

E19-2004-114

D. A. Kretov, Kh. T. Kholmurodov\*

**MD SIMULATIONS**  
**ON A FLEXIBLE CHAIN POLYETHYLENE:**  
**THE EFFECT OF THE ELECTROSTATIC FORCES**  
**IN THE DENSITY-TEMPERATURE BEHAVIOR**

Submitted to «Физика низких температур»

---

\*E-mail: mirzo@jinr.ru

Кретов Д. А., Холмуродов Х. Т.

E19-2004-114

МД-моделирование гибкой полиэтиленовой цепочки:  
влияние электростатических сил  
на температурно-плотностное поведение

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 проведено сравнение влияния короткодействующих (ван-дер-ваальсовых) и электростатических сил на динамику ПЭ-системы. С этой целью проводились три различных расчета для моделирования тепловых мод: быстрое, умеренное и медленное нагревание. Изучались особенности поведения основных термодинамических величин системы 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.

Препринт Объединенного института ядерных исследований. Дубна, 2004

Kretov D. A., Kholmurodov Kh. T.

E19-2004-114

MD Simulations on a Flexible Chain Polyethylene:  
the Effect of the Electrostatic Forces  
in the Density-Temperature Behavior

Molecular Dynamics (MD) simulations have been performed on the parallel-vector and special-purposes MD machines to study the dynamical behaviors of a flexible polyethylene (PE) chain subjected to various heating conditions. Both the effect of the short-range and electrostatic interactions on the dynamics of the PE system were estimated and compared. For this purpose three different simulations were performed regarding on the following regimes: fast, moderate and slow 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.

Preprint of the Joint Institute for Nuclear Research. Dubna, 2004

## INTRODUCTION

One of the most convenient techniques to study the polymer phase transitions and other technologically interesting phenomena (structural conformations, chain-folding processes, time and density-temperature behaviors, etc.) is molecular dynamics (MD) method. 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 [1–6]. The MD simulation allows one to estimate the density-temperature changes of polymer systems, to study their time-dependent thermodynamic properties in solvents and to explore polymer-surface interactions [1–5, 7]. In this work we have studied through computer MD simulations the density-temperature distribution and dynamical properties of a chain PE, subjected to various heating conditions. It is worth noting that for polymeric systems both temperature and density play crucial roles in their dynamics and formation of nontrivial phases. For example, it has long been appreciated that both temperature and density essentially determine the low-temperature behavior of polymeric chains (the extremely super-Arrhenius phase), the viscosity of the fragile liquids, etc. [8–10]. In several recent studies for a model polymeric material (see, for example, [8–13]) the computer simulations were performed on the basis of the MD to study the chain dynamics in bulk PE over a wide range of temperature (including the volumetric glass transition), the isobaric and isochoric cooling and other phenomena. It was found that simulation results, in general, are in excellent agreement with the existing experimental trends [10–12]. In 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 in the presence of the electrostatic interactions.

### 1. DETAILS OF SIMULATIONS

The computational details were the same as described in our previous study for the polyethylene (PE) model [14]. Briefly, the MD simulations were performed on the basis of the optimized general-purposes DL\_POLY code [15, 16] and generic DREIDING force field for the molecular simulations [17]. Within the DREIDING potential a single flexible PE chain of about 500 CH<sub>2</sub> units in

length was simulated, where each  $\text{CH}_2$  group treated as a united atom and satisfying charge neutrality. 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 configuration energy of the PE model is represented as a sum of the intramolecular valence (bonded)  $E_{\text{val}}$  and nonbonded  $E_{\text{nb}}$  interaction energies; the intramolecular energy  $E_{\text{val}}$  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 potential; the equation of motion was solved by the leapfrog Verlet algorithm; a constant temperature was attained using NPT ensemble and Nose–Hoover method.

## 2. RESULTS AND DISCUSSION

For the PE chain model, as in the previous work [14], we have simulated the following three processes: regime 1 — fast, regime 2 — moderate and regime 3 — slow heating modes. The temperature steps for those simulation regimes are displayed in Table 1.

**Table 1. The temperature increments for the three heating regimes**

Heating regime	Temperature increment $\Delta T$ , K
Fast	150
Moderate	50
Slow	10

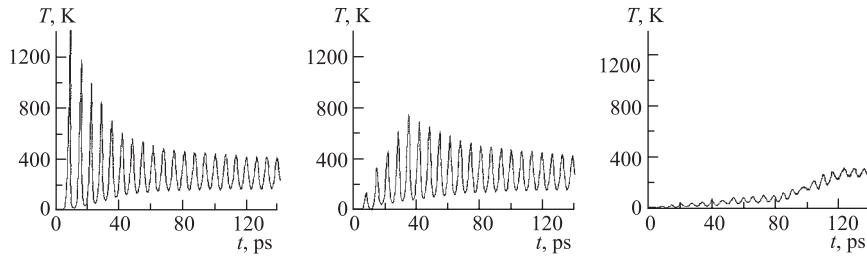
In Table 2 the mass and charge numbers of the PE model, used in the calculation of the Coulomb interactions are displayed.

**Table 2. The hydrocarbon mass and charge numbers**

Atomic index	Mass	Charge
C	12.011000	-0.053302
H	1.008000	0.026651

For each heating mode as described above the atomic interactions were estimated through the following stages: 1) the valence and VdW forces were calculated (viz., the results of [14], where the electrostatic interactions were neglected); 2) the valence, VdW and the electrostatic forces were calculated. Thus, the effect of the electrostatic interactions on the dynamics of the density-temperature behavior of PE system was compared to the valence and VdW interactions.

In Fig. 2 the temperature evolutions for three heating modes in the presence of the electrostatic interactions are presented.



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

It is easy to see from Fig. 2 that the evolution of the temperature has a 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. In comparison with the results of [14], we observe the small changes in the temperature dynamics. The peculiarities of the time evolutions of the temperature are easily distinguishable for the fast and moderate heating; for the slow heating mode the results are closely the same.

Fig. 3 displays the evolutions of the density of the PE chain in the presence of the electrostatic (Coulomb) interactions.

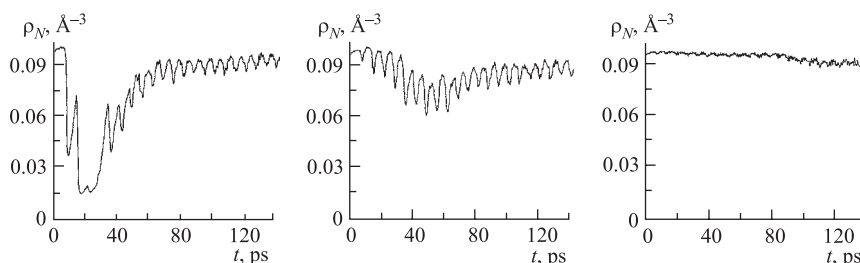


Fig. 3. The evolutions of the atomic density in the fast (left), middle (central) and slow (right) heating regimes

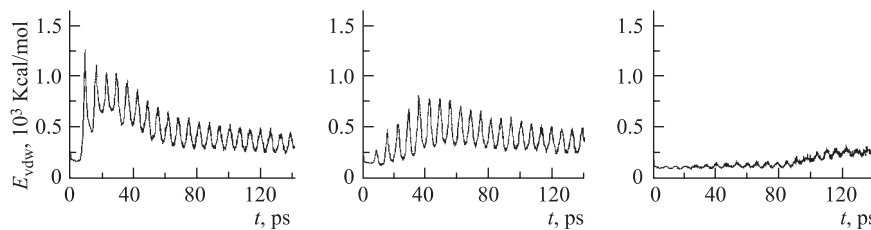


Fig. 4. Configuration energy due to the short-range (VdW) potential in the fast (left), middle (central) and slow (right) heating regimes

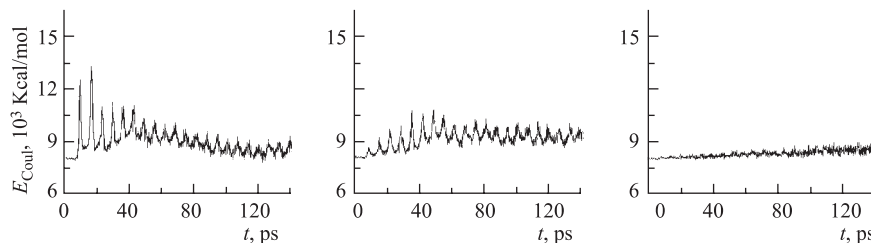


Fig. 5. The electrostatic energy of the PE system for the fast (left), moderate (central) and slow (right) heating regimes

In comparison with the behaviors of the temperature (viz., Fig. 2) inclusion of the electrostatic forces for the density leads to its nonlinear changes. From Fig. 3 it is seen that in the moderate and slow heating (middle and right pictures) the density reaches its maximum value very fast, from the start of the evolutions. Besides of this, the density oscillations in the moderate heating pass the extremum at later stages of the system dynamics. This result represents itself intriguing and it might be interpreted as a PE intermediate phase or in terms of the nonlinear dynamical transitions in the polymeric chain.

The MD calculation results of the VdW and Coulomb energies for the three heating regimes are shown in Figs. 4 and 5, respectively. The electrostatic energy of the PE chain, as it is seen from Fig. 5, possesses very small values. In comparison with the VdW energy (Fig. 4) contribution of the electrostatics is three orders smaller. Nevertheless, this small contribution changes the behavior of the basic quantities (temperature, density, energy) essentially.

In Fig. 6, *a-c* the peculiarities of the dynamical evolutions are presented for the intramolecular interactions: *a* — the bond  $E_B$ , *b* — the angular  $E_A$ , and *c* — the dihedral  $E_T$  energy.

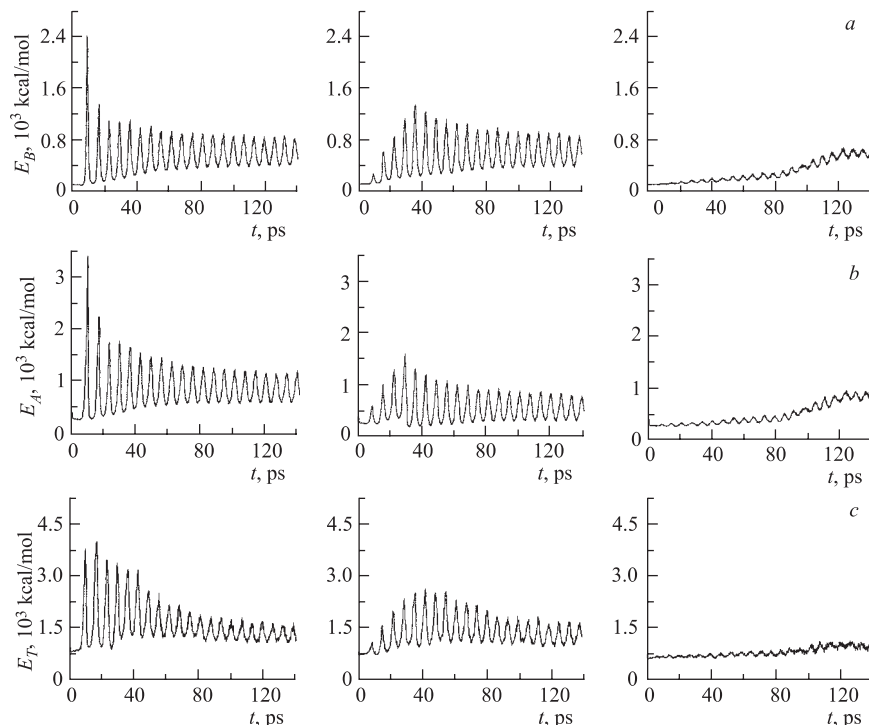


Fig. 6. Configuration energy due to intramolecular potential in the fast (left), middle (center) and slow (right) heating regimes: *a* — chemical bond; *b* — valence angle; *c* — dihedral

Analysis of results shown in Fig. 6, *a-c* indicates that the effects of the electrostatic forces have been observed for all heating modes. The largest change more obvious, however, for the moderate heating regime (the middle pictures in Fig. 6, *a-c*). It is easy to observe that the evolution curves of the moderate heating mode possess a nonlinear region, where VdW or bonded energy goes through a maximum value. In this temporal window (from 30 ps until 70 ps) all interaction potentials weakly increased simultaneously with the decreasing of the system density.

**Acknowledgements.** The special-purposes MDGRAPE-2 computer was provided by Ebisuzaki Computational Astrophysics Laboratory of RIKEN (Institute of Physical and Chemical Research), Japan. The authors are grateful to Prof. T. Ebisuzaki for the support on the MDGRAPE-2 machine and DL\_POLY optimization works. We acknowledge the helpful discussion and valuable comments by Dr. M. Altaisky.

## REFERENCES

1. *Allinger N. L.* // J. Comput. Chem. 1987. V. 8. P. 581.
2. *King S. M., Cosgrove T.* // Macromolecules. 1993. V. 26. P. 5414.
3. *Budzien J., Raphael C., Ediger M. D., de Pablo J. J.* // J. Chem. Phys. 2002. V. 116. P. 8209.
4. *Fukuda M., Kikuchi H.* // J. Chem. Phys. 2000. V. 113. P. 4433.
5. *Guo H. X., Yang X. Z., Li T.* // Phys. Rev. E. 2000. V. 61. P. 4185.
6. *Xia T. K., Landman U.* // Science. 1993. V. 261. P. 1310.
7. *Krishna Pant P. V., Han J., Smith G. D., Boyd R. H.* // J. Chem. Phys. 1993. V. 99. P. 597.
8. *Boyd R. H., Gee R. H., Han J., Jin Y.* // J. Chem. Phys. 1994. V. 101. P. 788.
9. *Ferrer M. L. et al.* // J. Chem. Phys. 1998. V. 109. P. 8010.
10. *Yang L., Srolovitz D. J., Yee A. F.* // J. Chem. Phys. 1999. V. 110. P. 7058.
11. *Bharadwaj R. K., Boyd R. H.* // J. Chem. Phys. 2001. V. 114. P. 5061.
12. *Koyama A., Yamamoto T., Fukao K., Miyamoto Y.* // J. Chem. Phys. 2001. V. 115. P. 560.
13. *Neelakantan A., Maranas J. K.* // J. Chem. Phys. 2004. V. 120. P. 465.



14. *Smith W., Forester T.R.* // Molecular Graphics. 1993. V. 14. P. 136; The DL\_POLY User Manual. Version 2.11; [http://www.dl.ac.uk/TCS/Software/DL\\\_POLY](http://www.dl.ac.uk/TCS/Software/DL\_POLY), 1999.
15. *Kretov D., Kholmurodov Kh.* JINR Preprint. E19-2004-112. Dubna, 2004.
16. *Kholmurodov Kh., Smith W., Yasuoka K., Ebisuzaki T.* // Comput. Phys. Commun. 2000. V. 125. P. 167;  
*Kholmurodov Kh. et al.* Fast Forces Calculations in the DL\_POLY Molecular Simulation Package // Proc. of the 6th World Multiconference on Systemics, Cybernetics and Informatics (SCI). Orlando, USA, July 14–18, 2002.
17. *Mayo S.L., Olafson B.D., Goddard III W.A.* // J. Phys. Chem. 1990. V. 94. P. 8897.

Received on July 13, 2004.

Корректор *Т. Е. Попеко*

Подписано в печать 18.08.2004.

Формат 60 × 90/16. Бумага офсетная. Печать офсетная.

Усл. печ. л. 0,68. Уч.-изд. л. 0,96. Тираж 220 экз. Заказ № 54569.

Издательский отдел Объединенного института ядерных исследований  
141980, г. Дубна, Московская обл., ул. Жолио-Кюри, 6.

E-mail: [publish@pds.jinr.ru](mailto:publish@pds.jinr.ru)

[www.jinr.ru/publish/](http://www.jinr.ru/publish/)