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Molecular-dynamics simulation of solitary waves in polyethylene

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We carry out molecular-dynamics simulation studies of two types of solitonlike defects, namely, twist elongation (TE) and twist compression (TC) of a polyethylene chain surrounded by a rigid crystal environment. We show that the TE can propagate smoothly with a wide range of velocities, but that in contrast the TC is easy to collapse into a sharply localized immobile defect. We observe that a free chain end has an attractive force to the TE soliton, which can be annihilated after interactions with the chain end. We briefly investigate the effects of thermal disorder on the soliton excitations. [S1063-651X(97)13910-1]

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I. INTRODUCTION

In recent years, large-amplitude nonlinear coherent excitations in molecular systems have attracted much attention. Solitary waves and localized modes have been used to explain many physical phenomena including energy transfer in DNA and proteins (see, e.g., Refs. [1]), and chain twistings in polymer crystals [2–8]. However, most earlier studies have been limited to simplified mathematical models, and little has been done to investigate the solitary wave dynamics in realistic molecular systems that involve not only many more degrees of freedom but also more complex interatomic interactions.

At low temperatures, crystalline polyethylene chains are packed in an orthorhombic array, where each of the repeating crystal units has two all-*trans* planar zigzag chains. At high temperatures the polymer chains contain various types of thermally created conformational defects, whose nature and role have been a subject of extensive study (see, e.g., Refs. [2–14]). In particular, some time ago Mansfield and Boyd proposed the existence of *twistons* [2], smooth 180° twists of a polyethylene chain stem accompanied with a CH_2 unit translation (so that far away from the twist region the chain goes back to the crystallographic register asymptotically). It was argued that the motion of twistons leads to dielectric relaxation and surface roughening in the high-temperature phase of polyethylene crystals by being created thermally at one chain end and traveling through to the other, leaving the chain translated along its axis by one CH_2 group and rotated through 180° relative to its original position. The solitonlike nature of the twist defects has been analyzed in the framework of idealized mathematical models such as the well known sine-Gordon equation [4] and the multicomponent generalized solitary wave models [5–8]. In these simplified soliton models the two types of twistons (twist elongation and twist compression) are entirely symmetric and equivalent, having the same energetics and dynamics.

In the present paper we study the properties of twistons in an *all-atom* polyethylene chain surrounded by a rigid crystal environment. Using molecular-dynamics techniques, we show that the twist elongation (TE) and twist compression (TC) of the chain have rather different energetics and dynamics. In particular, the TE can propagate smoothly along the chain with a wide range of velocities, but the TC defect can be easily broken into a sharply varying wave form and get pinned. In addition, we study the interactions of the TE soliton with free chain ends, and find that the chain ends have an attractive force to the TE soliton which, when near to the chain end, can be trapped and eventually annihilated. We also simulate the twiston dynamics under thermal fluctuation, and observe that the TE and TC have very different stabilities and mobilities.

II. POLYETHYLENE MODEL AND TWISTONS

We consider an all-atom polyethylene (PE) model, whose chemical formula is CH_3-$(CH_2)_n$-CH_3, n being a large integer ($n\sim 100$). The carbon and hydrogen atoms in this polymer interact with each other through the following intramolecular potential functions:

$$\text{bond stretching:}\quad E(r)=\tfrac{1}{2}K_l(l-l_e)^2, \tag{1}$$

$$\text{bond bending:}\quad E(\theta)=\tfrac{1}{2}K_\theta[\cos(\theta)-\cos(\theta_e)]^2, \tag{2}$$

$$\text{torsion:}\quad E(\tau)=K_\tau^1[1-\cos(\tau)]+K_\tau^2[1-\cos(2\tau)] +K_\tau^3[1-\cos(3\tau)], \tag{3}$$

$$\text{methyl-group rotation:}\quad E(\tau)=K_\tau[1-\cos(3\tau)], \tag{4}$$

where l is the covalent bond length, θ is the bond angle, τ is the torsional angle, and the subscript e refers to the equilibrium values. This intramolecular force field is similar to those used in Refs. [12,15,16]; the energy parameters, which are presented in Table I, are known to be determined by using experimental data such as infrared spectra and/or *ab initio* quantum-chemistry calculation results. (See Ref. [17] for more and general discussions on empirical force fields for molecular dynamics of polymers.)

The intermolecular (nonbonded) potential is taken as the exp-6 form:

$$\text{nonbonded:}\quad E(r)=A\exp(-Br)-C/r^6, \tag{5}$$

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TABLE I. Force field parameters for polyethylene.

Bond stretching
C-C: $l_e = 1.53$ Å, $K_l = 2580$ KJ/Å^2 mol
H-H: $l_e = 1.09$ Å, $K_l = 2830$ KJ/Å^2 mol

Bond bending
C-C-C: $\theta_e = 112.7°$, $K_\theta = 529$ KJ/mol
C-C-H: $\theta_e = 109.5°$, $K_\theta = 405$ KJ/mol
H-C-H: $\theta_e = 107.9°$, $K_\theta = 356$ KJ/mol

C-C-C-C torsion
$K_\tau^1 = 3.35, K_\tau^2 = -1.814, K_\tau^3 = 6.78$ KJ/mol

The end methyl-group (CH_3) rotation
$K_\tau = 6$ KJ/mol

Nonbonded interaction
C . . . C: $A = 363.6$ MJ/mol, $B = 3.6$/Å, $C = 2452$ KJ/mol Å^6
C . . . H: $A = 32.97$ MJ/mol, $B = 3.67$/Å, $C = 469$ KJ/mol Å^6
H . . . H: $A = 12.23$ MJ/mol, $B = 3.74$/Å, $C = 140$ KJ/mol Å^6

where r is the distance between the atoms. This interaction also acts as an intramolecular potential for atoms that belong to groups (CH_2 or CH_3) separated by more than three C-C bonds. The parameters for the nonbonded interactions are from Ref. [18]. Unlike the united-atom Lennard-Jones intermolecular potential used in Ref. [13], the force field (5) can reproduce the correct orthorhombic crystal structure for the polyethylene: each crystal unit contains two all-*trans* planar zigzag chains, the unit-cell dimensions are $a = 7.52$ Å, $b = 4.98$ Å, and $c = 1.274$ Å, and the chain setting angle is $\phi = 48°$ (see Refs. [2,7]).

Now we consider a single (central) PE chain surrounded by a fixed crystal environment. Any atom in the central chain will experience a force exerted by the atoms in the crystal environment via the nonbonded interactions. If we consider each CH_2 unit as a rigid group, and assume that the displacements (d_n, ψ_n, u_n) of the cylindrical coordinates for the CH_2 units are small, then the dynamics of the chain is governed by the following effective Lagrangian [5–8]:

$$\mathcal{L} = \tfrac{1}{2}(Md_t^2 + I\psi_t^2 + Mu_t^2) - \tfrac{1}{2}(K_1 d^2 + K_2 c^2 \psi_z^2 + K_3 c^2 u_z^2 + 2K_4 c d u_z) - U(\psi, u), \tag{6}$$

where $m = 14$ g/mol, $I = 2.5$ g Å^2/mol, $K_1 = 5296$ KJ/Å^2 mol, $K_2 = 83$ KJ/mol, $K_3 = 2024$ KJ/Å^2 mol, $K_4 = 1670$ KJ/Å^2 mol, and

$$U(\psi, u) = -\left[B_2\cos(2\psi) + B_4\cos(4\psi) + B_1\cos(\psi)\cos\left(\frac{\pi u}{c}\right)\right], \tag{7}$$

where $B_1 = 1.2$, $B_2 = 0.32$, and $B_4 = 1.48$ KJ/mol.

We note that the values for the force parameters K_i ($i = 1$, 2, 3, and 4) can be calculated from the (primary) intramolecular model parameters in Eqs. (1)–(4); B_i ($i = 1$, 2, and 3) depends on the intermolecular force parameters A, B, and C in Eq. (5) (see Refs. [7,8] for details).

The function $U(\psi, u)$ is an approximation to the total intermolecular potential energy for the CH_2 group in the central chain. This potential has a series of equivalent ground states due to the periodic structure of the crystal lattice. As a result, system (6) can support topological solitons. In particular, a traveling solitary wave has the following approximate solution [8]:

$$\psi(z) = \frac{\pi}{2} + \tan^{-1}\left[\frac{1}{\eta}\sinh\left(\frac{2\eta(z - z_0 - vt)}{c\sqrt{K_2/B_2}}\right)\right], \tag{8}$$

$$u(z) = \sigma\frac{2c}{\pi}\tan^{-1}[\exp\gamma(z - z_0 - vt)], \tag{9}$$

$$d(z) = -\sigma\frac{K_4\gamma c^2}{K_1\pi}\frac{1}{\cosh[\gamma(z - z_0 - vt)]}, \tag{10}$$

where $\eta = \sqrt{1 + 4B_4/B_2}$, $\gamma = (\pi/c^2)\sqrt{B_1/(K_3 - K_4^2/K_1)}$, v is the soliton's velocity, and z_0 denotes its initial location. This soliton configuration represents a smooth twist of the polymer chain: $\psi(z)$ describes the rotation of the chain around its long central axis; and $u(z)$ represents the translational mismatch (in the chain direction, or the z axis) accompanied with the twist. When z goes from $-\infty$ to ∞, the variables $\psi(z)$ and $u(z)$ go from (0,0) to $(\pi, \sigma c)$, where $\sigma = 1$ corresponds to the twist with elongation of the chain, and $\sigma = -1$ to the twist with compression. In the framework of the mathematical model (6), TE and TC are equivalent, i.e., they have the same energetic and dynamic properties [8]. However, in the full-atom molecular model, their properties can be considerably different, as will be shown below.

III. MOLECULAR-DYNAMICS SIMULATION RESULTS

We have carried out a molecular-dynamics (MD) simulation of a single polyethylene chain ($C_{100}H_{202}$) confined in a rigid shell (consisting of 16 chains) of crystal environment. In such a simulation we only need to follow the dynamics of the 302 atoms in the center chain. We have done some preliminary simulations including more dynamical chains (thus requiring much more computer memory and time), and we found that the results are similar to the case with only one dynamical chain. This is because the surrounding chains (with no twistons) are hardly affected by the introduction of a twiston in the central chain, and they remain planar zigzag and nearly motionless. The basic idea of the MD is to integrate the Hamiltonian equations of motion numerically for all the carbon and hydrogen atoms which interact among each other via the intramolecular and intermolecular force field (1)–(5).

First we determine the twiston conformation by a pseudo-molecular-dynamics method, which employs an artificial damping term to extract energy from the chain until it is sufficiently relaxed. The initial conditions (the position for each atom in the dynamic chain) are calculated from the analytical twiston solutions (8)–(10). The final twiston conformations are presented in Figs. 1 and 2. We observe that the TE involves elongated C-C bond lengths, and enlarged

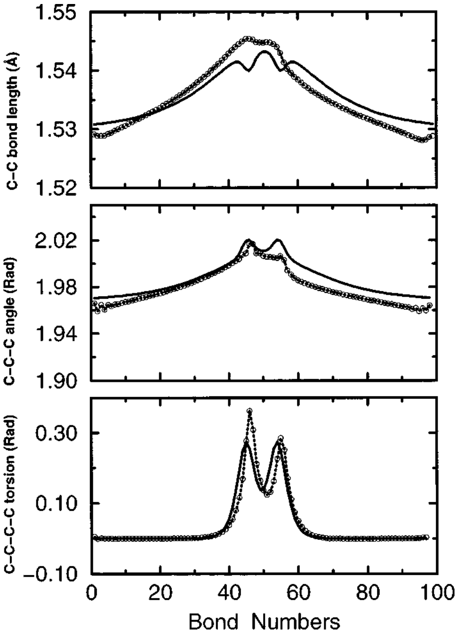

FIG. 1. The conformation of the twist elongation (TE). Shown are the internal coordinates of the carbon backbone of the polymer chain. The solid lines are from the analytical results (8)–(10), and the open circles are obtained numerically through the pseudo-MD. The bond length is in angstrom; the angles are in radian.

C-C-C bond angles from their equilibrium values. Similar to molecular-mechanics calculation results on short PE chains of Ref. [2], the torsional angles have double peaks which is a consequence of the fact that the effective intermolecular potential (7) is double-sine-Gordon-like. On the other hand, the TC involves shortened C-C bond length, reduced C-C-C bond angles, and larger torsional angles (Fig. 2). Note that TC is more localized than TE, especially in the torsional angles.

We find that TE has a conformational energy of about 95.3 KJ/mol, which is significantly higher than the energy of TC, which is about 73.8 KJ/mol. This is in contrast to previous works [2,4–8], where TE and TC have the same conformational energy. Moreover, from Figs. 1 and 2, we observe that although the torsional angle's deformation is localized in a few bonds, the distortion of the C-C bond lengths and angles spread over a wide range due to the high stiffness of the bond stretching and bending. Therefore the conformational energy of the twistons will strongly depend on the crystal thickness, or the chain length [2,9].

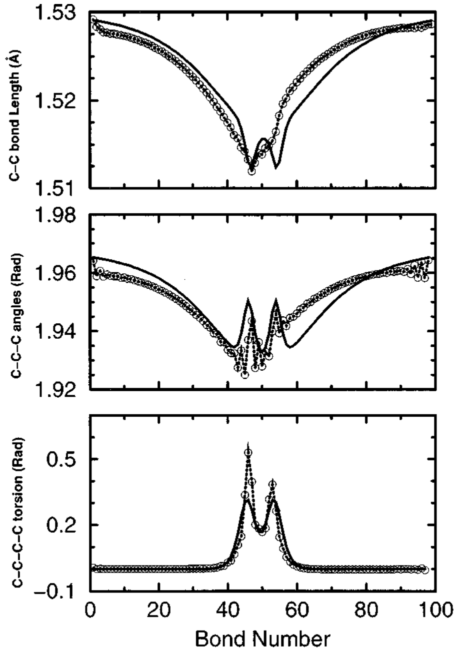

FIG. 2. The same as Fig. 1, but for the twist compression.

Given the twistons conformation, it is straightforward to investigate their dynamics and to examine whether they can really propagate like a solitary wave along the polymer chain. To this end, we carry out MD simulations with the initial atomic coordinates given by the configuration of the twistons obtained numerically through the pseudo-MD methods, and the atomic velocities computed by using the analytical solutions (8)–(10). The simulation results are summarized as follows.

The first feature of note is that (TE) can propagate along the chain for various initial velocities ranging from $v = 5$ Å/ps to $v = 20$ Å/ps (Fig. 3). In particular, if the twiston is launched at a low velocity ($\leqslant 10$ Å/ps) it will travel with little radiation of small-amplitude phonon waves (Figs. 3(a) and 3(b)]. However, if the twiston is given a high initial velocity, it will generate a lot of small-amplitude waves, and eventually the twiston will travel with a velocity lower than the initial one [Fig. 3(c)]. The TC, on the contrary, cannot travel freely along the chain. It will either be trapped if launched with a low velocity [Fig. 4(a)], or collapse into a sharp twist if given a high initial velocity [Fig. 4(b)]. (The sharp twist is similar to the intersitial-like dispiration defect of Ref. [9].)

Another qualitative feature observed in the simulation is that the chain end can create an effective attractive force to the TE twiston, because when the TE is near a chain end it will accelerate and then become trapped (Fig. 3). Moreover, the TE soliton cannot survive the interaction with a chain end; it will be destroyed, resulting a translation of the chain stem by a CH_2 unit and a rotation by 180°. This situation is in sharp contrast to the idealized soliton models [4–8], in which the interactions of a soliton with a free boundary are at least *semielastic*, i.e., the soliton may re-emerge and escape from the boundary.

The above simulation results are valid for low temperature phase of PE crystals. In the high-temperature phase the thermally introduced conformational disorder may have significant effects on the twiston dynamics. In Fig. 5 we present simulation results for the twistons under thermal fluctuations. It is seen that although the TE twiston is severely distorted, its identity can still be recognized as a group of large torsional angles diffusing along the chain [Fig. 5(a)]. In contrast, a TC is found to be very unstable under thermal fluctuations; it will soon break up into a sharp twist [Fig. 5(b)] whose diffusion is difficult because of the high-energy barrier experienced by such types of localized defects.

IV. CONCLUDING REMARKS

In conclusion, we have simulated the twistons in a long polyethylene chain surrounded by a fixed crystal environ-

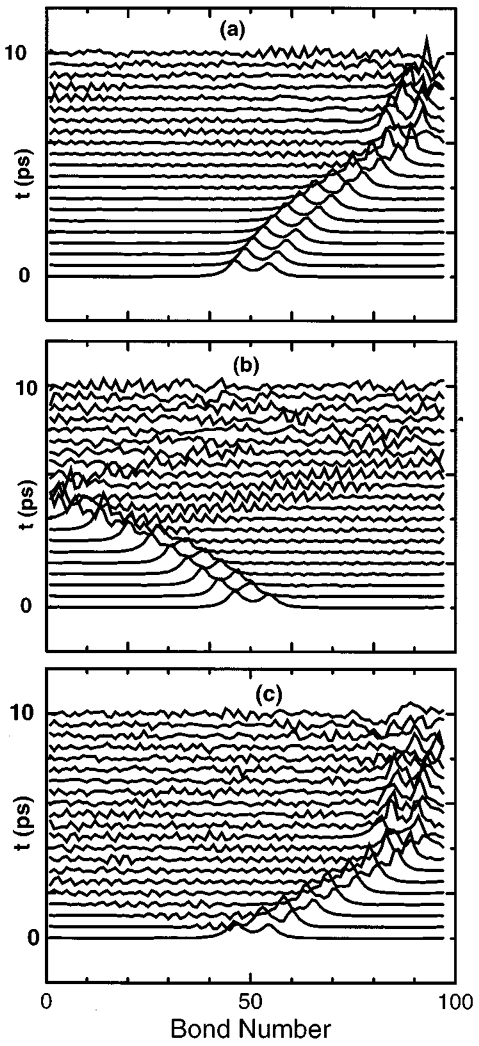

FIG. 3. The dynamics of the TE soliton for various initial velocities: (a) $v=5c/\mathrm{ps}$, (b) $v=-10c/\mathrm{ps}$, and (c) $v=20c/\mathrm{ps}$, where $c=1.274$ Å. Shown are the C-C-C-C torsional angles output every 0.5 ps.

ment. We have found that the twist elongation has a higher conformational energy than the twist compression. The twist elongation can propagate relatively smoothly along the chain, but the twist compression can easily be trapped and even broken into a sharply localized defect. Moreover, we have observed that the twist elongation experiences an attractive force when near to a free chain end, and it can be annihilated after highly inelastic interactions with the chain end.

We note that earlier investigations [2,9] of twist defects employed the molecular-mechanics method (and on much shorter PE chains), which cannot yield information on the twistons dynamics. Some researchers [13] used a united-atom model in which each CH_2 unit is represented by a structureless pseudoatom to simulate the twiston dynamics at different temperatures. Unfortunately, such a simple model cannot even reproduce the correct orthorhombic crystal structure, and thus cannot give an accurate solution for the twistons (see Ref. [7]). On the other hand, it is worth mentioning the recent constant temperature MD simulation of the rotator phase of an n-heneicosane ($C_{21}H_{44}$) bilayer [14], in which solitary waves describing 90° rotation (in contrast to the 180° rotation in the present paper) of a PE chain have been observed.

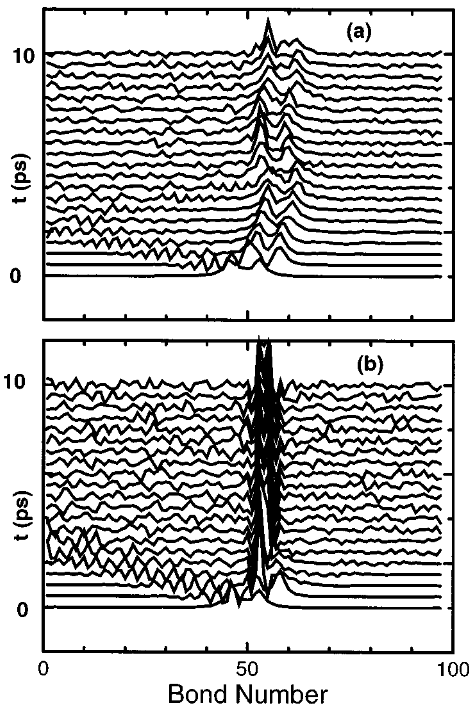

FIG. 4. The same as Fig. 3, but for the twist compression. (a) $v=30c/\mathrm{ps}$. (b) $v=40c/\mathrm{ps}$.

The present MD simulations with a realistic model have clearly established the high mobility and stability of the TE

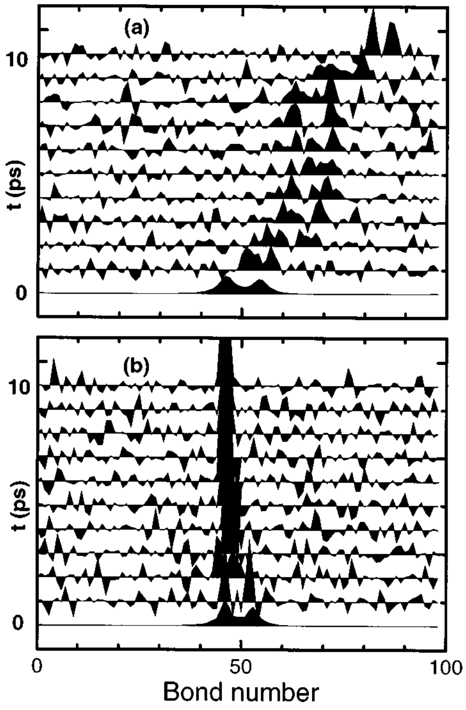

FIG. 5. The dynamics of the TE (a) and TC (b) under thermal fluctuation with an average temperature $T=300$ K. Shown are the C-C-C-C torsional angles output at every 1 ps. The larger polygons indicate the positions of the twistons.

in *long* polyethylene chains (thick crystals). Our results suggest that the TE can be an ideal candidate for explaining the dielectric relaxation phenomena observed experimentally in dipole-decorated polyethylene crystals. In addition, the propagation of the TE from one chain end to the other produces a CH_2 unit length translation of the chain; thus the creation and motion of the twist elongations can also lead to the surface roughening phenomena which have been observed in the premelting (high-temperature) phase of polyethylene crystals.

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