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MOLECULAR DYNAMICS SIMULATIONS
OF THE DENSITY-TEMPERATURE BEHAVIOR
OF A CHAIN POLYETHYLENE

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Молекулярно-динамическое моделирование
температурно-плотностного поведения
полиэтиленовой цепочки

Молекулярно-динамическое (МД) моделирование проводилось на основе параллельно-векторных вычислений и с помощью специализированного компьютера MDGRAPE-2 с целью изучения динамического поведения гибкой полиэтиленовой (ПЭ) цепочки при разных условиях нагревания. Было исследовано влияние температурных режимов на термодинамические параметры системы, такие как плотность и энергия. С этой целью проводились три различных расчета моделирования тепловых мод: быстрое, умеренное и медленное нагревания. Изучались особенности поведения вышеуказанных термодинамических величин для этих режимов нагревания полимерной цепочки. Молекулярно-механические и МД-моделирования ПЭ-системы проводились на базе оптимизированной версии пакета многоцелевого назначения DL_POLY, адаптированного для параллельно-векторных и специализированных компьютеров.

Работа выполнена в Отделении радиационных и радиобиологических исследований ОИЯИ.

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Molecular Dynamics Simulations
of the Density-Temperature Behavior of a Chain Polyethylene

Molecular Dynamics (MD) simulations have been performed on the parallel-vector and special-purposes MD machines to study the phase transitions and dynamical behaviors of a flexible polyethylene (PE) chain subjected to various environmental and heating conditions. Main objective of the study was to investigate the influence of the heating condition on a final state of the polymeric system and sensitivity of its thermodynamic quantities (density, energy, etc.) on the heating modes. For this purpose three different simulations were performed regarding on the following regimes: fast, moderate and low heating processes. The peculiarities of the main thermodynamic quantities of the system were estimated in detail and compared for all three processes. Molecular mechanical and MD calculations on the PE system were performed using the optimized version of the DL_POLY code, adapted for the vector- and special-purpose MDGRAPE-2 machines.

The investigation has been performed at the Division of Radiation and Radiobiological Research, JINR.

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INTRODUCTION

Simulations on the detailed structural changes of polymers, based on their microscopic transition behavior, provide the information valuable for the industry of polymer materials, for the material modification and technological innovations [1–3]. One of the most convenient techniques to study polymer phase transitions and other technologically interesting phenomena (structural conformations, chain-folding processes, time and temperature behavior, etc.) is the molecular dynamics (MD) method [4–6]. The MD method allows one to estimate the density-temperature changes of polymer systems, to study their time-dependent thermodynamic properties in solvents and to explore nontrivial polymer-surface interactions [1–5, 7]. In this work we have studied the density-temperature distributions and the dynamics of a chain polyethylene subjected to various environmental and heating conditions through the MD simulations. As a main objective of the present study we have investigated the influence of the heating condition on a final state of the polymeric system and sensitivity of the thermodynamic quantities (density, energy, etc.) on the heating processes. The MD simulations have been performed on the basis of the optimized general-purposes DL_POLY code [8, 9] and generic DREIDING force field for molecular simulations [10].

1. DETAILS OF SIMULATIONS

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



Fig. 1. Initial configuration of a polyethylene chain (black circles — carbon atoms, white circles — hydrogen atoms)

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

The configuration energy of the PE model is represented as a sum of the intramolecular valence (bonded) E_{val} and nonbonded E_{nb} interaction energies:

$$E = E_{\text{val}} + E_{\text{nb}}. \quad (1)$$

The intramolecular energy E_{val} includes bond stretching, bond angle bending, and torsion and inversion interactions

$$E_{\text{val}} = E_B + E_A + E_T + E_I, \quad (2)$$

nonbonded interactions consist of Van der Waals (VdW), electrostatic and hydrogen bonds

$$E_{\text{nb}} = E_{\text{vdw}} + E_Q + E_{\text{hb}}. \quad (3)$$

The VdW interactions were calculated by the pairwise 6–12 Lennard–Jones (LJ) potential. The LJ-parameters of the PE model are shown in Table 1.

Table 1. The LJ-parameters used in the MD simulations

Atomic pair	ε , kcal/mol	σ , Å
C C	0.0951	3.4730
C H	0.0380	3.1597
H H	0.0152	2.8464

We employed the NPT ensemble; a constant temperature of 300 K was attained using Nose–Hoover method. The equation of motion was solved by the leapfrog Verlet algorithm with a time step of 0.001 ps. The relaxation constant for the heat bath variable was 0.1 ps. In Table 2 the control parameters used in the MD simulations are shown.

Table 2. The setting control parameters of the MD simulations

Temperature, K	300
Pressure, kbar	0
Ensemble	NPT
R_cut, Å	10.5
Ewald precision	10^{-4}

2. RESULTS AND DISCUSSION

We have studied the influence of the heating processes on a final state of the PE system with periodic boundary conditions. Starting from the same initial state at $T_0 = 10$ K with the system equilibration we have reached a final state of $T_F = 300$ K through the following three different ways: regime 1 — fast; regime 2 — moderate; and regime 3 — slow heating processes. In Table 3 the temperature steps for those three simulation regimes are displayed.

Table 3. The temperature increments for the three heating regimes

Heating regime	Temperature increment ΔT , K
Fast	150
Moderate	50
Slow	10

In Fig. 2 the values of the temperature (T) vs time (t) are shown for three regimes: left picture displays fast regime; middle picture — moderate; and right picture — slow heating. The starting time $t = 4$ ps coincides with the end of the equilibration process. In each simulation run several thousands MD steps with the velocity scaling were performed to reach the equilibrium states, viz., the point $t = 4$ ps.

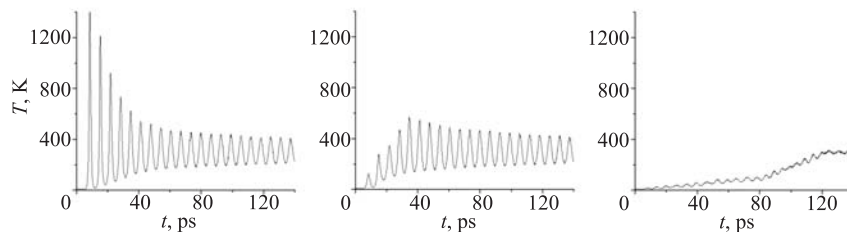


Fig. 2. The evolutions of the temperature of the system in the fast (left), moderate (middle) and slow (right) heating regimes

It is easy to see from Fig. 2 that the evolution of the temperature has a clearly different behavior between the heating regimes. During the fast and moderate heating modes we observe large oscillations of the temperature $T(t)$. For the same system, the slow heating yields satisfactory small oscillations of temperature. In other words, the slow heating mode «smoothly» forms the equilibrium state, which manifests itself as an important stage of the final dynamics. A final state achieved at $t = 140$ ps has the same value of T close for all heating regimes. For a larger MD time scales ($t > 140$ ps) a more significant changes of the temperature

values have not been observed, so far the PE system has been analyzed only at this time interval from 0 to 120 ps.

Next we have estimated the evolutions of the atomic density of the system for the three heating processes. In Fig. 3 the behavior of $\rho_N(t)$ is shown for the same regimes as displayed in Fig. 2 (left picture — fast; middle — moderate; and right — slow heating).

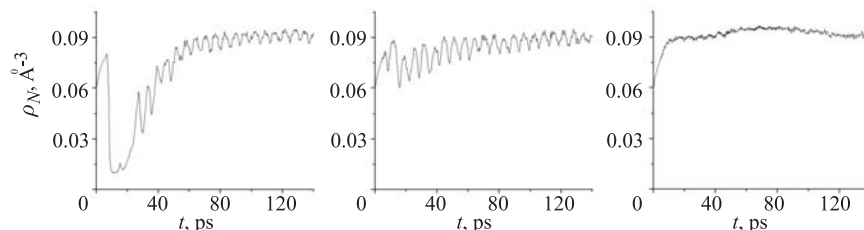


Fig. 3. The evolutions of the atomic density in the fast (left), moderate (middle) and slow (right) heating regimes

In the fast and moderate heating the visibly high oscillations of the density values were observed. In comparison to the pictures above for time dependences of $T(t)$, the high temperature oscillations result in a significant change of the density (see left and middle pictures). At the same time, the slow heating process leads to an equilibrium density monotonically. That is that the behavior of the system under consideration, as it is seen from Fig. 3, is essentially sensitive to the dynamics of the heating. The values of $\rho_N(t)$ at the final point $t = 140$ ps are the same for all heating regimes. The final equilibrium values for the three regimes are presented in Table 4.

Table 4. The calculated densities of the PE system for the three heating regimes

Regime	Fast	Moderate	Slow
$\rho, \text{g/cm}^3$	0.165532	0.160132	0.165256

The various energy contributions, which result in the density behavior as shown above, have been compared. We have separately estimated the energies of the nonbonded (VdW) and intramolecular (bonded) interactions for all heating regimes. In Fig. 4 the calculated values of the configuration energy due to the short-range potential E_{vdw} , as a function of time, are presented.

It is seen from Fig.4 that the changes of E_{vdw} at the beginning of the MD simulations for the fast and moderate heating processes (left and middle pictures) are approximately one order higher than those for the slow heating

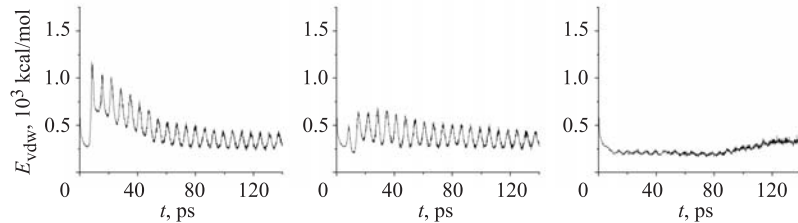


Fig. 4. Configuration energy due the short-range (Van der Waals) potential in the fast (left), moderate (middle) and slow (right) heating regimes

mode (shown in the right picture). Starting from the same value of about $E_{\text{vdw}} = 0.125 \cdot 10^3$ kcal/mol the energy grows up to $0.125 \cdot 10^3$ kcal/mol in regime 1 (left picture) and up to $0.75 \cdot 10^3$ kcal/mol in regime 2 (middle picture), respectively. At the same time, as it is seen from Fig. 4, the VdW energy for regime 3 (right picture) keeps about the average value of $E_{\text{vdw}} = 0.125 \cdot 10^3$ kcal/mol.

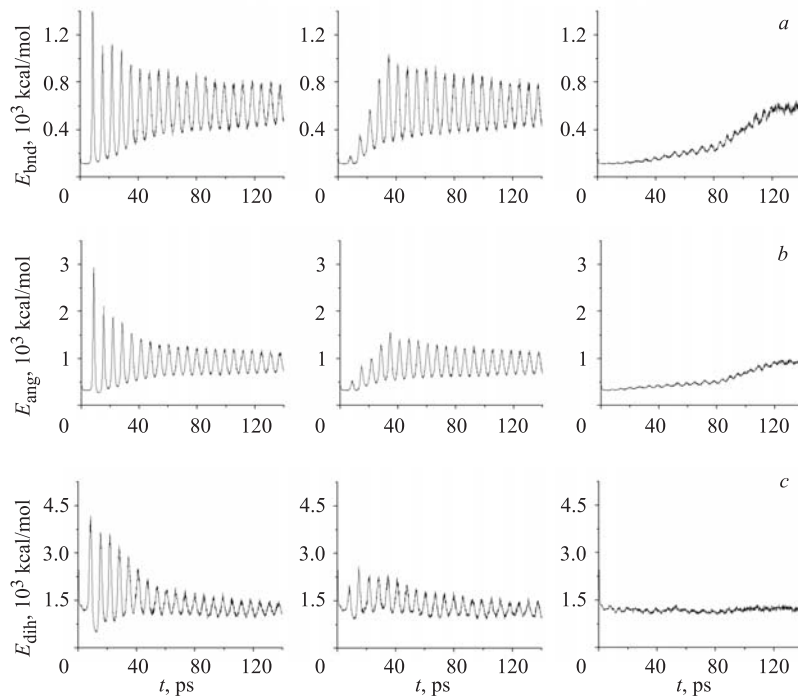


Fig. 5. Configuration energy due to intramolecular potential in the fast (left), moderate (middle) and slow (right) heating regimes: *a* — chemical bond; *b* — valence angle; *c* — dihedral

In Fig. 5 we present the values of the intramolecular energies due to the bond E_B (Fig. 5, *a*), angular (Fig. 5, *b*), and dihedral (Fig. 5, *c*) interactions as a function of time.

As it is seen from Fig. 5, *a-c* the behavior of the energy for the bond, angular and dihedral interactions could easily be distinguished, comparing those for the three heating regimes. For the fast and moderate heating modes the initial changes of the intramolecular energies are significantly larger than those for the slow heating process. The oscillations of the intramolecular energies for the slow heating behave monotonically. It is in accordance with the dynamics of the setting temperature shown in Fig. 2. The chemical bond potential gives a large contribution; next is the valence angle potential; and then goes the dihedral interaction potential. It is worth noting that the changes of the dihedral energy in slow heating mode are very small. This is an interesting dynamical behavior to be taken into account in similar studies performed on the PE system. The snapshots of the resultant configurations of the PE system for the three heating modes are presented in Fig. 6.

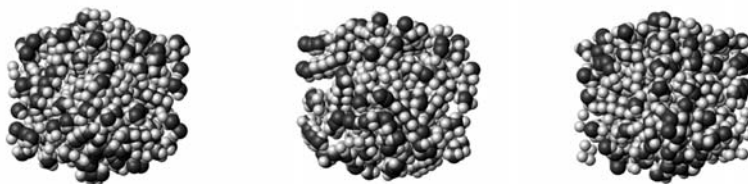


Fig. 6. Snapshots of the resultant configurations of the PE system for the fast heating (left), moderate (middle) and slow (right) regimes

Finally, in Fig. 7 the results of the total energies of the PE system for regimes 1 (left), 2 (middle) and 3 (right) are displayed.

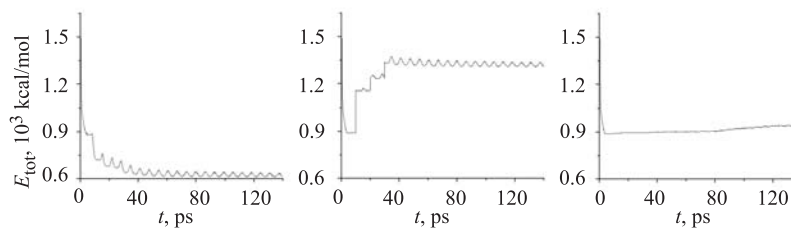


Fig. 7. The evolution of the total energy of the system for the fast (left), moderate (middle) and slow (right) heating regimes

From Fig. 7 we see that all displayed values of the total energy asymptotically go to a constant. Nevertheless, it is important that those values calculated for the

PE system differ from each other. The equilibrium energy E_{tot} is $0.6 \cdot 10^3$ kcal/mol for regime 1; $1.3 \cdot 10^3$ kcal/mol for regime 2; and $0.9 \cdot 10^3$ kcal/mol for regime 3, respectively. The most remarkable point, however, is that in the fast and moderate heating the total energy does not behave in the same manner, as it clearly was observed from the results of Figs. 2–5. In comparison to the above dependencies (see, for example, Figs. 4 and 5 for the nonbonded and the bonded potentials, respectively) the total energy starting at $t = 0$ from the close values (Fig. 7) decreases in the fast, but increases in the moderate heating mode (before reaching an asymptotics). It can rather be explained so that the total energy E_{tot} , as a conserved quantity of the system, contains all contributions including those coming from the thermostat. Thus, the PE system interacting with the thermostat forces reaches the different values of E_{tot} (see Fig. 7 for regimes 1 and 2). This is true even when the intra- or intermolecular energy parts possess the same law, comparing the fast and moderate regimes of Figs. 4–5. In other words, the thermostat contribution somehow «corrects» the final state, yielding the correct constant values of E_{tot} .

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