Supersonic motion of vacancies in a polyethylene crystal

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The possibility of supersonic motion of vacancies in a polyethylene crystal is revealed by means of analytical investigation and numerical simulation. It is demonstrated that in the crystalline field of immovable neighbors, a vacancy with a core size of about 70 CH_2 groups and a velocity in the range of 1.02–1.05 sound velocity preserves itself for the time scale of about 1 ns. It is demonstrated that this type of structural defect is similar to coupled supersonic solitons described earlier in the one-dimensional chains with combined gradient and nongradient nonlinearity. An analytic approach is proposed for prediction of their shape and velocity. The simulation of the crystal with all degrees of freedom released demonstrates that the supersonic vacancy is still distinguishable. Its lifetime is less than 5 ps but still may be significant for physical applications.

I. INTRODUCTION

The concept of vacancy as a structural defect in crystals related to the absence of one or more atoms or atomic groups is very important in various branches of solid state physics. Usually the vacancies are characterized by a single parameter (dilatation volume [1]), which may be evaluated empirically in different ways. For some physical problems nonisotropic vacancy-type defects should be considered and more parameters are required [2]. Still, these parameters remain free parameters of phenomenological theory. The determination of the parameters of vacancy from molecular potentials of interaction requires solution of a three-dimensional nonlinear problem, which usually is intractable.

Polymer crystals are believed to be an important exception. The simplification is possible due to strong anisotropy of the system, related to the difference between intramolecular and intermolecular interactions. The vacancy core with nonlinear interactions may be concentrated at one chain and the problem turns out to be effectively one dimensional with the interaction with neighboring chains considered as small perturbation [3–5].

Two types of such vacancies are explored. The first type constitutes one chain stretched in such a way that exactly two CH_2 groups are absent and crystalline order may be preserved at infinity [6]. This type is referred to as a bivacancy, since two units are absent. The second type is a combination of the chain twist and stretching, which makes it possible for only one group to be absent. This defect represents a simple vacancy. Both types of defects may be at rest or move with subsonic velocities—such behavior is rather typical for vacancies. Similar results were obtained for other polymer systems [7,8].

There exists one type of nonlinear excitation in an isolated polyethylene chain that propagates with supersonic velocity and constitutes the localized wave of tension. The rea-son for such behavior is the nonlinearity of valence angle interaction [9]. If such a localized wave of tension propagated in a chain surrounded by neighboring chains in a crystal, one would get the example of a vacancy moving with supersonic velocity. It is rather reasonable to expect that such a solution will exist. The chain surrounded by the immovable neighbors is very similar to the models of a chain with combined gradient and nongradient nonlinearities [10,11]. These models are shown to have supersonic localized solutions corresponding to coupled solitons. However, it is unknown whether such a solution will exist under concrete conditions of a polyethylene crystal.

The other question is whether the model of immovable neighbors is in any way realistic for the description of the excitation of this type in a crystal. In other words, it is unknown whether the supersonic excitation will persist in a polyethylene (PE) crystal with all degrees of freedom released. This type of wave motion seems to be absolutely impossible in common low-molecular crystals because any supersonic excitation would cause very strong radiation due to Cherenkovs effect. However, rather weak intermolecular interaction in a PE crystal allows for a sufficiently long lifetime of the supersonic excitation despite the radiation. Another unaddressed question (even in the case of a single chain) is the interaction of the supersonic vacancies.

The purpose of the present paper is to explore the properties of supersonic vacancy in a PE crystal. In the second section analytical treatment of the motion of the supersonic vacancy in a chain surrounded by immovable neighboring chains is presented. The third section deals with numerical simulation of the vacancy motion both in the case of immovable neighbors and when all degrees of freedom are released. Interaction of the vacancies is also investigated.

II. ANALYTICAL TREATMENT

Let us consider the nonlinear dynamics of a single PE chain in the plane trans-conformation (Fig. 1). The chain is composed of CH_2 groups having mass m. The lengths of the
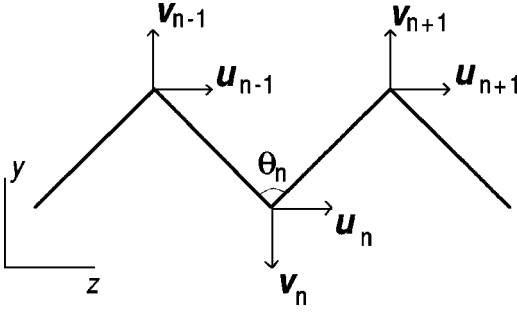
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FIG. 1. Scheme of the polyethylene chain in the transzigzag conformation (approximation of united atoms).

valence bonds are considered to be fixed and equal to l. This approximation is correct in the case considered since the rigidity of the valence bonds is about two orders more than the rigidity of the valence angles. The energy associated with the deformation of potential angles θ is determined by potential function

$$U_3(\theta) = \frac{1}{2}K_\theta(\theta - \theta_0)^2, \qquad (1)$$

where θ_0 is the equilibrium value of the valence angle.

The dynamics of the chain is considered in a continuum limit. The displacements of the masses in the direction of the z axis are denoted as u_n, and the displacements in the transversal direction as v_n (in Fig. 1, the arrows denote positive directions of the displacements).

The potential energy of the chain is presented as

$$\Pi = \frac{1}{2}K_\theta\sum_n (\theta_n - \theta_0)^2, \qquad (2)$$

and its kinetic energy as

$$K = \frac{1}{2}m\sum_n (\dot{u}_n^2 + \dot{v}_n^2). \qquad (3)$$

The changes of the angles $\theta_n - \theta_0$ may be expressed via the displacements of the masses. Then, the requirement of fixed length of the valence bonds makes the values of u_n and v_n not independent and allows us to express the Lagrange function of the chain,

$$L = K - \Pi, \qquad (4)$$

via the variables u_n and $\dot{u}_n$ only. Then, if it is supposed that u_n changes slowly with respect to n, it is possible to make a transition to continuum variables z and t and to express everything via function $u(z,t)$.

Let us introduce the notions

$$s = \sin\frac{\theta_0}{2}, \quad c = \cos\frac{\theta_0}{2}. \qquad (5)$$

The condition of fixed length of the valence bonds is thus expressed as

$$(ls + u_{n+1} - u_n)^2 + (lc + v_{n+1} + v_n)^2 = l^2. \qquad (6)$$

Consequently, we get

$$2ls(u_{n+1} - u_n) + 2lc(v_{n+1} + v_n) + (u_{n+1} - u_n)^2$$
$$+ (v_{n+1} + v_n)^2 = 0,$$

and, supposing v_n to be small compared to u_n and preserving small terms up to the second order, we finally get

$$v_{n+1} + v_n = -\frac{s}{c}(u_{n+1} - u_n) - \frac{1}{2lc^3}(u_{n+1} - u_n)^2. \qquad (7)$$

The relationship between θ_n and the displacements of the adjacent masses may be calculated as

$$l^2\cos\theta_n = -\mathbf{l}_{n-1}\cdot\mathbf{l}_n,$$

where

$$\mathbf{l}_n \equiv \{ls + u_{n+1} - u_n, lc + v_{n+1} + v_n\},$$

$$\mathbf{l}_{n-1} \equiv \{ls + u_n - u_{n-1}, -lc - v_n - v_{n-1}\}.$$

Then, the expression for the angle obtains the form

$$\cos\theta_n = \cos\theta_0 + \frac{c}{l}[(v_n + v_{n-1}) + (v_{n+1} + v_n)]$$

$$+ \frac{1}{l^2}(v_n + v_{n-1})(v_{n+1} + v_n) - \frac{s}{l}(u_{n+1} - u_{n-1})$$

$$- \frac{1}{l^2}(u_n - u_{n-1})(u_{n+1} - u_n). \qquad (8)$$

Substituting Eq. (7) into Eq. (8) and preserving the terms with appropriate order of magnitude, we get

$$\cos\theta_n - \cos\theta_0 = -\frac{2s}{l}(u_{n+1} - u_{n-1}) - \frac{1}{2l^2c^2}[(u_n - u_{n-1})^2$$

$$+ (u_{n+1} - u_n)^2] - \frac{\cos\theta_0}{l^2c^2}(u_n - u_{n-1})$$

$$\times (u_{n+1} - u_n). \qquad (9)$$

From the other side,

$$\cos\theta_n = \cos[\theta_0 - (\theta_n - \theta_0)]$$

$$= \cos\theta_0\cos(\theta_n - \theta_0) - \sin\theta_0\sin(\theta_n - \theta_0).$$

Preserving the terms up to the second order of magnitude, we obtain

$$\theta_n - \theta_0 = -\frac{\cos\theta_n - \cos\theta_0}{\sin\theta_0} - \frac{\cos\theta_0}{2\sin^3\theta_0}(\cos\theta_n - \cos\theta_0)^2. \qquad (10)$$
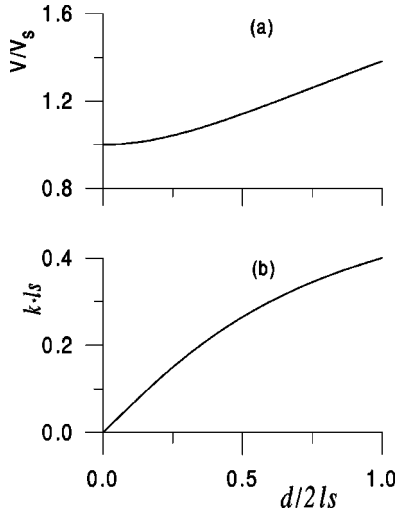
FIG. 2. Plots of the velocity (a) and inverse half-width (b) of the soliton versus overall displacement.

Substitution of Eq. (9) into Eq. (10) expresses $\theta_n - \theta_0$ via the displacements of masses in the direction of the chain axis.

Let us perform the transition to the continuum variables. The variables $u_{n\pm1}$ are expressed via the derivatives of $u(z)$ up to the fourth order,

$$u_{n\pm1} = u_n \pm ls\, u'_n + \frac{(ls)^2}{2} u''_n \pm \frac{(ls)^3}{6} u'''_n + \frac{(ls)^4}{24} u^{(4)}_n .$$

(11)

Using the expression for $\theta_n - \theta_0$ and retaining the terms of appropriate order of magnitude, we get the expression for the potential energy,

$$\Pi = \frac{2s^2}{c^2} K_\theta \int_{-\infty}^{\infty} \frac{dz}{ls} \left[u_z^2 + \frac{1}{3} s^2 l^2 u_z u_{zzz} + \frac{s^2}{c^2} u_z^3 \right]. \quad (12)$$

The condition (7) leads to the following relationship between u and v in the continuum limit:

$$\dot{v} = -\frac{ls^2}{2c} u_{zt}. \quad (13)$$
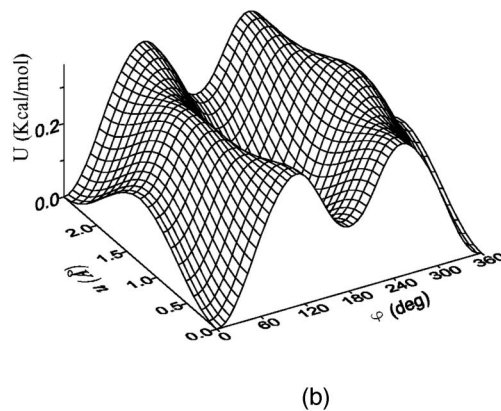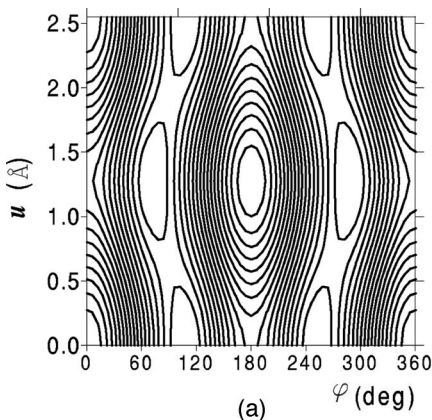
The kinetic energy is thus expressed as

$$K = \frac{1}{2} m \int_{-\infty}^{\infty} \frac{dz}{ls} (\dot{u}^2 + \dot{v}^2) = \frac{1}{2} m \int_{-\infty}^{\infty} \frac{dz}{ls} \left(u_t^2 + \frac{s^4 l^2}{4c^2} u_{zt}^2 \right).$$

(14)

The dynamical equation of the chain may be expressed via the Lagrange function in the following form:

$$\frac{\partial L}{\partial u} - \frac{\partial}{\partial t}\frac{\partial L}{\partial u_t} - \frac{\partial}{\partial z}\frac{\partial L}{\partial u_z} + \frac{\partial}{\partial t}\frac{\partial}{\partial z}\frac{\partial L}{\partial u_{zt}} - \frac{\partial^3}{\partial z^3}\frac{\partial L}{\partial u_{zzz}} = 0.$$

(15)

After simple calculations we get

$$u_{tt} - V_S^2 \left[u_{zz} + \frac{3s^2}{c^2} u_z u_{zz} + \frac{1}{3} s^2 l^2 u_{zzzz} \right] - \frac{s^4 l^2}{4c^2} u_{zztt} = 0,$$

(16)

where $V_S = (2s/c)\sqrt{K_\theta/m}$ is the sound velocity.

Equation (16) is not integrable but still its localized solutions may be computed in the form

$$u(z,t) = \frac{d}{2}\{1 + th[k(z - Vt)]\}. \quad (17)$$

Here V is the soliton velocity, k characterizes the inverse half-width of the soliton, and d is the overall displacement of the chain after the passage of the soliton. The relationship between these parameters of the solution is expressed as

$$k^2 + \frac{2}{d}\frac{c^2}{s^2}\left(\frac{4}{3}\frac{c^2}{s^2} + 1 \right)k - \frac{c^2}{s^4 l^2} = 0,$$

$$V^2 = V_S^2 \left(1 + \frac{s^2 d}{2c^2} k \right). \quad (18)$$

The concrete computations are performed with the following parameter values: $K_\theta = 79.15$ kcal mol^{-1}rad^{-2}; $\theta_0 = 113°$; $l = 1.53$ Å, $m = 14$ amu. The sound velocity in this case is equal to 14.71 km/sec. The plots $k(d)$ and $V(d)$ are presented in Fig. 2.

Let us take into consideration the field of immovable neighbors of the chain considered. The surface of the potential energy of the chain embedded in the crystal of equal

(a)

(b)

FIG. 3. Energetic surface of immovable neighbor chains [(a) and (b) are different representations].

chains is plotted in Fig. 3. The details of model used for numerical simulation incorporate with the parameters of intra- and intermolecular interaction are presented in the third section. We have considered the monoclinic structure of the crystal, where the planes of all macromolecules are parallel. The structure of the crystal was considered after the process of relaxation. The plots of potential energy of intermolecular interaction presented in Fig. 3 were obtained by artificial numerical rotation of the molecule chosen (the angle φ) and by the displacement along the axis (displacement u) in the field of immovable neighbors. The macromolecule shape that corresponds to the energy minimum is the transzigzag; therefore, we may consider only longitudinal displacement of the chain. The interaction potential related to this displacement $U(u)$ is characterized completely by the plots in Fig. 3, but for the purposes of the analytical treatment we need to know some parameters of this potential. The most natural values that characterize it are the height of the potential barrier at $\varphi = 0$ $H = 0.1753$ kcal mol^{-1} and the period of small vibrations of the chain as a whole near the equilibrium position $T = 1.5$ ps.

The intermolecular interaction may therefore be taken into account via the effective on-site potential $U(u)$. The motion equation for this case may be obtained easily from Eq. (16) by adding the appropriate right-hand side,

$$u_{tt} - V_S^2 \left[u_{zz} + \frac{3s^2}{c^2} u_z u_{zz} + \frac{1}{3} s^2 l^2 u_{zzzz} \right] - \frac{s^4 l^2}{4c^2} u_{zztt}$$

$$= -\frac{1}{m} \frac{\partial U(u)}{\partial u}. \qquad (19)$$

We do not know the exact analytical form of the potential $U(u)$. Moreover, Eq. (19) obviously has no chance to be solved analytically since it is a partial nonlinear differential equation of the fourth order. We will use for its solution the asymptotic procedure similar to one proposed in our paper [12]. First, the approximation of the propagating wave is introduced,

$$u \equiv u(z - Vt). \qquad (20)$$

Then, after substituting Eq. (20) into Eq. (19), we get

$$(V^2 - V_S^2) u'' - \frac{3s^2 V_S^2}{c^2} u' u'' - \left(\frac{1}{3} s^2 l^2 V_S^2 + \frac{s^4 l^2 V^2}{4c^2} \right) u''''$$

$$= -\frac{1}{m} \frac{\partial U(u)}{\partial u}. \qquad (21)$$

The apostrophe denotes the derivative with respect to the collective variable $z - Vt$.

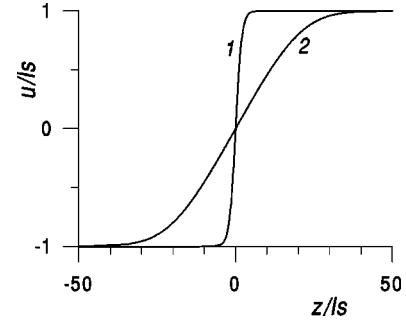Equation (21) may be simplified by substituting $p^{1/2}(u) = u'$ and one integration with respect to u,

FIG. 4. Plots $u(z)$ for two localized solutions of equation (21): $V = 1.385 V_s$ (1) and $V = 1.012 V_s$ (2).

$$(V^2 - V_S^2) p - \frac{2s^2 V_S^2}{c^2} p^{3/2} - \left(\frac{1}{3} s^2 l^2 V_S^2 + \frac{s^4 l^2 V^2}{4c^2} \right)$$

$$\times \left(p p_{uu} - \frac{1}{4} p_u^2 \right) = -\frac{2}{m} U(u). \qquad (22)$$

Now we have to take advantage of the information we have concerning the effective potential $U(u)$ (due to periodicity we restrict ourselves to consideration of the period $-ls \leq u \leq ls$). This information may be summarized as follows: (a) $U(0) = H$; (b) $U(ls + \varepsilon) = \frac{1}{2} m (2\pi\varepsilon/T)^2$ (to ensure period T of small vibrations, $\varepsilon \ll ls$); (c) $U'(0) = 0$; (d) $U^{(2k+1)}(\pm ls) = 0$ (the potential wells are symmetric with respect to inversion).

The conditions listed allow us to calculate the appropriate approximation for the function $p(u)$. This approximation is searched for in the following form:

$$p(u) = \frac{A^2 (u^2 - l^2 s^2)^2}{(1 - au^2)^2}. \qquad (23)$$

Substituting Eq. (23) into Eq. (22) and taking into account the information concerning the potential $U(u)$, one obtains the system of three algebraic equations for parameters A, a and for the velocity of the soliton V:
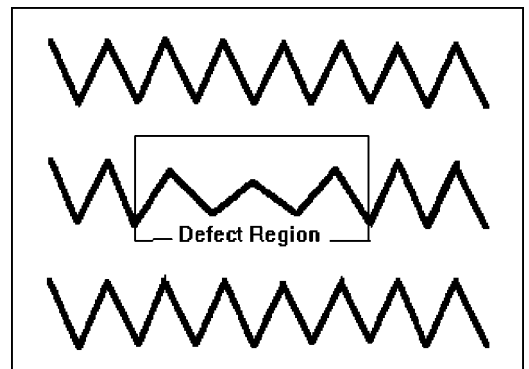

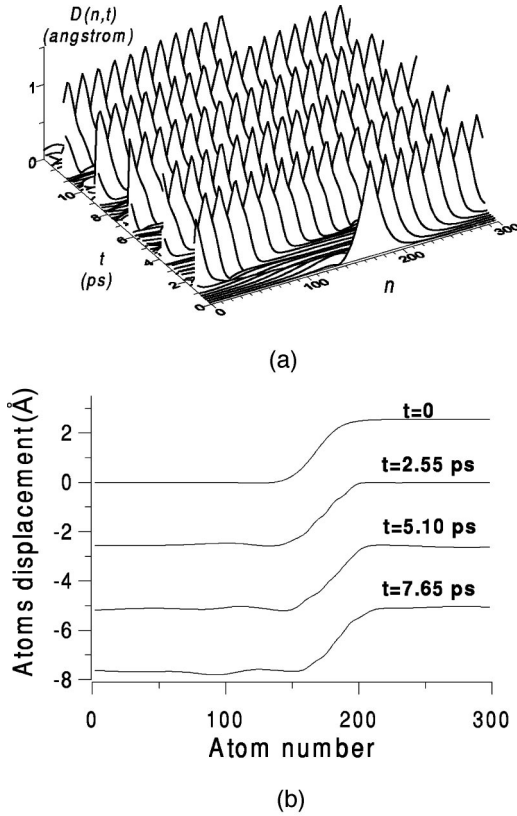FIG. 5. Schematic representation of a tensile defect.

(a)

(b)

FIG. 6. Propagation of the vacancy in the chain surrounded by the immovable neighbors: (a) deformation $D(n,t)$; (b) displacements of atoms in different time moments.

$$(V^2-V_S^2)\frac{4A^{*2}}{(1-a^*)^2}-\left(\frac{1}{3}V_S^2+\frac{s^2V^2}{4c^2}\right)\left[\frac{4A^{*2}}{(1-a^*)^2}\right]^2$$

$$=-\left(\frac{2\pi ls}{T}\right)^2,$$

$$(V^2-V_S^2)A^{*2}-\frac{2s^2V_S^2}{c^2}A^{*3}-4\left(\frac{1}{3}V_S^2+\frac{s^2V^2}{4c^2}\right)(1-a^{*2})A^{*4}$$

$$=-\frac{2}{m}H, \tag{24}$$

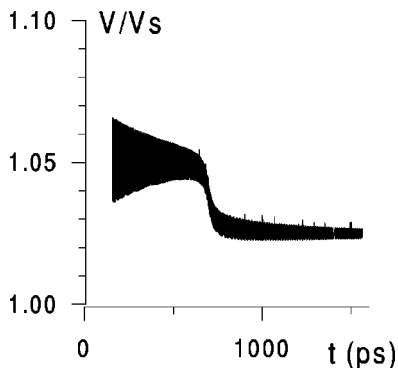

FIG. 7. Jump of the velocity of the vacancy.

$$(V^2-V_S^2)\frac{4A^{*2}}{(1-a^*)^2}\frac{1-5a^*}{1-a^*}-\frac{2s^2V_S^2}{c^2}\frac{8A^{*3}}{(1-a^*)^3}$$

$$-5\left(\frac{1}{3}V_S^2+\frac{s^2V^2}{4c^2}\right)\left[\frac{4A^{*2}}{(1-a^*)^2}\right]^2\frac{1-5a^*}{1-a^*}=0.$$

Here $A^*=Al^2s^2$, $a^*=al^2s^2$.

The system of equations (24) is solved numerically and has two sets of solutions in the supersonic region: (1) $V=1.385\,V_s\,(=20.38$ km/sec), $A^*=0.51$, $a^*=0.02$ (accuracy for this case is not very perfect, but the solution is rather nonsensitive); (2) $V=1.012\,V_s\,\,(=14.89$ km/sec), $A^*=0.047$, $a^*=0.52$.

The plots of both solutions [$u(z)$ versus z in units of ls] are presented in Fig. 4. The first solution may be predicted rather straightforwardly if considering the solutions (17),(18) for a single chain when the overall displacement is considered to be equal to $2ls$ (in other words, the surrounding chains preserve the long-range order but their effect in the core of the vacancy is neglected). This solution has rather high velocity and is very narrow—the continuum model used in the theoretical investigation is very doubtful for such a case.

The nature of the second solution is entirely different, since it obviously cannot be treated as a small perturbation of the solution for the chain without the crystalline field. It has comparatively small velocity and is sufficiently smooth to be in line with the continuum approximation used. Therefore, it may be a good candidate for the model of supersonic vacancy in a PE crystal. The next natural step is to check its applicability by means of numerical simulation.

III. NUMERICAL SIMULATION OF THE SUPERSONIC VACANCY

In order to proceed with the numerical simulation of a PE crystal, we have used the model developed earlier [13]. The rectangular cell of simulation consists of 23 polyethylene chains $(-\mathrm{CH}_2-)_{300}$ and one chain with two CH_2 groups less in order to generate the conditions for formation of the supersonic vacancy. Periodic boundary conditions are applied in all directions and therefore any excitations are allowed to move within infinitely large distances. Polymer chains were modeled in the transzigzag conformation. CH_2 groups were introduced as united atoms with mass $m=14$
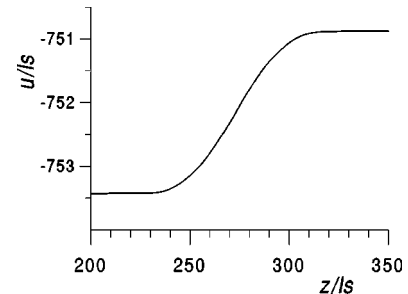

FIG. 8. Shape of the vacancy for the lower value of the velocity $V=1.03\,V_s$.
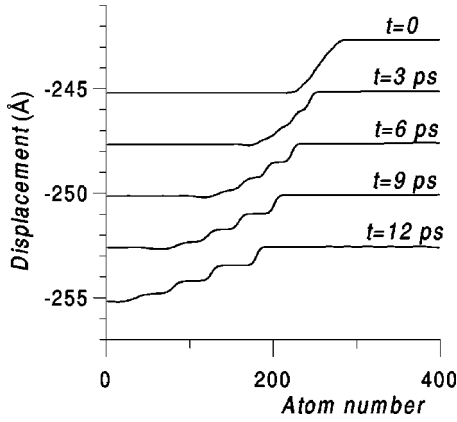
FIG. 9. Decay of the vacancy to four solitons—plots of displacements at different time moments.

amu. The valence bonds were supposed to have fixed length $l = 1.53$ Å. The interatomic interaction was described by means of potential function $U(\mathbf{r})$,

$$U(\mathbf{r}) = \sum U_3(\theta_i) + \sum U_4(\varphi_i) + \sum U_{nb}(|\mathbf{r}_i - \mathbf{r}_j|). \quad (25)$$

Here $\mathbf{r} \equiv \{\mathbf{r}_1, \ldots, \mathbf{r}_N\}$ are the position vectors of all united atoms in the cell; the first term in the right-hand side contains the summation over all valence angles, the second one over all conformational angles, and the third over all pairs of particles connected neither by valence angle nor by conformational angle interactions. The model takes into account not only the interactions within the cell but also the interactions with the particles of image cells due to periodic boundary conditions. The valence angle potential is introduced as

$$U_3(\theta) = \frac{1}{2} K_\theta (\theta - \theta_0)^2. \quad (26)$$
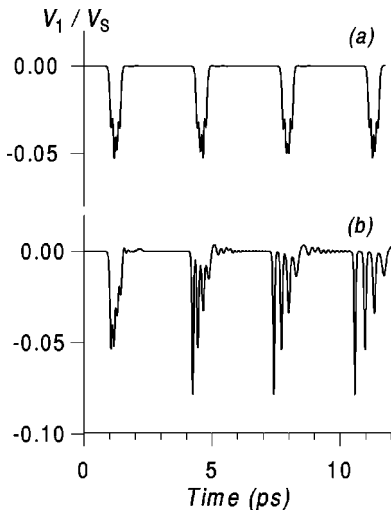

FIG. 10. Velocity of the first atom at successive passages of the supersonic vacancy in the surrounding of immovable neighbors (a) and in isolated chain (b).

Here $\theta_0 = 113°$ is the equilibrium value of the valence angle and $K_\theta = 79.15$ kcal mol^{-1} rad^{-2} is the force constant. The potentials of the torsion angles were computed as

$$U_4(\varphi) = \alpha \cos(\varphi) + \beta \cos^3(\varphi) + \gamma, \quad (27)$$

where $\alpha = 4.397$ kcal/mol, $\beta = 6.398$ kcal/mol, $\gamma = 1.998$ kcal/mol. All atoms not connected by either of the two above potentials interact via the following Lennard-Jones type potential:

$$U_{nb}(r) = \begin{cases} U_{LJ}(r) - U_{LJ}(R), & r \leq R \\ 0, & r \geq R \end{cases}. \quad (28)$$

Here $U_{LJ}(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6]$ is standard Lennard-Jones potential; R is the limit distance of interaction. We have used the following parameter values: $\varepsilon = 0.12$ kcal/mol, $\sigma = 3.8$, and $R = 2.25\sigma$.

The equations of motion of the system with geometrical constraints imposed by fixed valence bonds are written in Cartesian components as Lagrange equations of the first type,

$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = -\frac{\partial U}{\partial \mathbf{r}_i} + \sum_\nu \lambda_\nu \frac{\partial f_\nu}{\partial \mathbf{r}_i}. \quad (29)$$

These equations, together with algebraic conditions of fixed valence bonds

$$f_\nu(\mathbf{r}) = 0, \quad \nu = 1, \ldots, N, \quad (30)$$

provide a complete description of the dynamics of the system, provided that the appropriate initial conditions are also determined. The algorithm of integration is presented in detail elsewhere [13]. The sizes of the calculation cell were $3a \times 4b \times 150c$, $3a \times 4b \times 200c$, and $3a \times 4b \times 300c$, where $a = 7.031$, $b = 4.510$, and $c = 2.554$ Å are the parameters of the cell corresponding to the energy minimum.

The first series of numerical experiments was the investigation of the vacancy motion in the field of immovable neighbors. To perform this calculation the initial conditions of the particles of the short chain were introduced according to the formula (17) with different initial velocities. The other chains were artificially fixed. The initial situation for the simulation is schematically plotted in Fig. 5.

Starting from very different initial situations, the supersonic vacancy almost always (excluding the cases with relatively small initial energy) tended to a steady-shaped solution having a velocity of about 15.5 km/sec ($\approx 1.054 V_s$) and a width of about 90 Å or 70 bonds (see Fig. 6). This parameter is in rather good agreement with the results of the analytical treatment presented above, although the width of the vacancy turns out to be about 30% more. Probably the accuracy of the analytical procedure may be increased by consideration of further approximations but such treatment is extremely difficult from a technical point of view.

Great efforts were made to establish the exact shape of the solution, or, in other words, to eliminate phonons from the system in order to get pure soliton. Special friction was introduced far from the core of the vacancy and the shape has
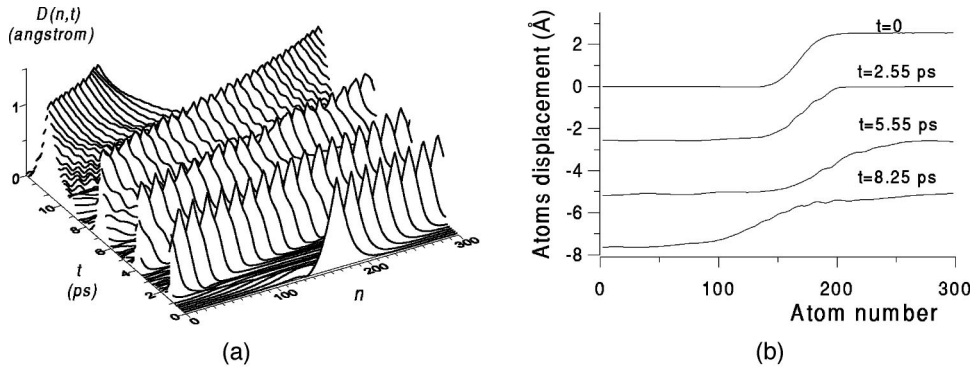
FIG. 11. Motion of the supersonic vacancy in the crystal with all degrees of freedom: (a) deformation $D(n,t)$; (b) displacements of atoms in different time moments.

repeated itself for a long time. However, the discreteness of the lattice leads to small irradiation of energy and the soliton loses its energy.

Interestingly, this loss does not occur smoothly. The energy of the vacancy decreases very slowly until it jumps to a new supersonic state with lower velocity (about 15.15 km/sec or $1.03V_s$) and even larger lifetime (we did not observe any further decay of this solution). The jump of the soliton velocity in presented in Fig. 7 and the shape of the vacancy with lower velocity in Fig. 8. The lifetime of the vacancy in the field of immovable neighbors was proved to be not less than 1 ns.

As mentioned above, the analytic solution with higher velocity (which cannot persist in the crystal) corresponds to a single soliton of a single chain with appropriate overall displacement. If the supersonic vacancy is transferred to the chain not interacting with the neighbors, it decays to a sequence of four solitons moving with close but different velocities, the lowest one corresponding to the velocity of the vacancy (Figs. 9 and 10). This result means that the supersonic vacancy represents the coupled state of few solitons of the polyethylene chain. Such coupling is impossible in a single chain and occurs due to on-site potential of the neighboring chains. The possibility of such coupling was discussed earlier in [14], but a PE crystal is the first physical system where this effect may be at least simulated. The phenomenon of the soliton coupling allows us to explain the effect of smooth decay and subsequent "drop" of the energy of the vacancy. The additional energy may be attributed to a alternative metastable coupled state of the soliton forming the vacancy. Both coupled states correspond to the same ana-

lyticsolution, as it considers only the smooth approximation of the vacancy shape and does not take into account its fine structure.

The crucial physical question to be solved by means of numerical simulation is whether the supersonic vacancy investigated in the model system of immovable neighbors will persist in a realistic model with all degrees of freedom released. The results of appropriate simulations are presented in Fig. 11. It is demonstrated that within the characteristic times of about 5 ps (or at characteristic distances of about 75 nm) the supersonic vacancy does not lose its individuality and propagates with a velocity close to 15 km/sec. This fact substantiates the idea of considerable effect of the supersonic vacancies investigated above on all processes in a polymer crystal where the vacancies are involved.

The soliton nature of the supersonic vacancy considered justifies the investigation of collision of two such vacancies. The appropriate numerical simulation (see Fig. 12) demonstrates that both in the case of immovable neighbors and in the case of all degrees of freedom released the vacancies interact almost elastically. Such behavior is typical to soliton solutions although the equations describing the motion of the vacancies are not integrable.

IV. CONCLUSION

New types of structural defects in a polyethylene crystal have been investigated. These structural defects are vacancies (more exactly, bivacancies, because they require two
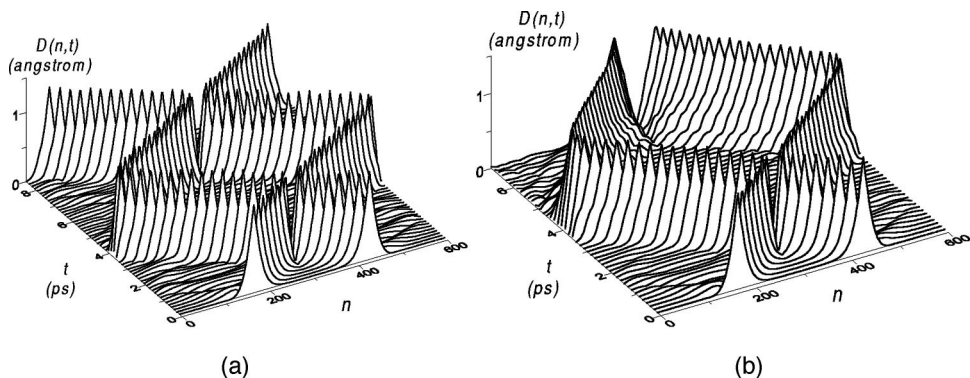

FIG. 12. Collision of two vacancies: (a) immovable neighbors; (b) movable neighbors.

CH_2 groups being absent) that move with supersonic velocity. They have a considerable lifetime and therefore may participate in all the processes related to the motion of vacancies. The asymptotic analytical procedure developed in the present paper is a reasonable tool for prediction of the properties of the vacancies investigated.

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