Computer simulation of energy flow in polyethylene

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The behaviour of energy flow in a model chain of amorphous polyethylene is discussed. The rate of energy flow through the backbone of a polyethylene chain was studied as a function of density, stretching force constant and temperature. It is found that the energy flow rate is initially fast and then becomes slower.The dispersion of excitation energy is found to be accelerated by energy transfer through non-bonded interactions. The rate of energy flow is also sensitive to the stretch force constant and temperature of the system.

(Keywords: energy transfer; amorphous; polyethylene)

INTRODUCTION

The determination of pathways of energy flow within molecules has been the focus of intense research for several years[1–12]. The pathways of energy flow are important in chemical reaction dynamics. For macromolecules, the energy flow behaviour is more complicated. Graener and Laubereau[4] studied the vibrational decay of crystalline polyethylene (PE) with time-resolved vibrational spectroscopy. The CH vibrational modes were excited using laser pulses. They observed that the time of excitation energy to flow out of the modes is ~5 ps. They suggested that this energy flow is due to Fermi resonance between CH stretches and HCH bends. Sumpter and co-workers[5,6] studied theoretically the energy flow behaviour of CH stretches in the PE chain, where the excitation energy was added to the CH stretching mode. They found that the rate of energy flow from an excited CH stretching mode occurs in <0.5 ps and increases with temperature. Their result demonstrates that the energy flow involves strong resonant pathways. In short-time dynamics, the CH stretching-HCH bending resonance is dominate. For long-time dynamics, redistribution of the initial excitation energy is the major process involved. This energy redistribution is complete within 2 ps.

Unlike the above-mentioned authors, we are interested in the energy flow through the backbone of a polymer chain. In this study, amorphous PE was examined. Simulations were performed below the glass transition temperature of PE (-40°C)[13,14]. The PE chain was excited by adding kinetic energy on the methyl group of one end of the chain. The rate of energy flow was studied as a function of density, stretching force constant and temperature.

METHOD

Molecular dynamics (MD)

A PE chain is modelled as sequences of 800 beads, each bead representing a methylene or methyl group, which are placed in the middle and the two ends of the chain, respectively. These beads are connected to their neighbours by spring-like C–C bonds. The cubic MD cell contains a single PE chain. The periodic boundary conditions produce replication of the basic cell in the three Cartesian directions. All the beads are subject to the bond stretching potential, bending potential, torsional potential and truncated Lennard–Jones 6-12 potential. This force field is adopted from reference 15. The individual potentials are as follows:

1. Bond stretching potential

$$E_b = (1/2)k_b(l - l_0)^2$$

where k_b is a force constant, and l and l_0 are the instantaneous and equilibrium bond distances between two neighbouring beads.

2. Bending potential

$$E_\theta = (1/2)k_\theta(\cos\theta - \cos\theta_0)^2$$

where k_θ is a force constant, and θ and θ_0 are the instantaneous and equilibrium bond angles.

3. Torsional potential

$$E_\phi = k_\phi \sum_{n=0}^{5} a_n \cos^n \phi$$

where k_ϕ is a force constant, a_n is a constant and ϕ is the instantaneous torsional angle.

4. Lennard–Jones potential for non-bonded interactions

$$E_{nb} = 4\varepsilon^*[(r^*/r)^{12} - (r^*/r)^6]$$

where ε^* and r^* are Lennard–Jones parameters and

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r is the distance between two non-bonded beads. The force constants and parameters are the same as in reference 15.

The cut-off distance in this work is $3.1r^*$, which is larger than that in reference 15 ($1.5r^*$), to improve the precision of our simulation. The standard MD simulation is carried out. The Newtonian equations of motion for all beads have been solved numerically by using Beeman's algorithm[16]. The integration time step is 1.2 fs.

Preparation of system

A single chain containing 800 methylene (or methyl) beads was put into a large MD box. The beads were connected as follows; the bead-to-bead distance was randomly chosen in the range $0.7–1.3l_0$ and the angle between consecutive beads was set up in the range of $0.7–1.3\theta_0$ in a random direction. After the configuration of the chain was constructed, the velocities of the beads were chosen according to a Gaussian distribution. The MD simulation was then started at the given temperature and the chain was moved under the given force field (including long range interaction and torsional terms). The system was allowed to 'equilibrate' until the kinetic energy of the system was fluctuating within a predetermined range ($\sim 3/2Nk_BT$, where N is the total number of beads, k_B is the Boltzmann constant and T is the absolute temperature). The size of the box was then reduced slightly, and the system was again allowed to equilibrate. This process was repeated until the density of the system matched the desired density. (The purpose of this procedure is to avoid overcrowding of the system at the starting point of the MD run.)

The dynamics of the model chain was simulated in four different systems in order to examine various effects on the energy flow: the 'normal system' was a system of amorphous solid with a density of 0.9 g cm^{-3} at 100 K; the 'high temperature system' was the same as the normal system but the temperature of the system was raised to 200 K; the 'reduced system' was the same as the normal system but the stretching constant was reduced to half of its original value; the 'free system' was a system in which the model chain was within a large MD box with a box length of 500 σ at 100 K. (In the free system, the box size is much larger than the chain dimension so that no chain-to-chain interaction is possible.)

Analysis

To excite the model chain, excitation energy was added to the kinetic energy of the methyl group on one end of the chain. The excitation energy was selected as 210 kJ mol^{-1}, which is the same magnitude as that used by Bintz and co-workers in the excitation of benzene[17]. While the systems were excited, parallel simulations without excitation were carried out. These unexcited systems were used as references to investigate the changes of energies for the excited systems.

In order to analyse the energy transfer in the model chain, the segmental energies were examined. Each segment was composed of six consecutive beads. The first segment was constituted by the 1st to the 6th bead, the second segment by the 2nd to the 7th bead, and so on. Overall, the model chain contained 795 segments. The segment was chosen for convenience to include all types of interaction. The segmental energy was taken as the sum of the kinetic and of all the interaction energies of the beads. The interaction energy included five bond stretches, four angle bends, three torsions and three Lennard–Jones interactions.

RESULTS AND DISCUSSION

In all simulations, the changes of segmental energies were obtained by taking the energy difierence between the excited and unexcited systems. This was used to determine the energy transfer behaviour. *Figure 1* shows a plot of activated segments *versus* time after excitation for the free system. The activated segment is determined when the energy difference is $>5\varepsilon$. The figure shows that the rate of activated segment formation in the chain is fast in the initial 0.4 ps. In the initial 0.4 ps and again between 0.4 ps and 1.8 ps the activation rate is linear. Therefore, at least two distinct rates of energy flow are observed. By 2.4 ps, the energy has been transferred to the 85th bead.

Figure 2 shows the changes of segmental energies of the model chain for the free and normal systems at four different times (0.012, 0.24, 0.84 and 2.4 ps) after excitation. *Figure 2a* shows that in both systems the excitation energy is accumulated in the first segment within 0.012 ps. *Figure 2b* shows that at 0.24 ps the excitation energy is dispersed into other segments. The energy has flowed to the 15th segment in both systems. In the free system, most of the energy is still accumulated within the first 5 segments at this time, but in the normal system the majority of the energy is dispersed among the first 13 segments. This indicates that the rate of energy dispersion for the normal system is faster than for the free system. This energy dispersion on the backbone of the chain is obviously influenced by its surroundings. In *Figure 2b*, some additional bumps on the later part of the chain are also observed. These bumps correspond to the energy differences of the 65th, 90th and 145th segments. These bumps arise from the non-bonded energy transfer. *Figure 2c* shows the energy differences at 0.84 ps after excitation. In both systems, the excitation energy flows into the 35th segment. For the free system, most of the excitation energy is accumulated within the first 20 segments. For the normal system, the majority of the excitation energy is accumulated within the first 30 segments. Aside from this, the rest of the chain is also affected. This is due to the influence of the bumps in

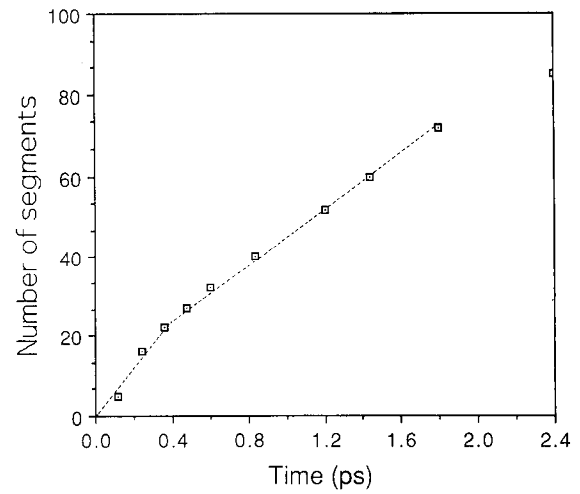

Figure 1 Number of activated segments within 2.4 ps for the free system

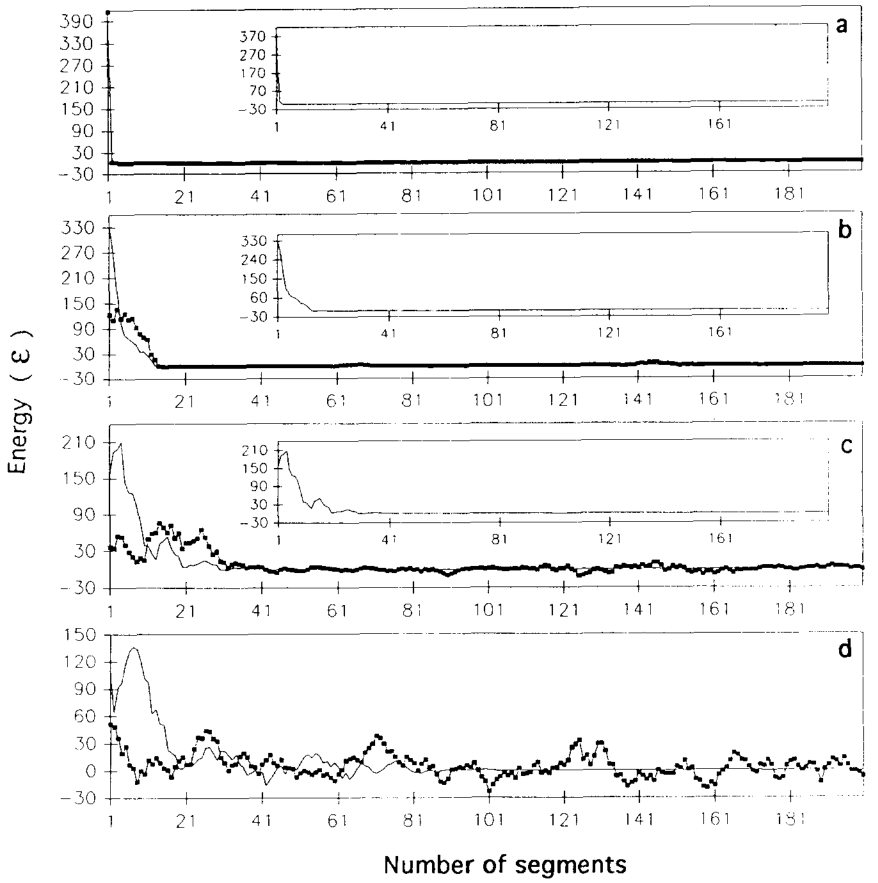

Figure 2 Differences of segmental energies for the normal system (■) and the free system (———) at: (a) 0.012 ps, (b) 0.24 ps, (c) 0.84 ps and (d) 2.4 ps. For clarity, the insets show the energy differences of the free system

Figure 2b and further non-bonded energy transfers. *Figure 2d* shows that in the normal system all the excitation energy is dispersed through the chain by 2.4 ps, while in the free system the energy has only flowed to the 90th segment. This indicates that the non-bonded interaction process is very important in energy transfer behaviour. It will accelerate the dispersion of the excitation energy. *Figure 3* shows the relationship between bead and distance for the normal and free systems. The figure shows the distance from the first bead to the nth bead before excitation. This provides information on how the PE chain is packed in systems. In the free system a linear relationship is observed, which indicates a stretched PE chain structure. In the normal system the distances oscillate in a range of 2–6σ, indicating a lump-like structure for the PE chain in the amorphous solid. This structure allows energy transfer through non-bonded interactions over short distances. *Figure 2b* shows bumps in the early stage after excitation. These bumps occurred around special beads which were close to the first bead according to *Figure 3*. This is the evidence of non-bonded energy transfer, even in the early stage after excitation.

In order to understand the effect of force field in the chain on the energy transfer process, simulation of the reduced system was also carried out. *Figures 4a* and *b* show the energy difference of a PE chain for the reduced and normal systems, respectively, after excitation. *Figure 4a* shows that at 0.84 ps the majority of the excitation energy is accumulated within the first 30 segments. The maximum is found around the 6th segment with the energy difference being ~100ε. Other distinct maxima within an energy difference of >60ε are found around the 3rd and the 20th segments. *Figure 4b* shows that at the same time the majority of the excitation energy is accumulated within the first 40 segments. The maximum is found around the 15th segment with the energy difference being ~75ε. Two other maxima with an energy difference of >60ε are found around the 16th and the 24th segments. Therefore, the rate of energy transfer for the reduced system is slower than for the normal system.

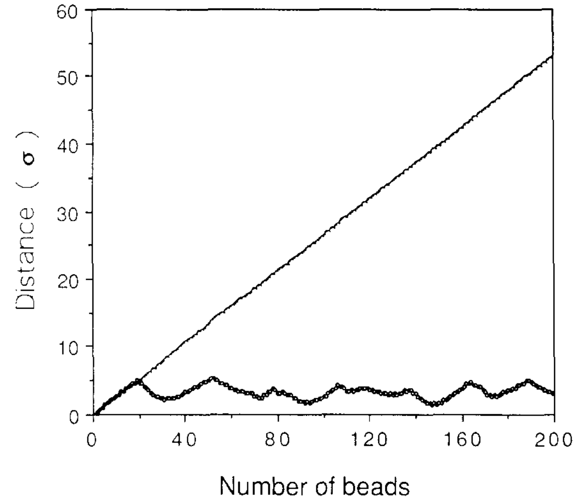

Figure 3 Distance from the first bead to the nth bead of the model chain for the unexcited free system (———) and the unexcited normal system (○)

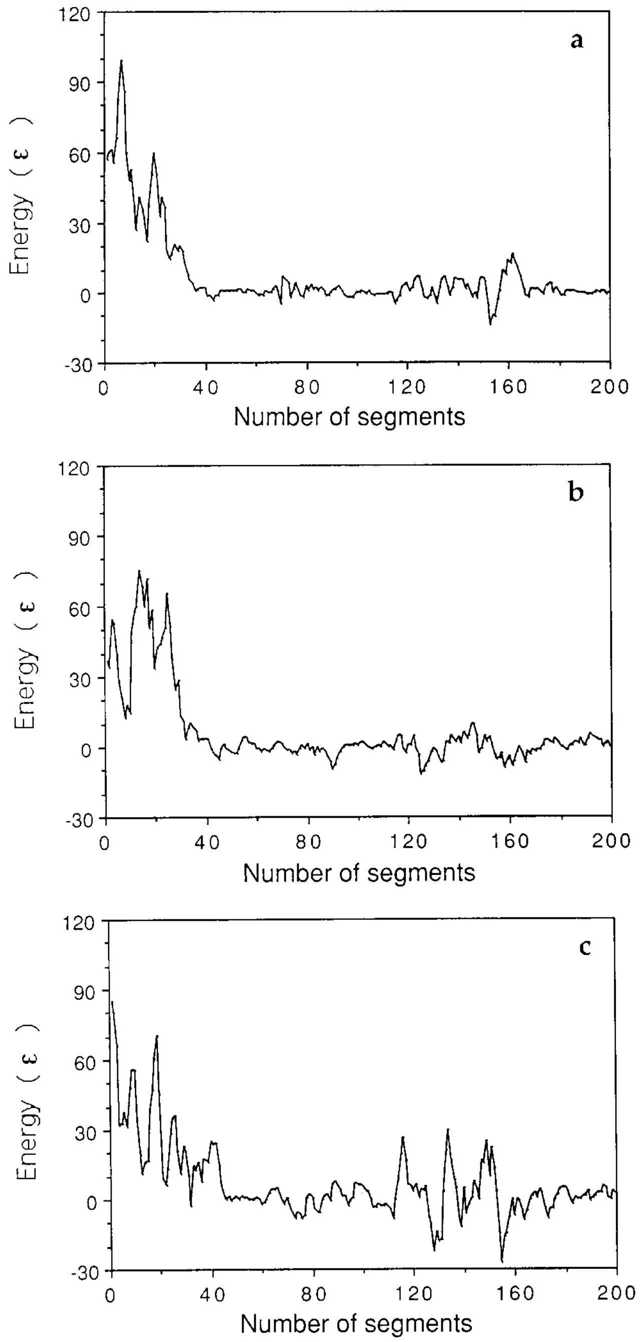

Figure 4 Differences of segmental energies between excited and unexcited systems for (a) the reduced system, (b) the normal system and (c) the high temperature system at 0.84 ps

This indicates the significant effect that the stretching force constant has on the energy transfer process. Unlike the potential used by Sumpter *et al.*[5,6], in our force field the stretching and bending potential were harmonic, so no anharmonic stretch–bend coupling existed. Therefore, the energy flow could only be caused by the dynamic coupling and non-bonded interactions. Dynamic coupling refers to the coupling of two internal motions involving the same atoms. The magnitude of coupling implicitly depends on the force constant. For example, Wilson's G matrix element[18] of a polyatomic molecule indicates the magnitude of coupling of internal modes. We found that energy flow is faster if the stretching force constant is larger.

Figure 4c shows the energy difference at 0.84 ps for the high temperature system at 200 K. According to the figure, the majority of the excitation energy is accumulated within the first 40 segments. Another high energy region is found between the 110th and 155th segments with a peak height of ~30ε. As previously described, the bumps are due to the non-bonded energy transfer processes. In comparison with the normal system at low temperature (*Figure 4b*), in which the majority of the excitation energy is accumulated within the first 30 segments and there is only a small bump around the 140th segment, both the rates of energy flow and non-bonded energy transfer are faster at higher temperature. This is in agreement with Sumpter and co-workers[5] for their simulation of PE.

CONCLUSIONS

The behaviour of energy flow in a model PE chain has been examined by using molecular dynamics simulation. The model chain is excited by increasing its kinetic energy and the rate of energy flow is analysed by comparing the energy differences of segments to the unexcited system. In the free system, we found that the rate of energy flow is fast in the initial 0.4 ps and then the rate becomes slower and is approximately constant within 2 ps. In the normal amorphous system, we found that the rate of energy flow is faster than in the free system. In addition to this, the energy is also transferred through non-bonded interactions. This non-bonded energy transfer accelerates the dispersion of the excitation energy through the chain. In the reduced system, we found that reducing the stretching force constant will slow down the rate of energy flow. In the high temperature system, we found that increasing temperature will accelerate both the rates of energy flow and non-bonded energy transfer.

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