A theoretical approach to structural change of a polymer induced by beta decays of substituted tritium based on the linear response theory

Susumu Fujiwara^{1*}, Ryuta Kawanami², Haolun Li², Hiroaki Nakamura^{3,4},
Kazumi Omata^{5,6}

¹Faculty of Materials Science and Engineering, Kyoto Institute of Technology

²Graduate School of Science and Technology, Kyoto Institute of Technology

³Department of Helical Plasma Research, National Institute for Fusion Science

⁴Department of Energy Engineering and Science, Nagoya University

⁵National Center for Global Health and Medicine

⁶Kumamoto University Hospital

*fujiwara@kit.ac.jp

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Abstract. Molecular dynamics simulations of the hydrogen-removed polyethylene are carried out to study the structural change of polyethylene induced by beta decays of substituted tritium. Our simulations show that the folded structure of the hydrogen-removed polyethylene becomes more disordered as the number of removed hydrogen atoms becomes larger. We also propose a theoretical approach to explaining and predicting our molecular dynamics simulation results of hydrogen-removed polyethylene on the basis of the linear response theory. We derive the time derivative of the dynamical quantity, which is conjugate to the force applied as perturbation in the framework of the linear response theory, required to calculate the response function. The dynamical quantity in this study is the total potential energy difference of polyethylene before and after removal of hydrogen. Preliminary results of the response function for the total potential energy of polyethylene after removal of hydrogen are presented.

Keywords: Linear response theory, Molecular dynamics simulation, Structural change, Polyethylene, Substituted tritium, Decay effect

1. Introduction

Since Fukushima nuclear accident in 2011, the treatment of large amount of contaminated water containing tritium has become an urgent problem. Tritium (T or ^3H) is a radioactive isotope

of hydrogen with a half-life of 12.32 years [1,2]. When tritium is taken into the human body, it may replace hydrogen in biomolecules. It is also found that hydrogen-tritium exchange reactions can occur between proteins or small organic molecules and HTO molecules [3,4], which suggests that, in tritiated water, hydrogen in polymeric molecules can be replaced by tritium. The substituted tritium in biomolecules and polymeric molecules decays into helium-3 (^3He) due to beta decay with emissions of a low energy beta electron (beta ray) and an antineutrino [1,2], and the chemical bonds between helium-3 and other atoms break because of the chemical inertness of helium-3.

Radiation effects on biomolecules and polymeric molecules are mainly classified into two types: direct and indirect effects [1,2]. In the direct effect, the radiation hits directly to the molecules and disrupts their molecular structures. In the indirect effect, on the other hand, free radicals and active oxygen induced by radiation strike and disrupt the molecules. In addition to these two effects, the decay effect should also be taken into account when hydrogen in the molecules is substituted by tritium [1,2]. In the decay effect, the chemical bonds break by beta decay of substituted tritium in the molecules to helium-3. Although several experimental and simulation studies have so far been conducted on radiation effects on biomolecules [5,6] and polymeric molecules [7,8], the molecular mechanism of radiation effects on biomolecules and polymeric molecules is not fully understood yet.

In our previous work, the structural change of a telomeric DNA by beta decay of substituted tritium to helium-3 was studied using molecular dynamics (MD) simulations and it is found that the fragility of the DNA structure increases as the number of substituted tritium atoms or the temperature of the system becomes larger [9,10]. We also performed MD simulations of polyethylene to investigate its structural change by beta decay of substituted tritium to helium-3 and found that the structure of polyethylene becomes more unstable as the number of substituted tritium atoms becomes larger [9,11,12].

In this paper, besides performing MD simulations, we propose a theoretical approach to the structural change of polyethylene induced by beta decays of substituted tritium based on the linear response theory [13] to explain and predict our simulation results. Based on this theoretical approach, when investigating the structural change of a polymer due to beta decays of substituted tritium to helium-3 by MD simulation, it is possible to calculate the post-decay structural relaxation only by performing the pre-decay simulation, i.e., without performing the post-decay simulation. We also show our preliminary results of the response function for the total potential energy of polyethylene after removal of hydrogen based on the linear response theory.

Figure 1: Schematic illustration of damage process after the substitution of tritium in polyethylene. The chemical bond between ${}^3\text{He}^+$ and C breaks because of the chemical inertness of helium-3. The remaining -CH- is treated as an sp^2 hybrid orbital.

2. Molecular dynamics simulation

In this section, the simulation model and method are described in detail and the simulation results of the hydrogen-removed polyethylene are shown.

2.1. Simulation model and method

The polyethylene model is similar to that used in Refs. [9,11]. The model polyethylene chain consists of a linear chain of 2998 CH_2 groups with 2 terminal CH_3 groups which are all treated as united atoms. The masses of CH_2 and CH_3 groups are 14 and 15 g/mol, respectively. As described in Sec.1, the chemical bonds (C-T bonds) break after beta decay of substituted tritium in the polyethylene chain to helium-3 since helium-3 is inert (Fig. 1). To simulate the decay effect on the polyethylene chain, the generated helium-3 is assumed to be removed quickly. In this study, hydrogen atoms are removed randomly from the polyethylene (not from the end CH_3 groups and no more than one bonded hydrogen for every carbon) and the remaining CH group is treated as a united atom with an sp^2 hybrid orbital [9,11]. The mass of CH group is 13 g/mol.

The united atoms interact with each other via bonded potentials (bond-stretching, bond-bending and torsional potentials) and a non-bonded potential (Lennard-Jones potential). The atomic force field used here is the modified DREIDING potential [14,15]. The total potential energy E_{pot} consists of four parts: bond-stretching potential energy E_{B} , bond-bending potential energy E_{A} , torsional potential energy E_{T} , and the Lennard-Jones potential energy E_{LJ} .

The bond-stretching potential energy E_{B} is given by

$$E_{\text{B}} = \sum_{i=1}^{N-1} \frac{1}{2} K_{\text{B}} (d_{i,i+1} - d_{i,i+1}^0)^2, \quad (1)$$

where N is the number of united atoms, $d_{i,i+1}$ is the bond distance between united atom i

Table 1: The values of the equilibrium bond distance $d_{i,i+1}^0$.

i	$i+1$	$d_{i,i+1}^0$ (Å)
CH ₂ or CH ₃	CH ₂ or CH ₃	1.53
CH ₂ or CH ₃	CH	1.43
CH	CH	1.33

Table 2: The values of the equilibrium bond angle θ_i^0 .

i	θ_i^0 (deg)
CH ₂ or CH ₃	109.471
CH	120.000

Table 3: Parameters used for the torsional potential.

i	$i+1$	$V_{i,i+1}$ (kcal/mol)	$n_{i,i+1}$	$\phi_{i,i+1}^0$ (deg)
CH ₂ or CH ₃	CH ₂ or CH ₃	2.0	3	180
CH ₂ or CH ₃	CH	1.0	6	0
CH	CH	45	2	180

and united atom $i + 1$, and $d_{i,i+1}^0$ is the equilibrium bond distance. The force constant is $K_B = 700$ (kcal/mol)/Å². The values of $d_{i,i+1}^0$ are given in Table 1.

The bond-bending potential energy E_A is expressed by

$$E_A = \sum_{i=2}^{N-1} \frac{1}{2} K_A (\theta_i - \theta_i^0)^2, \quad (2)$$

where θ_i is the angle between bonds $i - 1$, i and i , $i + 1$, and the force constant is $K_A = 100$ (kcal/mol)/rad² and θ_i^0 is the equilibrium bond angle. The values of θ_i^0 are shown in Table 2.

The torsional potential energy E_T takes the form of the following equation

$$E_T = \sum_{i=2}^{N-2} \frac{1}{2} V_{i,i+1} \{1 - \cos[n_{i,i+1}(\phi_{i,i+1} - \phi_{i,i+1}^0)]\}, \quad (3)$$

where $\phi_{i,i+1}$ is the dihedral angle between the planes $i - 1$, i , $i + 1$ and i , $i + 1$, $i + 2$, $V_{i,i+1}$ is the energy barrier to rotation, $n_{i,i+1}$ is the periodicity, and $\phi_{i,i+1}^0$ is the equilibrium dihedral angle. Table 3 shows the values of $V_{i,i+1}$, $n_{i,i+1}$, and $\phi_{i,i+1}^0$.

The Lennard-Jones potential energy E_{LJ} is expressed by the following common equation

Figure 2: Snapshots of polyethylene at 330 K for (a) $f_H = 0$, (b) $f_H = 0.01$, and (c) $f_H = 0.1$. Red balls represent CH groups.

$$E_{LJ} = \sum_{i=1}^{N-1} \sum_{j=i+1}^N 4\varepsilon_{i,j} \left\{ \left(\frac{\sigma_{i,j}}{r_{i,j}} \right)^{12} - \left(\frac{\sigma_{i,j}}{r_{i,j}} \right)^6 \right\}, \quad (4)$$

with a cutoff of 10.5 Å, where $r_{i,j}$ is the distance between united atom i and united atom j , $\varepsilon_{i,j}$ is the depth of the potential well and $\sigma_{i,j}$ is the finite distance at which the interparticle potential energy is zero. In the modified DREIDING potential [15], the values of $\varepsilon_{i,j}$ and $\sigma_{i,j}$ are respectively $\varepsilon_{i,j} = 0.0951$ (kcal/mol) and $\sigma_{i,j} = 3.4730$ (Å) for all types of united atoms (CH, CH₂, and CH₃).

We used the velocity version of the Verlet algorithm [16] to solve the equations of motion for all united atoms numerically. NVT ensemble was employed and the Nosé-Hoover method [13-15] was applied to keep the temperature of the system constant. The integration time step was 1 fs. The total linear momentum and angular momentum were set to be zero in order to cancel overall translation and rotation of a polyethylene chain. The MD simulations were carried out in the following way. First of all, we prepared the folded orientationally-ordered structure of a single polyethylene chain at 100 K by cooling from a random conformation at 800 K at a cooling rate of 50 K/ns. Next, the system was heated from 100 K to 200 K at a heating rate of 5 K/ns and was subsequently heated from 200 K to 400 K at a heating rate of 2 K/ns. We then randomly removed a certain amount of hydrogen atoms from a polyethylene chain at 250 K, 330 K, and 400 K. The ratio of the number of removed hydrogen atoms to the number of carbon atoms, f_H , was set at $f_H = 0, 0.001, 0.01$ and 0.1 . After that, the MD simulations of the hydrogen-removed polyethylene were performed for 10 ns at each temperature. The Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) was used for all simulations [20].

2.2. Simulation results

The snapshots of the hydrogen-removed polyethylene at 330 K for $f_H = 0$, 0.01 and 0.1 are shown in Figure 2. It is found from this figure that the polyethylene chain still maintains a folded orientationally-ordered structure for $f_H = 0$ and 0.01 whereas the folded structure becomes slightly disordered for $f_H = 0.1$. In fact, the global orientational order parameter P_2 [11,21-24], which indicates the degree of orientational order in the polyethylene chain, is $P_2 = 0.284$ for $f_H = 0$, $P_2 = 0.261$ for $f_H = 0.01$, and $P_2 = 0.138$ for $f_H = 0.1$, respectively.

3. Linear response theory

In this section, we give an explanation for the theoretical framework to treat the structural change of polyethylene induced by beta decays of substituted tritium based on the linear response theory, derive the time derivative of the dynamical quantity conjugate to the applied force required to calculate the response function, and show an example of our preliminary results of the response function calculated for the total potential energy.

3.1. Theoretical framework

The substituted tritium in polyethylene decays to inert helium-3 by beta decays and CHT changes to CH (Fig. 1), which leads to the structural change of polyethylene. In this study, hydrogen atoms are assumed to be removed simultaneously from the polyethylene instead of being exchanged to helium-3 since it is not necessary to treat helium-3 to study the decay effect of tritium-substituted polyethylene. Consequently, the interactions between the united atoms including substituted tritium (CHT) and other united atoms switch to those between the united atoms including one hydrogen atom (CH) and other united atoms immediately after the beta decays of substituted tritium. After that, the polyethylene, which was in non-equilibrium due to beta decays, relaxes to equilibrium. When perturbation is applied to the system, the relaxation of physical quantities can be examined by non-equilibrium statistical mechanics [13,24,25]. We suppose that the perturbation energy $H'(t)$ is described by the following equation when an external force $F(t)$ is applied to the system:

$$H'(t) = -A \cdot F(t), \quad (5)$$

where A is the dynamical quantity conjugate to the applied force. In this study, the external force $F(t)$ is the Heaviside step function and the dynamical quantity A is calculated by

$$A = E_{\text{pot}}^{\text{before}} - E_{\text{pot}}^{\text{after}}, \quad (6)$$

where $E_{\text{pot}}^{\text{before}}$ and $E_{\text{pot}}^{\text{after}}$ represent the total potential energy E_{pot} before and after beta decays of substituted tritium, respectively. According to the linear response theory [13], the ensemble average of the change $\langle \Delta B \rangle$ of a physical quantity B is given by

$$\langle \Delta B \rangle = \int_0^t dt' \phi_{BA}(t - t') \quad (8)$$

when the motion of the system is perturbed by weak force. Here, $\phi_{BA}(t)$ is the response function which is calculated by

$$\phi_{BA}(t) = \frac{1}{k_B T} \langle B(t) \dot{A}(0) \rangle, \quad (8)$$

where k_B is the Boltzmann constant and T is the absolute temperature. Note that the ensemble average is taken over the unperturbed equilibrium state. The description of $\dot{A}$ is given in the following section, Sec. 3.2.

3.2. Derivation of $\dot{A}$

We need to derive the expression of the time derivative $\dot{A}$ of the dynamical quantity conjugate to the applied force to calculate the response function from (8). $\dot{A}$ has four terms $\dot{A}_B$, $\dot{A}_A$, $\dot{A}_T$, and $\dot{A}_{LJ}$, which are calculated by

$$\dot{A}_B = \dot{E}_B^{\text{before}} - \dot{E}_B^{\text{after}}, \quad (9)$$

$$\dot{A}_A = \dot{E}_A^{\text{before}} - \dot{E}_A^{\text{after}}, \quad (10)$$

$$\dot{A}_T = \dot{E}_T^{\text{before}} - \dot{E}_T^{\text{after}}, \quad (11)$$

$$\dot{A}_{LJ} = \dot{E}_{LJ}^{\text{before}} - \dot{E}_{LJ}^{\text{after}}, \quad (12)$$

respectively. Here, E_B^{before} , E_B^{after} , E_A^{before} , E_A^{after} , E_T^{before} , E_T^{after} , E_{LJ}^{before} , and E_{LJ}^{after} represent the bond-stretching, bond-bending, torsional potentials and a Lennard-Jones potential before and after beta decays of substituted tritium, respectively. In this study, $\dot{A}_{LJ} = 0$ because E_{LJ} does not change before and after beta decays of substituted tritium in the case of the modified DREIDING potential [14,15]. We arrive at the following expressions for $\dot{A}_B$, $\dot{A}_A$, and $\dot{A}_T$ after simple but cumbersome calculation.

$$\dot{A}_B = K_B \sum_{i=1}^{N-1} \left(d_{i,i+1}^{0'} - d_{i,i+1}^0 \right) \hat{\mathbf{d}}_{i,i+1} \cdot \dot{\mathbf{d}}_{i,i+1}, \quad (13)$$

where $\mathbf{d}_{i,i+1} = \mathbf{r}_{i+1} - \mathbf{r}_i$ is the bond vector between the i -th united atom and the $(i+1)$ -th united atom, $\mathbf{r}_i$ is the position vector of the i -th united atom, $\hat{\mathbf{d}}_{i,i+1}$ is the unit vector of $\mathbf{d}_{i,i+1}$, and $d_{i,i+1}^0$, $d_{i,i+1}^{0'}$ are the equilibrium bond lengths before and after beta decays of substituted tritium, respectively. As for $\dot{A}_A$, we have

$$\dot{A}_A = K_A \sum_{i=2}^{N-1} \left(\theta_i^{0'} - \theta_i^0 \right) \dot{\theta}_i, \quad (14)$$

$$\dot{\theta}_i = \frac{\left(\frac{\dot{\mathbf{d}}_{i-1,i}}{d_{i-1,i}} \cdot \hat{\mathbf{d}}_{i,i+1} + \hat{\mathbf{d}}_{i-1,i} \cdot \frac{\dot{\mathbf{d}}_{i,i+1}}{d_{i,i+1}} \right) - \hat{\mathbf{d}}_{i-1,i} \cdot \hat{\mathbf{d}}_{i,i+1} \left(\hat{\mathbf{d}}_{i-1,i} \cdot \frac{\dot{\mathbf{d}}_{i-1,i}}{d_{i-1,i}} + \hat{\mathbf{d}}_{i,i+1} \cdot \frac{\dot{\mathbf{d}}_{i,i+1}}{d_{i,i+1}} \right)}{\sqrt{1 - \hat{\mathbf{d}}_{i-1,i} \cdot \hat{\mathbf{d}}_{i,i+1}}^2}, \quad (15)$$

where θ_i^0 and $\theta_i^{0'}$ represent the equilibrium bond angles before and after beta decays of substituted tritium, respectively. A_T is expressed as the following equations:

$$A_T = \frac{1}{2} \sum_{i=2}^{N-2} \{ n_{i,i+1} V_{i,i+1} \sin[n_{i,i+1}(\phi_{i,i+1} - \phi_{i,i+1}^0)] - n_{i,i+1}' V_{i,i+1}' \sin[n_{i,i+1}'(\phi_{i,i+1} - \phi_{i,i+1}^{0'})] \} \dot{\phi}_{i,i+1}, \quad (16)$$

$$\dot{\phi}_{i,i+1} = \frac{C - D}{\sin \phi_{i,i+1}}, \quad (17)$$

$$C = \frac{1}{|\mathbf{d}_{i-1,i} \times \mathbf{d}_{i,i+1}| |\mathbf{d}_{i,i+1} \times \mathbf{d}_{i+1,i+2}|} \times \{ (\mathbf{d}_{i-1,i} \times \mathbf{d}_{i,i+1}) \cdot (\dot{\mathbf{d}}_{i,i+1} \times \mathbf{d}_{i+1,i+2} + \mathbf{d}_{i,i+1} \times \dot{\mathbf{d}}_{i+1,i+2}) + (\mathbf{d}_{i,i+1} \times \mathbf{d}_{i+1,i+2}) \cdot (\dot{\mathbf{d}}_{i-1,i} \times \mathbf{d}_{i,i+1} + \mathbf{d}_{i-1,i} \times \dot{\mathbf{d}}_{i,i+1}) \}, \quad (18)$$

$$D = \frac{(\mathbf{d}_{i-1,i} \times \mathbf{d}_{i,i+1}) \cdot (\mathbf{d}_{i,i+1} \times \mathbf{d}_{i+1,i+2})}{|\mathbf{d}_{i-1,i} \times \mathbf{d}_{i,i+1}|^2 |\mathbf{d}_{i,i+1} \times \mathbf{d}_{i+1,i+2}|^2} \times \left\{ \frac{|\mathbf{d}_{i,i+1} \times \mathbf{d}_{i+1,i+2}|}{|\mathbf{d}_{i-1,i} \times \mathbf{d}_{i,i+1}|} (\mathbf{d}_{i-1,i} \times \mathbf{d}_{i,i+1}) \cdot (\dot{\mathbf{d}}_{i-1,i} \times \mathbf{d}_{i,i+1} + \mathbf{d}_{i-1,i} \times \dot{\mathbf{d}}_{i,i+1}) + \frac{|\mathbf{d}_{i-1,i} \times \mathbf{d}_{i,i+1}|}{|\mathbf{d}_{i,i+1} \times \mathbf{d}_{i+1,i+2}|} (\mathbf{d}_{i,i+1} \times \mathbf{d}_{i+1,i+2}) \cdot (\dot{\mathbf{d}}_{i,i+1} \times \mathbf{d}_{i+1,i+2} + \mathbf{d}_{i,i+1} \times \dot{\mathbf{d}}_{i+1,i+2}) \right\}, \quad (19)$$

$$|\sin \phi_{i,i+1}| = \sqrt{1 - \left\{ \frac{(\mathbf{d}_{i-1,i} \times \mathbf{d}_{i,i+1}) \cdot (\mathbf{d}_{i,i+1} \times \mathbf{d}_{i+1,i+2})}{|\mathbf{d}_{i-1,i} \times \mathbf{d}_{i,i+1}| |\mathbf{d}_{i,i+1} \times \mathbf{d}_{i+1,i+2}|} \right\}^2}. \quad (20)$$

where $\phi_{i,i+1}^0$ and $\phi_{i,i+1}^{0'}$, $n_{i,i+1}$ and $n_{i,i+1}'$, $V_{i,i+1}$ and $V_{i,i+1}'$ denote the equilibrium dihedral angles, the periodicities and the energy barriers to rotation before and after beta decays of substituted tritium, respectively. The sign of $\sin \phi_{i,i+1}$ is decided by that of $\{(\mathbf{d}_{i-1,i} \times \mathbf{d}_{i,i+1}) \times (\mathbf{d}_{i,i+1} \times \mathbf{d}_{i+1,i+2})\} \cdot \mathbf{d}_{i,i+1}$.

3.3. Preliminary results of the response function

We performed some preliminary calculations of the response function $\phi_{BA}(t)$ using (8) to show an example of the results obtained on the basis of the linear response theory. The average in (8) was done with 100 samples. Figure 3 shows the response function calculated for the total

Figure 3: Temporal evolution of the preliminary calculated response function for the total potential energy at 250 K in the case of $f_H = 0.1$.

Figure 4: Temporal evolution of the preliminary calculated ensemble average of the change $\langle \Delta B \rangle$ for the total potential energy at 250 K in the case of $f_H = 0.1$.

potential energy at 250 K in the case of $f_H = 0.1$. This figure tells us that $\phi_{BA}(t)$ stays almost constant after 2.0 ps although there is large fluctuation around the constant value. The constant value is found to be not zero although it should be theoretically zero. Large fluctuation and non-zero constant value are due to the small number of samples. We show, in Fig. 4, the ensemble average of the change $\langle \Delta B \rangle$ calculated using (7) for the total potential energy at 250 K in the case of $f_H = 0.1$. When performing the integral in (7), we shifted $\phi_{BA}(t)$ in the vertical axis direction so that $\phi_{BA}(t)$ converges to zero at long time. It is found from Fig. 4 that the total potential energy of polyethylene after removal of hydrogen decreases by about 400 kcal/mol within 0.3 ps.

4. Summary and future work

In this paper, we performed the MD simulations of the hydrogen-removed polyethylene to investigate the structural change of the polyethylene by beta decay of substituted tritium. By analyzing the global orientational order parameter, the folded structure of the hydrogen-removed polyethylene is found to become less ordered as the number of removed hydrogen atoms becomes larger. We also developed a theoretical approach to describe the structural change of tritium-substituted polyethylene induced by beta decays of substituted tritium in the framework of the linear response theory and showed our preliminary results of the response function for the total potential energy of the hydrogen-removed polyethylene. In this theoretical approach, the ensemble average of the difference of a physical quantity before and after beta decays of substituted tritium can be expressed by the time integration of the response function. We derived the time derivative of the dynamical quantity conjugate to the applied force needed to calculate the response function, where the dynamical quantity in this study is the total potential

energy difference before and after beta decays of substituted tritium. The advantage of this theoretical approach is that when investigating the structural change of a polymer due to beta decays of substituted tritium to helium-3 by MD simulation, it is possible to calculate the post-decay structural relaxation only by performing the pre-decay simulation, i.e., without performing the post-decay simulation. This suggests the possibility of improving the efficiency of simulation research.

For future work, we will perform calculations of the response function using (8) from our long time MD simulation of the unperturbed (i.e., hydrogen-unremoved) polyethylene which is in equilibrium at a constant temperature. As a physical quantity B , we choose the potential energy, the global orientational order parameter, the root mean square deviation of the unperturbed polyethylene, and so on. We will also compare the ensemble average of the change $\langle \Delta B \rangle$ of B calculated from (7) with that calculated using our MD simulation data of the perturbed (i.e., hydrogen-removed) polyethylene to evaluate the validity of the theoretical approach proposed in the further study.

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References

- [1] T. Tanabe: “Characteristics of Tritium” in *Tritium: Fuel of Fusion Reactors* (T. Tanabe ed.), Springer Japan, Japan, 2017, 27-48.
- [2] P. C. Souers: *Hydrogen Properties for Fusion Energy*, University of California Press, California, 1986.
- [3] S. L. Laiken, M. P. Printz, L. C. Craig: Tritium-hydrogen exchange studies of protein models. I. Gramicidin S-A, *Biochemistry*, 8:2 (1969), 519-526.
- [4] T. Udagawa, M. Tachikawa: Reaction mechanism of hydrogen-tritium exchange reactions between several organic and HTO molecules: a role of the second HTO, *RSC Adv.*, 8 (2018), 3878-3888.
- [5] M. Higuchi, M. Pinak, K. Saito: Effects of Abasic Site and 8oxoG Lesions on DNA Molecule, *Jpn. J. Health Phys.*, 42:2 (2007), 166-174.
- [6] J. Zálešák, M. Lourdin, L. Krejčí, J.-F. Constant, M. Jourdan: Structure and Dynamics

- of DNA Duplexes Containing a Cluster of Mutagenic 8-Oxoguanine and Abasic Site Lesions, *J. Mol. Biol.*, 426:7 (2014), 1524-1538.
- [7] K. Ema, Y. Izumi: Interaction of Tritium with Polyethylene, *Fusion Sci. Technol.*, 41:3P2 (2002), 378-381.
- [8] E. B. Fox, M. D. Kranjc, T. E. Skidmore: , *Fusion Sci. Technol.*, 71:4 (2017), 507-513.
- [9] S. Fujiwara, H. Nakamura, H. Li, H. Miyanishi, T. Mizuguchi, T. Yasunaga, T. Otsuka, Y. Hatano, S. Saito: Computational strategy for studying structural change of tritium-substituted macromolecules by a beta decay to helium-3, *J. Adv. Simulat. Sci. Eng.*, 6:1 (2019), 94-99.
- [10] H. Nakamura, H. Miyanishi, T. Yasunaga, S. Fujiwara, T. Mizuguchi, A. Nakata, T. Miyazaki, T. Otsuka, T. Kenmotsu, Y. Hatano, S. Saito: Molecular dynamics study on DNA damage by tritium disintegration, *Jpn. J. Appl. Phys.*, 59 (2020), SAAE01.
- [11] H. Li, S. Fujiwara, H. Nakamura, T. Mizuguchi, T. Yasunaga, T. Otsuka, T. Kenmotsu, Y. Hatano, S. Saito: Structural change of tritium-substituted polymeric materials by a beta decay: A molecular dynamics study, *Plasma Fusion Res.*, 14 (2019), 3401106.
- [12] H. Li, S. Fujiwara, H. Nakamura, T. Mizuguchi, A. Nakata, T. Miyazaki, S. Saito: Structural change of damaged polyethylene by beta-decay of substituted tritium using reactive force field, *Jpn. J. Appl. Phys.*, 60 (2021), SAAB06.
- [13] R. Kubo: *J. Phys. Soc. Jpn.*, 12:6 (1957), 570-586.
- [14] S. L. Mayo, B. D. Olafson, W. A. Goddard III: DREIDING: A Generic Force Field for Molecular Simulations, *J. Phys. Chem.*, 94:26 (1990), 8897-8909.
- [15] K. Hagita, S. Fujiwara, N. Iwaoka: Structure formation of a quenched single polyethylene chain with different force fields in united atom molecular dynamics simulations, *AIP Advances*, 8:11 (2018), 115108.
- [16] L. Verlet: Computer "Experiments" on Classical Fluids. I. Thermodynamical Properties of Lennard-Jones Molecules, *Phys. Rev.*, 159:1 (1967), 98-103.
- [17] S. Nosé: A molecular dynamics method for simulations in the canonical ensemble, *Phys. Rev.*, 52:2 (1984), 255-268.
- [18] S. Nosé: A unified formulation of the constant temperature molecular dynamics methods, *J. Chem. Phys.*, 81:1 (1984), 511-519.
- [19] W. G. Hoover: Canonical dynamics: Equilibrium phase-space distributions, *Phys. Rev. A*, 31:3 (1985), 1695-1697.

- [20] S. Plimpton: Fast Parallel Algorithms for Short-Range Molecular Dynamics, *J. Comput. Phys.*, 117:1 (1995), 1-19.
- [21] S. Fujiwara, T. Sato: Molecular dynamics simulations of structural formation of a single polymer chain: Bond-orientational order and conformational defects, *J. Chem. Phys.*, 107:2 (1997), 613-622.
- [22] S. Fujiwara, T. Sato: Molecular Dynamics Simulation of Structural Formation of Short Polymer Chains, *Phys. Rev. Lett.*, 80:5 (1998), 991-994.
- [23] S. Fujiwara, T. Sato: Molecular Dynamics Study of the Structural Formation of Short Chain Molecules: Structure and Molecular Mobility, *Mol. Simul.*, 21 (1997), 271-281.
- [24] R. Kubo, M. Toda, N. Hashitsume: *Statistical Physics II*, Springer-Verlag Berlin Heidelberg, 1985.
- [25] K. Kitahara: *Nonequilibrium Statistical Physics* (in Japanese), Iwanami Shoten Publishers, Tokyo, 1997.