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Molecular Dynamics Simulation of Twist Motion in Polyethylene[†,‡]

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ABSTRACT: The molecular dynamics technique to simulate polyethylene crystals, described earlier, is used with minor modifications to study the mobility of the defect in crystal environment proposed by Mansfield and Boyd. A gradual 180° twist is added to the central atoms of a polyethylene chain before the beginning of the simulation. It is shown that the defect is mobile and when started below the barrier moves quickly to the nearest edge of the crystal.

I. Introduction

Molecular dynamics (MD) has been recently used to simulate the change of the crystal to a condis crystal,[1] the crystal to melt[2,3] transitions, and the correlation of very localized defects in polyethylene-like crystals.[4] Defect motion is an important topic since it is thought to be involved in molecular mechanisms involved in diffusion along polymer chains as observed during deformation and annealing, to cause transfer of free volume, accommodation of structural singularities, and the approach of reactive sites. Various models of the motion of rotational isomers have been presented in the polymer literature. The main tool has in the past been molecular mechanics calculations. Various types of defects have been proposed in the research literature over the last 30 years to explain the relaxation of processes such as observed by mechanical and dielectric relaxation.[5-8] Defects encompassing larger portions of the chain have also been described. The most prominent is a soft 180° twist of an all-trans chain proposed by Mansfield and Boyd extending over 12 CH_2 units as a transition state for the α process in polyethylene (PE). Figure 1 illustrates the appearance and proposed motion of the defect. The motion of the defect has been proposed to be rapid and interpreted in terms of solitons[9,10] or twistons.[11]

It is thus of interest to simulate the time dependence of defects in a polymer crystal by molecular dynamics. In our model we consider initial, dynamic defects and follow dynamically using MD the motion of this defect. This defect has not been previously studied by this technique, and in the next section we briefly present our model. The results from the molecular dynamics calculations are presented in the form of spatial plots in a time sequence appropriate for its lifetime. This is followed by analysis and discussion of the data and a number of preliminary conclusions.

II. Theoretical Methods

The technique of molecular dynamics simulation is well-known and has recently been reviewed,[1-4] so that only a minimum of detail needs to be presented here. Basically, one needs to solve Hamilton's equations or any other formulation of the classical equations of motion, starting with some initial positions and momenta of all atoms in the crystal involved, and to propagate the solution in a series of (usually) equally spaced time steps. The initial positions for rings of 6 and 12 chains are shown at the top of Figure 1. The PE chains occupy the appropriate positions in an orthorhombic crystal structure. The central chain has a gradual 180° twist as proposed by Boyd[5] and detailed in Figure 2. The effective temperature of the simulation is based on the calculated average kinetic energy

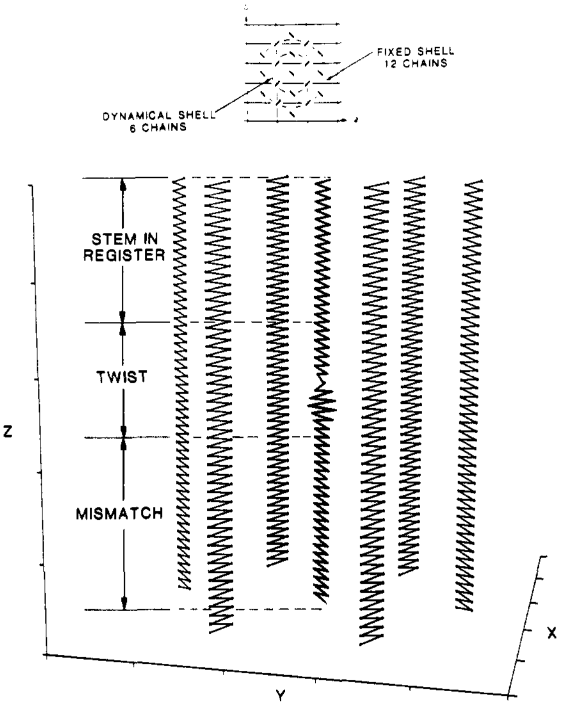

Figure 1. Diagram showing the defect modeled in our simulation in a polymer crystal environment. As time progresses, in a successful barrier crossing the defect is proposed to travel through the crystal in the upward direction.

$$\frac{3}{2}NKT = \sum_{i=1} \frac{p_x^{\,2} + p_y^{\,2} + p_z^{\,2}}{2M}$$

For the potential energy required in the classical equations, we have used the Hamiltonian previously described:

$$H = T + \sum_{\substack{\text{bonded}\\ \text{two}\\ \text{body}}} V_{2b} + \sum_{\substack{\text{bend}\\ \text{three}\\ \text{body}}} V_{3b} + \sum_{\substack{\text{torsion}\\ \text{four}\\ \text{body}}} V_{4b} + \sum_{\substack{\text{nonbonded}\\ \text{for}\\ \text{dynamic}\\ \text{atoms}}} V_{NB} + \sum_{\substack{\text{nonbonded}\\ \text{for}\\ \text{dynamic–}\\ \text{static}\\ \text{interactions}}} V_{NB} \qquad (1)$$

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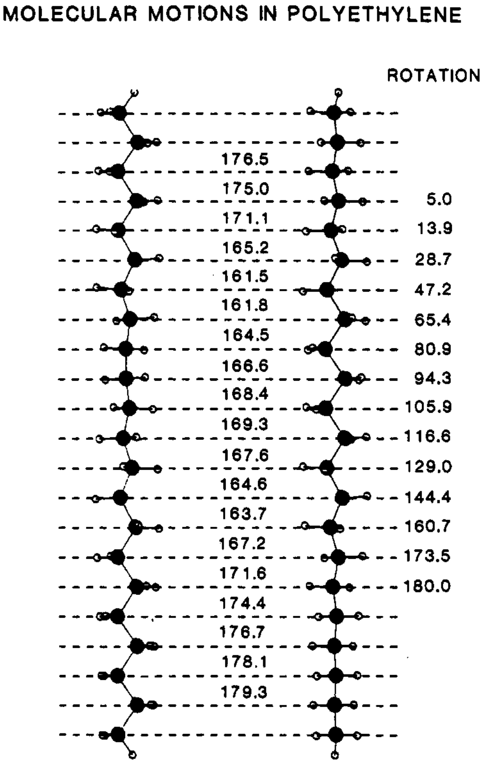

Figure 2. Two views of the defect chain with the torsional coordinate value for each of the 20 atoms in the Boyd defect and 14 atoms in our simulations. (See Figure 4 of ref 5.)

Table I
Potential Energy Parameters

two-body bonded constants	two-body nonbonded constants
$D = 334.72$ kJ/mol	$\epsilon = 0.4937$ kJ/mol
$r_e = 0.153$ nm	$\sigma = 0.4335$ nm
$\gamma = 19.9$ nm^{-1}	four-body bonded constants
three-body bonded constants	$\alpha = -18.4096$ kJ/mol
$K_3 = 130.22$ kJ/mol	$\beta = 26.78$ kJ/mol
$\cos\theta_0 = \cos 113° = 0.3907$ rad	

The potential functions are

$$V_{2B}(r_{ij}) = D[1 - \exp(-\alpha(r_{ij} - \hat{r}))]^2 \qquad (2)$$

for the adjacent bonded atoms

$$V_{NB}(r_{ij}) = 4\epsilon[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6] \qquad (3)$$

for the interaction between any two atoms *not* directly bonded (only 1–4 type interactions and larger), and

$$V_{3B}(\theta_{ijk}) = {}^1/_2\gamma_\theta(\cos\theta_{ijk} - \cos\theta_0)^2 \qquad (4)$$

for the bending of a three-atom sequence. The four-body term is the one developed by Boyd:

$$V_{4B}(\cos\tau) = 8.3 + \alpha\cos\tau + \beta\cos 3\tau \qquad (5)$$

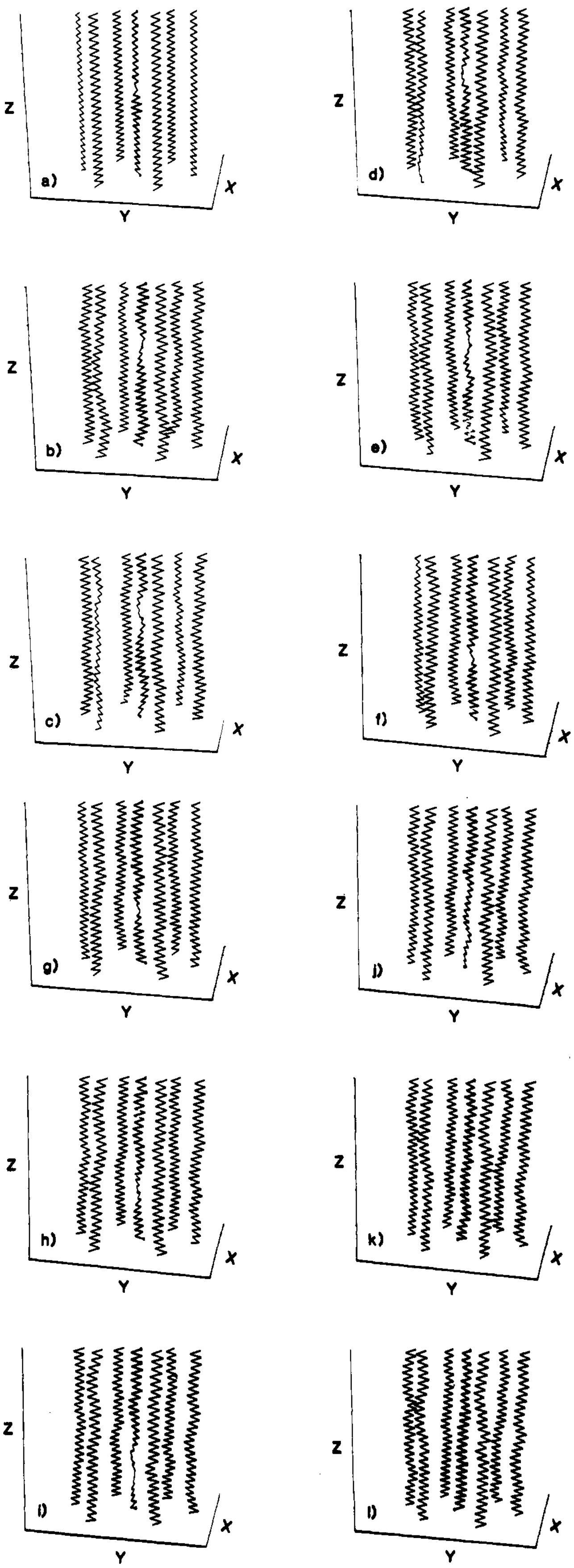

Figure 3. Movie of the first 2 ps of the defection motion for the lower 50 atoms of the 7 dynamic chains. The average temperature of the simulation was 50 K. Time sequence is in steps of 0.3 ps for a–e, f is at $t = 1.4$ ps, and the steps are 0.1 ps thereafter.

D, α, and $\hat{r}$ (see eq 1) represent the usual Morse oscillator parameters, and ϵ and σ (eq 3) represent the Lennard-Jones parameters. The bending force constant is γ_θ and θ_0 is the equilibrium value of the angle formed by the three atoms of interest in a particular bond. The values of α and β are potential parameters for the barrier to rotational isomerization. The barrier for the trans–gauche transition is 16 kJ/mol, with the trans conformation being 4 kJ/mol more stable than the gauche. The values of all the parameters are listed in Table I.[12] The model of PE consists of seven dynamic chains of 100 atoms each. Hamilton's equations $\dot{q} = \partial H/\partial P$ and $\dot{p} = -\partial H/\partial q$ were solved on a CRAY XMP using ODE.[13] Two chains make up a unit cell in crystalline PE (see Figure 1). In the orthorhombic phase of PE, it is very useful to view the crystal as consisting of consecutive cylinders of PE chains. The

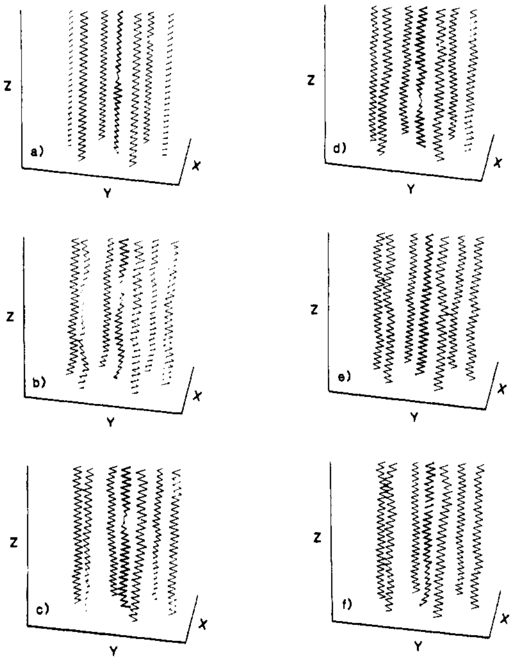

Figure 4. As in Figure 3, but with Δt = 0.5 ps.

number of chains in each cylinder is determined by repeating the unit cell. The unit cell lengths along the *a*, *b*, and *c* axes were taken as 0.74, 0.49, and 0.26 nm, respectively. The central seven chains were the only chains allowed to move in this preliminary model. Nonbonded interactions between the central chain and all stationary chains were taken into account, as well as the intrachain nonbonded interactions in the seven chains. The details of the defect proposed by Boyd are shown in Figure 2, where a gradual 180° twist is spread over 14 atoms in the central chain. Each atom in our simulation of the 14-atom segment is rotated by the cumulative rotational angle calculation from the torsion coordinate in Figure 2. For example, the first atom is rotated 5.0°, the second atom 13.9°, etc., up to 180° for the 14th and following atoms. Expansion of the crystal model to three and four mobile cylinders has been considered in ref 14, and it was found that little additional insight is offered by these considerably larger computational efforts.

III. Results

For the first set of simulations, the defect begins at atom 17 and runs to atom 30 from the bottom in a 100-atom-thick crystal. This point is well to one side of the potential energy barrier of the defect, about 25 kJ/mol below the top, which is expected for a defect in the center of the chain.[5] The bottom 50 atoms are plotted in a time sequence. The simulation with the smallest time increments is shown in Figure 3a. The plots are not equally spaced in time until Figure 3f; then the figures are at Δt = 0.1 ps per frame. At T = 50 K the chain snapped back into a perfect zigzag chain at t = 1.8 ps. Figures 4–7 show a similar simulation sequence with a lower simulation accuracy (smaller cutoff range for the nonbonded interactions, nm) at time spacing of 0.5 ps. In Figure 4, the simulation with T = 50 K is repeated. The chain isomerized to the crystal structure between t = 1.5 and 2.0 ps as before. In Figure 5, data for T = 150 K are shown. This time the chain does not flip before 2.5 ps. In Figures 6 and 7, T = 320 and 420 K, respectively, are simulated. The chain flips occur at about 1.5 and 2.0 ps, respectively. For these last two cases, the conformational disorder, typical in this temperature region, washes out the smooth twist almost immediately. Below this temperature, one can observe a smooth motion of part of a twist, but only for 1.0–2.0 ps. In all cases the motion of the twist was downhill energetically to the nearby crystal surface. In order to determine if the previous calculations were very dependent on the location of the defect, another simulation was run with the defect centered in the crystal. For this, the temperature was chosen to be 150 K and corresponded to the results in Figure 5. We observed that this defect condition reduced the amount of time needed to flip the chain. Because more energy is stored in the part of the stem out of register, it can relax at a faster rate.

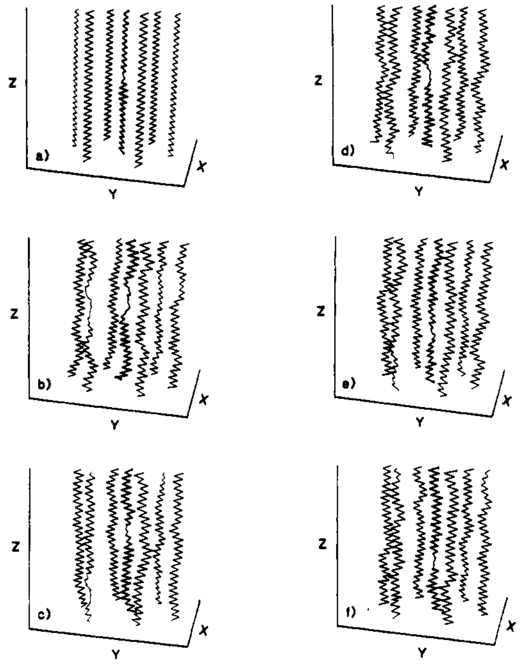

Figure 5. As in Figure 4, but with T = 150 K.

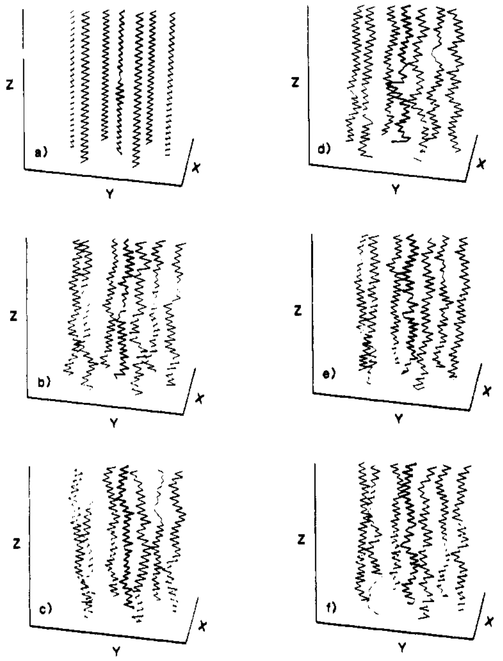

Figure 6. As in Figure 4, but with T = 320 K.

Overall, the simulations have thus shown that the initially introduced defect has a lifetime of no more than 2 ps. Its travel direction is that of the least resistance. At

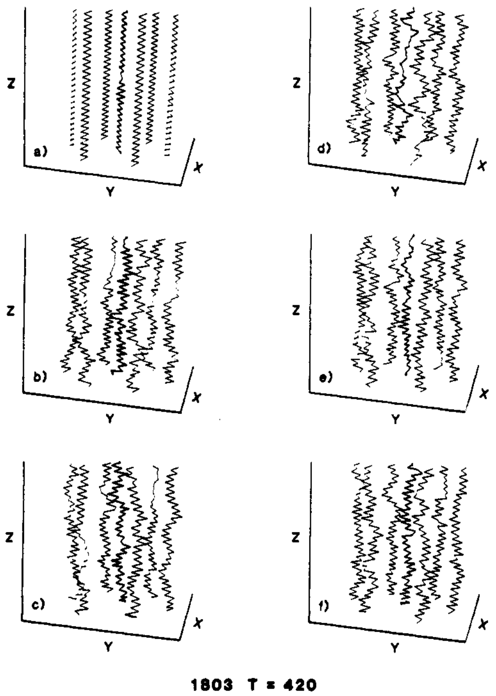

Figure 7. As in Figure 4, but with T = 420 K.

temperatures above 320 K, randomly produced local torsional defects of more than 90° rotation angle are so frequent that one expects that any diffusion processes will make use of the drift of such random defects in a free energy gradient. More details of the thermally introduced conformational disorder have been reported earlier.[15]

IV. Conclusions

In this paper we have presented a simulation of a defect first proposed by Mansfield and Boyd to explain the α-relaxation process in dipole-decorated polyethylene. In our calculations and model we have several conclusions: (1) The proposed defect motion is downhill energetically to the nearby crystal surface. (2) The defect proceeds very rapidly to the crystal edge and becomes quenched on a picosecond time scale. In our simulations, no special soliton-like transmission of the defect was observed. (There may be several reasons for this. (1) The defect may require a slightly different form. (2) Chaotic dynamics may destroy coherent motion required for solitons.) (3) At a sufficiently high-temperature conformation, defects are introduced randomly that may, in the presence of an electric field, enhance the formation of twist defects.

In future work, we plan to study the spectral changes for this defect. Because of the very short lifetime of the defect, it would be impossible to compute dispersion curves by the normal FFT method coupled with MD calculations. However, the MUSIC method recently introduced in the polymer dynamics literature[16,17] is capable of determining spectral shift for even such short-lived defects.

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