such perturbation theory cannot be used to take into account kink radiation loss which appears when its velocity increases. Indeed, it is easy to show that, in a system of two interacting chains, the introduction of the $\varepsilon_0\beta(\partial u_1/\partial y)(\partial u_2/\partial y)$ term results in that the lowest phase velocity of phonons common to both chains equals $v_{1,2} = \sqrt{1 \pm \beta}$ (in v_s units) for two branches corresponding to phonons synphase and antiphase in chains, respectively. It follows that, regardless of the sign of β, the velocity of phonons on one branch is always smaller than unity, and if a kink exceeds this velocity, Vavilov–Cherenkov-type radiation appears. Conversely, the term

$$-\varepsilon_0\alpha\left[1 - \cos\left(\frac{2\pi}{c}(u_1 - u_2)\right)\right]$$

only influences the width of the phonon spectrum gap rather than v_1 and v_2. We therefore see that two terms in (4) have different physical meanings.

Note also that Eq. (4) is internally contradictory. Indeed, the expression for energy only contains one harmonic, and this expression is obtained in the continual approximation, in which displacements $(u_1)_n$ and $(u_2)_n$ are replaced by fields $u_1(y)$ and $u_2(y)$, and the summation over atoms is replaced by the integration over the chain. This is the result of using the Poisson summation formula. The condition that allows us to retain a single harmonic in the obtained Fourier expansion of the potential is the collective character of interactions, when substrate for a given atom is formed by many neighboring chain atoms. On the other hand, it follows from (4) that the interaction between the fields is quasi-local; that is, the equation for field $u_1(y_0)$ contains field u_2 and its second derivative with respect to the coordinate only at the same y_0 point.

As (4) is extensively used to study interactions between kinks in various polymeric crystal chains and the influence of the mobility of neighboring chains on the dynamics of kinks [18] and to describe the dynamics of a fluxon in one of two interacting Josephson lines (see [21–23] and the references therein), it is interesting to determine if there exists a region of system parameters in which this equation is not physically meaningless.

The interaction energy between two chains in a crystal (see Fig. 3) is the sum of interactions of all pairs of atoms,

$$W_{1-2} = \sum_{n=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} U_{LJ}$$

$$\times\left(\sqrt{b^2 + \left[\frac{c}{2} + lc + (u_1)_{n+l} - (u_2)_n\right]^2}\right).$$

Replacing the summation over l by integration over θ in the Poisson formula,

$$W_{1-2} \approx U_0 \sum_{n=-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{d\theta}{c}$$

$$\times u\left(\sqrt{b^2 + (\theta + u_1(nc+\theta) - u_2(\theta))^2}\right) \tag{6}$$

$$\times\left[1 - 2\cos\left(\frac{2\pi}{c}\theta\right) + 2\cos\left(\frac{2\pi}{c}2\theta\right) - \dots\right],$$

we see that terms depending on the difference of fields $u_1(nc) - u_2(nc)$ at a single point nc can only appear in the expression for energy if, in calculating the integral over θ, $u_1(nc + \theta)$ can be expanded into a Taylor series and the corrections depending on θ can be assumed to be small,

$$u_1(nc+\theta) \approx u_1(nc) + \theta u_1'(nc) + \frac{\theta^2}{2}u_1''(nc) + \dots, \tag{7}$$

that is, on the segment of length $N_s c/2$, where the $u(\sqrt{b^2+\theta^2})$ function strongly varies (Fig. 4), the $u_1(\theta)$ function should be almost constant. If we are interested in the dynamics of vacancies, the characteristic spatial scale of substantial changes in $u_1(\theta)$ is the $L_k c$ kink half-width. The condition formulated above is then written as

$$L_k \gg N_s/2. \tag{8}$$

If this condition is satisfied, we can change variables

$$\zeta \equiv u_1(nc) - u_2(nc) + \theta(1 + u_1'(nc)) + \frac{\theta^2}{2}u_1''(nc),$$

$$d\zeta = d\theta(1 + u_1'(nc) + \theta u_1''(nc)),$$

$$\theta \approx \frac{\zeta - [u_1(nc) - u_2(nc)]}{1 + u_1'(nc)} \approx \zeta - [u_1(nc) - u_2(nc)],$$

$$d\theta \approx d\zeta\{1 - u_1'(nc)$$

$$- [\zeta - (u_1(nc) - u_2(nc))]u_1''(nc) + \dots\}$$

to obtain

$$W_{1-2} \approx U_0 \sum_{n=-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{d\zeta}{c}$$

$$\times\{1 - u_1'(nc) + [u_1(nc) - u_2(nc)]u_1''(nc)\}u(\sqrt{b^2+\zeta^2})$$

$$\times\left[1 - 2\cos\left(\frac{2\pi}{c}\zeta\right)\cos\left(\frac{2\pi}{c}[u_1(nc) - u_2(nc)]\right) + \dots\right].$$

Comparing this equation with (2) and (3), replacing the summation over n by the integration along the chain, and only retaining the largest terms describing the interaction of the fields, we obtain

$$W_{1-2} \approx U_0\frac{3\pi}{8\delta}\int_{-\infty}^{\infty}\frac{d\xi}{c}$$

$$\times\left\{W_0 u_1'(\xi)u_2'(\xi) + f\cos\left(\frac{2\pi}{c}[u_1(\xi) - u_2(\xi)]\right)\right. \tag{9}$$

$$\left. - fu_1'(\xi)\cos\left(\frac{2\pi}{c}[u_1(\xi) - u_2(\xi)]\right)\right\}.$$

The last term in this equation is seemingly asymmetric with respect to fields u_1 and u_2, but it can easily be reduced to the symmetrical form

$$-\frac{1}{2}f[u_1'(\xi) + u_2'(\xi)]\cos\left(\frac{2\pi}{c}[u_1(\xi) - u_2(\xi)]\right)$$

by adding the total derivative with respect to the coordinate to energy density. The first term is transformed to the symmetrical form via the integration by parts. On the assumptions made above, the third term is much smaller than the first two ones.

The first two terms in Eq. (9) for the energy density are familiar to us because they are present in (4). However in (9), "phenomenological" constants are expressed in terms of interatomic potential parameters,

$$\varepsilon_0\alpha = U_0\frac{3\pi}{8\delta}f(\delta, y) < 0,$$

$$\varepsilon_0\beta = U_0\frac{3\pi}{8\delta}W_0(y) < 0,$$

$$\frac{\alpha}{\beta} \ll 1.$$

We see that, in the terminology of [18], the interaction between two linear chains of atoms that we are considering is interchain attraction. We now know which of many variants of interactions between kinks in neighboring chains considered in [18] (depending on signs of and the ratio between α and β) corresponds to the Lennard-Jones interatomic potential.

It is known that a discrete linear chain of atoms linked by springs and lying on a sine substrate (for instance, created by immobile neighboring chains) can be described by the continual sine-Gordon equation if the static kink half-width in interatomic distance units, L_k, which is proportional to the square root of the ratio between the rigidities of springs and substrate, is much larger than one. Numerical simulation [24] shows that, already at $L_k \approx 2$–4, the kink virtually does not emit and moves at an almost constant velocity (at a not too high velocity, $v_k = 0.5v_s$). However, if the substrate is created by mobile rather than immobile chains, it is necessary that the interaction energy between chains be representable in form (9) for the kink not to radiate; that is, the $\beta(\partial u_1/\partial y)(\partial u_2/\partial y)$ term resulting in radiative friction should be small. This requires condition (8) to be satisfied, namely, the kink half-width in the chain should greatly exceed not unity but half the number of particles, N_s, that really form substrate for each atom. The table shows that, in the collective case far from the boundary, N_s can be large, whereas in real polymers, intrachain rigidity can exceed the rigidity of substrate ten times but not ten thousand times. It follows that even the necessary condition of correctness of the Frenkel–Kontorova model requires nontrivially checking it for every real polymeric crystal.

In addition, in a polymeric crystal with all free chains, collective (involving many chains) phonon modes exist which have very narrow if any frequency gaps, and the lower boundary of phase velocity equals or approaches zero. Further, because any polymeric chain consists of several atomic rows linked with each other, the $\omega = \omega(k)$ dispersion curves (ω and k are the phonon frequency and wave vector) even of an isolated chain can be bent downward in the $k \longrightarrow 2\pi/c$ region (c is the chain period). Such dispersion curves also have no lower bound of phase velocities. Note that the existence of these modes is a direct consequence of the three-dimensional character of real polymeric crystals. A kink always emits radiation into these modes by the Vavilov–Cherenkov-type mechanism (when the velocity of the kink coincides with the phase velocity of some phonon mode), but the intensity of this radiation depends on the strength of coupling between the kink and such modes. For instance, numerical simulation of the dynamics of vacancies in zigzag chains of polyethylene crystals [16] for model [25] with united atoms in place of CH_2 groups shows that this radiation is only noticeable at velocities $v_k \gtrsim 0.6v_s$, and even at such velocities, its intensity is low.

5. AN EXAMPLE OF A CRYSTAL WHOSE DYNAMICS OF VACANCIES CAN BE DESCRIBED BY THE FRENKEL–KONTOROVA ONE-DIMENSIONAL MODEL

We have shown that, there exists a simple criterion for determining the amplitude and form of the potential generated by a row of atoms. This criterion is the $\delta = c/2r_0$ parameter value relating intrachain distances to the optimal r_0 distances of interchain interactions. At $\delta < 0.4$–0.55 (the collective case), this periodic potential is close to purely sinusoidal.

An arbitrary polymeric chain consists of several rows of almost rigidly fixed atoms, and the potential of such a chain can be obtained by summing the contributions of these rows. If the $\delta < 0.4$–0.55 condition is satisfied, each such contribution has a simple analytic form, which is important for calculating crystal unit cell parameters and the form and parameters of the interchain interaction potential.

Remarkably, in the simplest model of zigzag polyethylene chains [16, 25] with united atoms in place of CH_2 groups, the δ parameter for each row constituting a zigzag approximately equals 0.299. In a more realistic complete polyethylene model [26], which well reproduces the density, structure, and unit cell parameters of the orthorhombic polyethylene phase at room temperature, the δ parameters for carbon–carbon, hydrogen–hydrogen, and carbon–hydrogen interactions between rows are

$$\delta_{\text{C-C}} \approx 0.31, \quad \delta_{\text{H-H}} \approx 0.48, \quad \delta_{\text{C-H}} \approx 0.38,$$

which also falls into the category of collective interactions (although $\delta_{\text{H-H}}$ is close to the boundary value).

On the other hand, for a kink to emit no phonons into neighboring mobile crystal chains, it is necessary that the number of atoms over the $2L_k$ kink width be much larger than the N_s number of atoms that form substrate at the given chain point. In the collective case, $N_s \geq 4$. It follows that the $L_k \gg N_s/2 \geq 2$ inequality is the necessary condition for applying the continual (rather than discrete) sine-Gordon equation and for ignoring mobility of neighboring chains in describing the nonlinear dynamics of a chain with a kink.

For instance, in the same polyethylene model [16, 25, 26], $L_k \approx 16$ and $N_s \approx 4$ (for $\delta \sim 0.3$–0.5). As polyethylene parameters are at the boundary of the collective case, the rigidity of its chains is sufficiently large for the necessary condition $L_k \approx 16 \gg N_s/2 \approx 2$ to be satisfied.

We, however, know that this is not the sufficient condition. Molecular dynamics studies of this model [16] show that, at high ($v_k \gtrsim 0.6v_s$) kink velocities, there appears weak Vavilov–Cherenkov-type radiation to collective phonon modes of the crystal, the existence of which is a direct consequence of the three-dimensional character of real physical systems.

We nevertheless see that there exists at least one polymeric crystal, polyethylene, the behavior of vacancies in which can, with caution (at not very high velocities $v_k < 0.6v_s$), be described by the Frenkel–Kontorova model (using the approximation of immobile neighboring chains plus the continual sine-Gordon equation for the nonlinear dynamics of the chain under consideration).

6. CONCLUSION

The type of the dynamic behavior of a vacancy in a polymeric crystal is determined by the N_s number of neighboring chain atoms actually forming the substrate potential near each atom of the chain containing the defect. If this number is small ($N_s < 4$), the vacancy experiences deceleration and transmits energy to atoms of the chain containing it. If N_s is larger than the $2L_k$ vacancy width, the vacancy also experiences deceleration and transmits energy to atoms of the nearest neighboring chains. Only if the condition

$$4 \leq N_s \ll 2L_k$$

is satisfied, the type of the dynamic behavior of vacancies is close to that of solitons, although, because of the three-dimensional character of systems, the energy of the defect is always slowly (in comparison with the characteristic period of chain vibrations) emitted into collective crystal phonon modes by the Vavilov–Cherenkov-type mechanism.

To summarize, we studied the possibility of applying the one-dimensional nonlinear integrable model to describe the dynamics of a topological localized soliton-type excitation in a real physical three-dimensional system. We found that there existed an interval of three-dimensional system parameters in which the one-dimensional model correctly predicted the soliton type of the dynamic behavior of defects. On the other hand, at other parameter values, defects, as distinguished from solitons, could not retain a constant velocity.

ACKNOWLEDGMENTS

The author thanks Prof. L.I. Manevich for support and fruitful discussions and the referee for valuable comments. The Mapple package was used to obtain numerical estimates and to construct plots. This work was financially supported by the Russian Foundation for Basic Research (projects nos. 01-03-33122 and 00-15-97431) and the Commission for Work with Young Scientists of the Russian Academy of Sciences (grant 123 of the 6th expert competition, 1999).

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Translated by V. Sipachev