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MOLECULAR DYNAMICS SIMULATIONS
OF A FLEXIBLE POLYETHYLENE:
A PROTEIN-LIKE BEHAVIOUR
IN A WATER SOLVENT

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Молекулярно-динамическое моделирование гибкой
полиэтиленовой цепи: протеин-подобное поведение в воде

Представлено молекулярно-динамическое (МД) моделирование гибкой полиэтиле-новой цепи (ПЭ), подвергнутой различным условиям нагревания, с целью изучения ее плотностного и температурного поведения. Также исследовались структурные измене-ния ПЭ в присутствии воды. Сначала было рассмотрено влияние процесса нагревания на конечное состояние полимера и исследована чувствительность его термодинамиче-ских величин, таких как плотность и энергия, к различным условиям нагрева. С этой целью были проведены три вида моделирования: «быстрое», «умеренное» и «медленное» нагревания. Было найдено, что термодинамические параметры сильно чувствительны к условиям нагрева. Затем была исследована структурная динамика ПЭ в воде при раз-личных условиях моделирования. Было обнаружено протеин-подобное поведение ПЭ в воде, подобное поведению в воде ДНК и белков. Была исследована динамика измерения структуры ПЭ. Для молекулярно-динамического моделирования использовался оптимизи-рованный пакет общего назначения DL_POLY и потенциал силового поля DREIDING. Расчеты проводились на специализированном компьютере MDGRAPE-2.

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Molecular Dynamics Simulations of a Flexible Polyethylene: A Protein-Like
Behaviour in a Water Solvent

We used molecular dynamics (MD) simulations to study the density and the temperature behaviour of a flexible polyethylene (PE) subjected to various heating conditions and to inves-tigate the PE chain conformational changes in a water solvent. First, we have considered the influence of the heating process on the final state of the polymeric system and the sensitivity of its thermodynamic characteristics (density, energy, etc.) for different heating regimes. For this purpose three different simulations were performed: fast, moderate, and slow heating. Second, we have investigated the PE chain conformational dynamics in water solvent for var-ious simulation conditions and various configurations of the environment. From the obtained results we have got the pictures of the PE dynamical motions in water. We have observed a protein-like behaviour of the PE chain, like that of the DNA and the proteins in water, and have also estimated the rates of the conformational changes. For the MD simulations we used the optimized general-purpose DL_POLY code and the generic DREIDING force field. The MD simulations were performed on the parallel computers and special-purpose MDGRAPE-2 machine.

INTRODUCTION

Flexible protein molecules are well known to roll up in water to take more structured forms or optimal conformations [1–3]. A protein or an arbitrary polypeptide chain due to the hydrophobic interactions with water turns into a secondary or even a tertiary structure, therefore allowing itself to perform its specific and unique biological functions. Thus, the hydrophobic interactions, as results of the hydrogen bonding of the corresponding groups or side chains and water, play a central role in the structural conformations and functions of biological structures [2–5]. From the experimental point of view the measurement on the protein conformation is an extremely difficult and an ambiguous task [6, 7]. Moreover, the experimental data do not provide a unique answer on a valid structural behaviour of proteins. On one hand, the protein structure can be well measured in the form of the crystal only (or as a dense solvent). On the other hand, being defined in the state of crystal, the protein structure may essentially deviate from that existing *in vitro*. It turns out that the conformations of the biological macromolecules (DNA, RNA and proteins) in water solvent are most suitable for computer molecular modelling, as well as for the design of the synthetic copolymers [8–10]. There has been a new trend in nanostructural simulations to make possible the observation of a protein-like behaviour of synthetic copolymers (with the inclusion of water and other ionic solvents) [8, 9, 11]. In the computer molecular simulations such protein-like copolymers with desired properties are easy to generate, thereby playing a huge number of the configurations efficiently.

For the polymeric materials the nature of the dynamical changes in water is similar to the hydrophobic interactions of DNA and proteins [8–12]. Thus, simulations of the flexible polymeric chains may provide useful insight into the mechanisms of the protein-water dynamics and related phenomena. Synthetic copolymers have to collapse, e. g., in a nanostructed globules with well-shaped hydrophobic cores wrapped in hydrophilic envelopes [5, 11]. The behaviour of the polymeric chains (say, in water) allows for a direct exhibition of the hydrophobic (or hydrophilic) parts. So, the simulation of the polymer and water structural dynamics is useful stage of the understanding of proteins functions and their conformational dynamics. Synthetic copolymers with a protein-like behaviour cause a special interest in material sciences due to the modern innovations in nano- and biopolymer technology. The detailed structural pictures of polymers,

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their microscopic transition behaviour, are of interest for the industry of polymer materials, for the material modification and technological aspects, etc. [12–14]. It is worth noting that the MD simulation method is one of the most convenient techniques for studying the polymer phase transitions and other technologically important phenomena (structural conformations, chain-folding processes, the time and the temperature behaviour, etc.) [15–20]. The MD simulation allows one to estimate the density-temperature changes of polymeric chains, to study their time-dependent thermodynamic properties in solvents and to explore nontrivial polymer-surface interactions [1–5, 7].

In the present work we aim to investigate the density and temperature behaviours of a flexible polyethylene (PE) via MD simulations and to investigate for a PE chain a protein-like behaviour in an explicit (water) solvent. The MD simulations have been performed on the base of the optimized general-purposes DL_POLY code [21, 22] and the generic DREIDING force field for molecular simulations [10].

DETAILS OF SIMULATIONS

The MD simulations of a single flexible polyethylene (PE) chain of about 500 (mixed CH_2+CH_3) units in length (each of CH_2 or CH_3 group is treated as a united atom) were performed using DREIDING force field. A snapshot of the initial configuration of the PE chain used in our simulations is shown in Fig. 1.

Fig. 1. Initial configuration of a flexible polyethylene chain

The initial PE configuration was constructed with the help of the built-in Java interface provided by the DL_POLY package that supports a number of the utilities for the analyzing of the results and visualization purposes.

The configuration energy of the PE model is a sum of the intramolecular valence (bonded) E_{val} and nonbonded E_{nb} interaction energies. The intramolecular energy E_{val} includes bond stretching, bond angle bending, and torsion and

inversion interactions. Nonbonded interactions consist of Van der Waals (VdW), electrostatic and hydrogen bonds. The VdW interactions were calculated by the pairwise 6–12 Lennard–Jones (LJ) potential. The LJ-parameters of the PE model were: C–C — ε = 0.0951, σ = 3.4730; C–H — ε = 0.0380, σ = 3.1597; H–H — ε = 0.0152, σ = 2.8464 (ε, kcal/mol; σ, Å). We employed the NPT ensemble; a constant temperature of 300 K was attained with the Nose–Hoover method; VdW forces cutoff was 10.5 Å and Ewald precision parameter α was set to 10^{-4}. The equations of motion were solved by the leapfrog Verlet algorithm with a time step chosen from the interval of [0.0004–0.001] ps. The relaxation constant for the heat bath variable was 0.1 ps.

RESULTS AND DISCUSSION

A Flexible PE Chain Subjected to Various Conditions

We have first considered the influence of different heating processes on the final state of the chain PE under the periodic boundary conditions. In Fig. 2 the dependence of the temperature (T) vs time (t) is shown for three heating
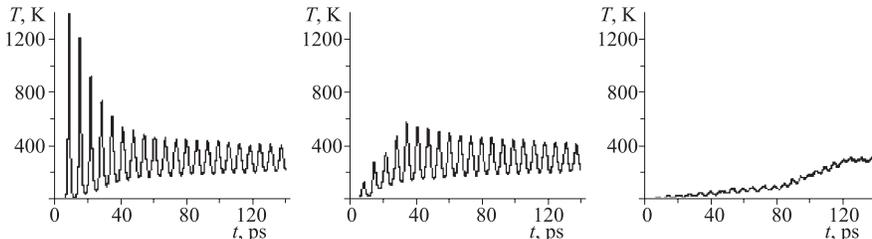
Fig. 2. The evolutions of the temperature of the system. The fast (left), moderate (middle) and slow (right) heating regimes are shown

regimes: left picture displays the fast; middle picture – the moderate; and right picture – the slow heating. Starting from the same initial state at $T(0)$ = 10 K during the system equilibration we have reached a final state of $T(t)$ = 300 K; the temperature step (ΔT) was chosen for the fast heating mode — 150 K, for the moderate — 50 K, for the slow — 10 K. The starting time t = 4 ps coincides with the end of the equilibration process.

For the above three heating processes we have estimated the evolutions of the atomic density of the system. In Fig. 3 the behaviours of the particle density are shown for the same three regimes as displayed in Fig. 2 (from left to right).

The resultant PE configurations for the above three heating modes are presented in Fig. 4 (from left to right).

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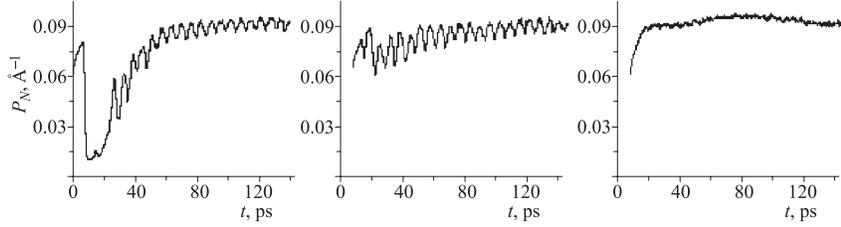
Fig. 3. The evolutions of the atomic density in the fast (left), moderate (middle) and slow (right) heating regimes
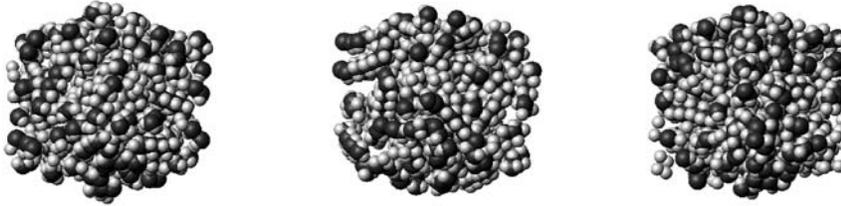
Fig. 4. The resultant PE configurations in the fast (left), moderate (middle) and slow (right) heating regimes

Summarizing the results presented above, we observe that the evolution of the temperature has a clearly different behaviour for these three heating regimes. During the fast and moderate heating we observe large temperature changes. At the same time, the slow heating yields satisfactorily small temperature $T(t)$ oscillations. In other words, the slow heating mode «smoothly» forms the equilibrium state, which manifests itself as an important stage for the final dynamics. A final state, achieved at the instant $t = 140$ ps, has approximately the same value of T for all heating regimes. For a larger MD time scales (t > 140 ps) more significant changes of the temperature values have not been observed, so far the PE system has been analyzed only at the interval from 0 to 140 picoseconds. Next, the evolutions of the atomic density of the system, shown in Fig. 3, indicate that the slow heating process leads to an equilibrium density monotonically. In the fast and moderate heating the visibly high oscillations of the density values are observed. The behaviour of the PE system under consideration is sensitive to the dynamics of the heating mode. The high temperature oscillations (the left and the middle pictures in Figs. 2, 3) are result in significant change of the particle number density. However, it is remarkable that the PE chain does not respond to these significant temperature changes. The resulting particle number densities are the same for all heating modes. In the equilibrium state ($t = 140$ ps) we have the following values, respectively: ρ_{fast}=0.165532, $\rho_{\text{moderate}} = 0.160132$, $\rho_{\text{slow}} =$

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0.165256 (g/cm^3). Thus, the large temperature oscillations, which occur in a very short period of time (viz. 10–20 ps), do not break the PE chain on constitutive fragments, so that the polymeric chain keeps its stability over a wide range of the temperature oscillations.

A Protein-Like Behaviour of the Flexible PE Chain in Water

Next, we simulated the conformation dynamics of the PE chain in a solvent. For the solvent molecules we have used the TIP4P water in the different configurations and for the different cell geometries. In Fig. 5 an example of the initial configuration of the PE chain and water is shown.

Fig. 5. The initial configuration of a polyethylene chain with cubic ice (left bottom)

To reach an equilibration for the PE chain and cubic ice, the system temperature was gradually increased from 0 to 300 K under the different heating conditions described above. A remarkable observed property of the PE chain is that, as described above, the latter keeps its stability as a whole even under the significant temperature oscillations (viz. in the fast heating process). We present the PE + ice water dynamics for the fast (initial) heating, where during the equilibration process the temperature step has chosen to be T = 150 K. In Fig. 6 the six sequential snapshots of the PE + water system at the moments of t = 5, 10, 20, 30, 40, 50 ps are displayed. Starting from the well-separated state, the PE chain is brought in contact with water. The PE chain, however, does not mix with the solvent molecules: it rather hides their fragments inside a central region («a hydrophobic core»). Such a behaviour is similar to that of a DNA or a protein interacting with water.

The dynamical behaviour of the PE chain is affected by the water conformation. The shape of the water configuration becomes visibly non-symmetric due to the PE-water interactions. In Fig. 6 a cavern-like formation is seen: the size of

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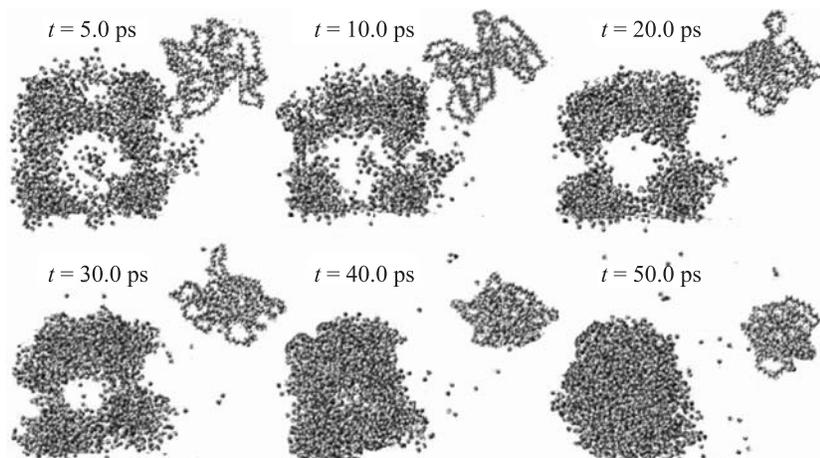
Fig. 6. The six sequential snapshots of the PE chain + water configurations are presented. For the water solvent we have employed TIP4P water model at the different configuration and geometry of the initial cell

the latter correlates with a PE-water contact distance. These two parameters, the cavern diameter and the PE-water distance, are drawn in Fig. 7.
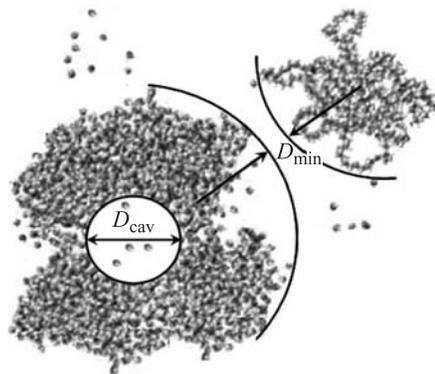
Fig. 7. The distance correlation PE chain + water configurations are presented through the two distances: diameter of the water cavern and PE-water contact distance

The calculated values of the D_{cav} (water cavern diameter) and D_{min} (PE-water contact distance) are presented in Figs. 8 and 9, respectively. Starting from the formation stage at $t = 0$ the diameter of the water cavern grows up to the time $t \sim 20$ ps (Fig. 8). That temporal point is also correlates with a PE-water

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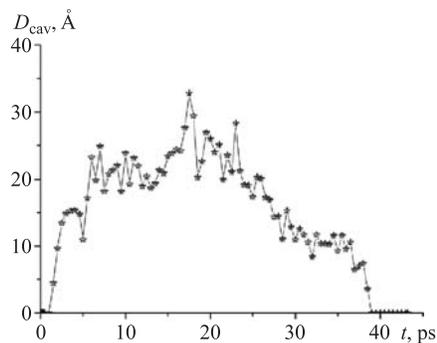
Fig. 8. The dependence of the diameter of the water cavern on time in the presence of the PE chain
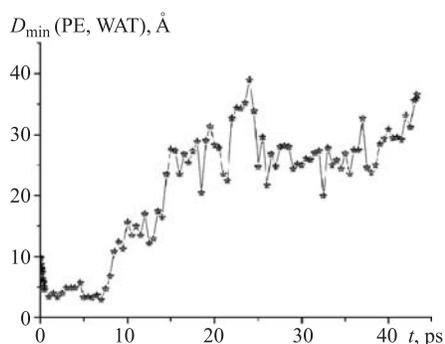
Fig. 9. The PE-water contact distance vs time for the PE chain + water configuration shown in Fig. 7

distance (Fig. 9) to reach a maximum value: within the same period we observe the increase of the PE-water contact distance.

Starting from the instant of about $t \sim 20$ ps the water cavern closes gradually; also starting from this point the PE-water contact distance becomes constant. In other words, the PE chain folds into a preferable state which is similar to the protein conformation in water solution.

The Dynamics of a Cavern-Like Formation

To make comparison with the behaviour of a cavern-like formation, presented in Figs. 5–8, we have investigated the dynamical changes of water without the PE chain at the same simulation conditions and the cell size as considered above.

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Briefly, we have fulfilled one more set of calculations just excluding the PE chain from the system. In Fig. 10 the initial configuration of water, a cubic ice, is shown.
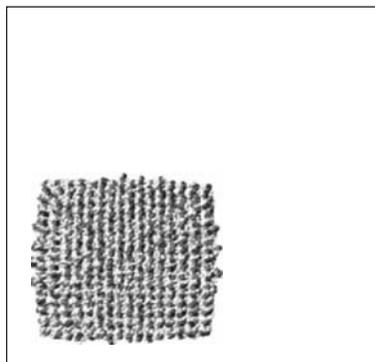
Fig. 10. The initial configuration of a polyethylene chain with cubic ice (left bottom)

In Fig. 11 the six sequential snapshots of the water solvent are displayed. If to compare these pictures with those in Fig. 6, it is easy to see that the water

$t = 3.75$ ps $\qquad$ $t = 7.50$ ps $\qquad$ $t = 11.25$ ps

$t = 15.0$ ps $\qquad$ $t = 18.75$ ps $\qquad$ $t = 22.70$ ps
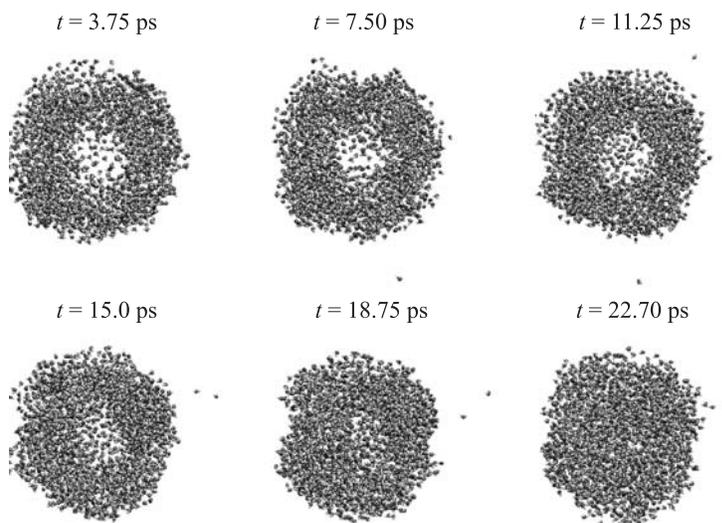
Fig. 11. The six sequential snapshots of the water configurations are presented. For the water solvent we have employed TIP4P water model at the same initial configuration and geometry of the cell, as in Fig. 6

configurations are almost spherically shaped. It is also worth noting that in the absence of the PE chain the changes in size of the cavern-like formation can be distinguished well. Thus, the influence of the flexible PE chain on the cavern configuration (or vice versa) we estimated via the changes of a cavern diameter.

In Fig. 12 the water cavern diameter is shown for the same cell and distant positions as in Fig.7.
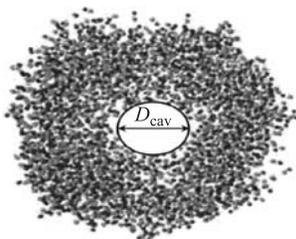
Fig. 12. The water cavern diameter in the same cell size as in Fig. 7

The calculated values of the cavern diameter are presented in Fig. 13. From the time dependences for the D_{cav} (viz. Fig. 13 and Fig. 8) it can be easily
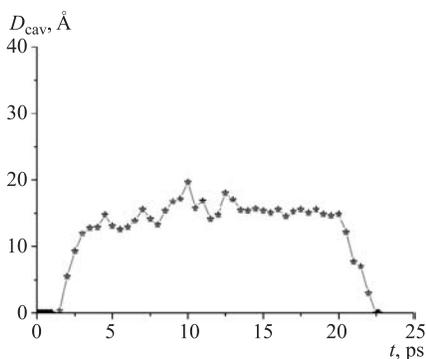
Fig. 13. The diameter of the water cavern vs time

observed that the values of the cavern diameter are possessed the visibly different behaviours. The most interesting point is that the D_{cav} in the absence of the PE chain keeps around of some average value (15 Å). In other words, the water cavern goes through the long oscillations before to close abruptly. Also the values of D_{cav}, as seen from Fig. 13, have to be approximately two times smaller in comparison with Fig. 8. Thus, the presence of the PE chain essentially changes the dynamics of the water cavern and «modifies» the cavern diameter. The process of the cavern-like formation under almost the same thermodynamical and cell-geometry conditions without the PE chain has to be characterized by

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a fast dynamics. It is remarkable that the influence of the PE chain on the water dynamics is accompanied by its protein-like hydrophobic behaviour, which should be taken into account for the studies of the flexible biomolecular systems involving solvent.

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