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Molecular dynamics study on the thermal conductivity of a single polyethylene chain: Strain dependence and potential models' effect

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ARTICLE

Molecular dynamics study on the thermal conductivity of a single polyethylene chain: Strain dependence and potential models' effect



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ABSTRACT

The thermal conductivity of a single polymer chain, which is an important factor in the rational design of polymer-based thermal management materials, is strongly affected by the strain state of the chain. In the present study, using non-equilibrium molecular dynamics simulations, the thermal conductivity of a single polyethylene chain, representing a typical polymer chain, was calculated as a function of strain. To investigate the effect of different modeling of covalent bonds, the results were compared for reactive and non-reactive potential models, the AIREBO and NERD potentials, respectively. When the strain ε was as small as $\varepsilon < -0.03$, i.e., under slight compression, the thermal conductivity values were similar regardless of the potential model and increased with increasing strain. However, the two potential models showed qualitatively different behaviors for larger strains up to $\varepsilon < 0.15$: the thermal conductivity calculated by the non-reactive potential continually grows with increasing strain, whereas that by the reactive potential model is saturated. The analysis of internal stress and vibrational density of states suggested that the saturation behavior is due to the weakening of the covalent bond force as the C–C bond elongates, and thus, the result of the reactive model is likely more realistic. However, for $\varepsilon > 0.1$, the reactive potential also produced unphysical results due to the effect of the switching function, describing the formation and breaking of covalent bonds. The present results indicate that careful selection of the potential model and deformation range is necessary when investigating the properties of polymers under tensile strain.

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I. INTRODUCTION

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Polyethylene is known to have a low thermal conductivity of 0.1 W/(m K)¹⁻³ in its amorphous phases at room temperature, but the thermal conductivity of a single chain polyethylene is reported to be more than 200 W/(m K).⁴⁻⁶ Many studies have tried to develop various materials that utilize this potentially high thermal conductivity of a single polyethylene chain. Polyethylene nanofibers are one such material and have also been actively researched because of their high mechanical strength, corrosion resistance, and low manufacturing cost. In particular, highly oriented polyethylene nanofibers have a high thermal conductivity of $50-100 W/(m K)^{7-9}$ and are expected to play an important role in situations where directional heat conduction is important, such as

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in the fins of heat exchangers. The alignment of molecular chains has been shown to improve the thermal conductivity of amorphous polymer bulk, indicating its potential application as a polymerbased thermal interfacial material.^{10,11} In addition, polyethylene can be used as a surface modifier of filler particles, such as graphene, to enhance the interfacial heat transfer between matrix and filler particles in nanocomposites.^{12,13}

Studies have shown that the thermal conductivity of a single polyethylene chain increases as the chain length is elongated by increasing the number of carbon atoms in the chain^{3,4,14–16} or by applying tensile stress.^{1,17–20} Such an enhancement of the single chain thermal conductivity is also an important factor in improving the thermal conductivity of materials. To investigate the molecular scale mechanism of heat conduction in polyethylene chains and the relevant materials, molecular dynamics (MD) simulation is typically used.

In classical MD simulation, molecules are represented by either reactive or non-reactive potential models. The main difference between the two potential models lies in the way covalent bonds are represented. A reactive potential, while having a rather complex functional form, can describe the formation and breaking of covalent bonds so that a dynamic change between different bond orders can be dealt with by a single potential function. A non-reactive potential mainly represents covalent bonds as the sum of bond stretching, bond angle bending, and dihedral angle interactions. In particular, the bond stretching potential is most often modeled by a harmonic potential, and the formation and breaking of covalent bonds are not allowed to occur.

The reactive and non-reactive potential models for polyethylene can give similar results as long as the lengths of covalent bonds are not far from the equilibrium one. However, if a molecular chain is significantly elongated by tensile stress, the two potential types produce different results. In the case of harmonic bond potentials, force along the bond is always proportional to its displacement from the equilibrium length. The bonding force, i.e., the gradient of the bond potential, becomes stronger with increasing bond distance, and the bond can never be broken even at an infinitely long distance. In contrast, the bonding force described by a reactive potential becomes weaker with increasing bond distance until the bond finally dissociates. Due to this difference, reactive and non-reactive potential models could result in different heat conduction characteristics in a polyethylene chain under tensile strain. Some MD studies investigated the thermal transport properties and stress-strain relation of a single polyethylene chain using a non-reactive potential model based on harmonic potentials for covalent bonds; however, a similar study using a reactive potential has not been conducted to the authors' knowledge.

In this study, non-equilibrium MD (NEMD) simulations were used to analyze the thermal conductivity of a single polyethylene chain in relation to strain. Polyethylene chains were represented by both the AIREBO²¹ potential, which is a reactive potential, and the NERD²² potential, which is a non-reactive potential, with the bond stretching interaction being modeled by a harmonic potential. Our simulation results demonstrated that the two potential models give qualitatively different results, and based on that, we will discuss the criteria for selecting appropriate potential models and simulation conditions.

II. MOLECULAR MODEL AND SIMULATION PROCEDURE

MD simulations were performed using the Large-scale Atomic/Molecular Massively Parallel Simulator $(LAMMPS)^{23,24}$ software package. We used two potential models, the NERD²² and AIREBO²¹ potentials, to investigate the difference in heat conduction characteristics depending on different modeling of covalent bonds. The NERD potential is a united atom model and considers a hydrocarbon group (CH_x) as a single interaction site. The intermolecular van der Waals interaction is described by Lennard–Jones (LJ) potential, whereas the intramolecular interaction is represented by the sum of bond stretching, angle bending, and dihedral interactions. The bond stretching and angle bending interactions are

modeled by a harmonic potential. On the other hand, the AIREBO potential treats each of carbon and hydrogen atoms as an individual interaction site, and the interaction energy is expressed as

$$E = \frac{1}{2} \sum_{i} \sum_{j \neq i} \left[E_{ij}^{\text{REBO}} + E_{ij}^{\text{LJ}} + \sum_{k \neq i,j} \sum_{l \neq i,j,k} E_{kijl}^{\text{tors}} \right], \tag{1}$$

where *i* and *j* are atom indices, E_{ij}^{REBO} is Brenner's REBO potential²⁵ for covalent bonding, which can deal with the bond formation and breaking, E_{ij}^{LJ} is the intermolecular interaction expressed by LJ potential, and E_{ij}^{tors} is the intramolecular dihedral (torsion) potential. In Eq. (1), E_{ij}^{REBO} contains a switch function shown in Eq. (2) so that the covalent bond interaction is smoothly turned off at the cutoff interatomic separation r_{ii}^{max} ,

$$f_{ij}(r) = \begin{cases} 1 & (r < r_{ij}^{\min}) \\ \frac{1}{2} + \frac{1}{2} \cos\left(\pi \frac{r - r_{ij}^{\min}}{r_{ij}^{\max} - r_{ij}^{\min}}\right) & (r_{ij}^{\min} < r(r_{ij}^{\max}), \\ 0 & (r > r_{ij}^{\max}) \end{cases}$$
(2)

where *r* is the distance between the two interacting atoms, and r_{ij}^{\min} is the inner cutoff distance. We used the original settings for r^{\min} and r^{\max} , which, for the pair of carbon atoms, are $r^{\min} = 1.7$ Å and $r^{\max} = 2.0$ Å. The cutoff distance of the LJ potential was 15 Å for the NERD potential and 10.2 Å for the AIREBO potential. The timestep was set to 1 fs for the NERD potential, whereas a shorter timestep of 0.2 fs was used for the AIREBO potential, considering the fast vibration of hydrogen atoms.

In this study, we used polyethylene chains with two different lengths composed of 85 and 165 CH₂ units and hereafter denoted by $N_{\rm C}$ = 85 and $N_{\rm C}$ = 165, respectively. The polyethylene chain is placed elongated in the z direction. Thus, as in other MD studies, D ^{7–20} we consider extended chains, even though folded states may be energetically more stable.²⁶ The chain length L was defined by the difference of the z coordinates between the two terminal carbon atoms at both ends. Prior to the MD simulations, we performed potential energy minimization based on the conjugate gradient algorithm to find the optimized geometry at 0 K for the two chains. The chain length at the optimized geometry was defined as the reference chain length L_0 . Both before and after the minimization, the polymer chains retained a straight chain shape. The value of L_0 determined for each potential model is presented in Table I. This reference chain length is used to define the strain ε of a chain with length *L* as $\varepsilon = (L-L_0)/L_0$, when we investigate the strain dependence of stress and thermal conductivity at 300 K. We note that L_0 gives zero stress at 0 K but not at 300 K.

TABLE I. Reference length L_0 of a polyethylene chain containing 85 and 165 carbon atoms, $N_C = 85$ and $N_C = 165$, respectively.

	<i>L</i> ₀ (nm)	
	$\overline{N_{\mathrm{C}}} = 85$	N _C = 165
AIREBO	10.69	20.88
NERD	10.84	21.16

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We, nevertheless, adopted this definition because the chain length of zero stress at 0 K is strictly defined, while the length at 300 K was ambiguous as we will see later [Fig. 4(a)]. If necessary, one can easily convert the strain ε' defined by another reference length L'_0 using the equality $L = L_0(\varepsilon + 1) = L'_0(\varepsilon' + 1)$.

Thermal conductivity was calculated using NEMD simulation. First, a single polyethylene chain was placed in a vacuum. The terminal carbon and hydrogen atoms at both ends were fixed. Then, the temperature was increased at a constant rate from 5 to 300 K in 2 ns via Nosé-Hoover thermostat^{27,28} with a temperature damping parameter of 1 ps. Afterward, the system was equilibrated for 2 ns to produce a canonical (NVT) ensemble at temperature T = 300 K using a Nosé–Hoover thermostat. Then, the Nosé–Hoover thermostat was turned off, and a relaxational calculation was performed for 2 ns to generate the microcanonical (NVE) ensemble. Finally, a NEMD simulation was performed for 10 ns, where the two hydrocarbon groups adjacent to the terminal groups were considered as the heat source and sink and were coupled with Langevin thermostats²⁹ with the damping coefficient set to 0.2 ps, as shown in Fig. 1. The temperature of the heat source was set to 310 K and that of the heat sink to 290 K, in order to generate a temperature gradient along the molecular axis (z direction).

Of the 10 ns NEMD simulation, the first 2 ns were used to impose a steady state with a temperature gradient, and the following 8 ns were used to calculate thermal conductivity in the *z* direction and the vibrational density of states (VDOS). In addition to the NEMD simulation, an *NVE* simulation without any temperature control was also performed for 10 ns after the *NVT* relaxation mentioned above, from which the stress tensor inside the chain and the probability distribution of C–C bond distance were calculated.

The NEMD and *NVE* simulations were conducted for different values of the chain length *L* by contracting or elongating the chain: 11 different *L* values for the chain with $N_{\rm C}$ = 85 and 21 values for $N_{\rm C}$ = 165 were examined.

The stress tensor σ is expressed as^{30,31}

$$\sigma V = -\left(\sum_{i \in V} m_i \mathbf{v}_i \otimes \mathbf{v}_i\right) - \left(\frac{1}{2} \sum_{i} \sum_{j \neq i} \frac{\partial \phi_j}{\partial \mathbf{r}_i} \otimes (\mathbf{r}_i - \mathbf{r}_j)^*\right), \quad (3)$$

where *V* is the control volume, and m_i , \mathbf{r}_i , and \mathbf{v}_i are the mass, position vector, and velocity vector of the *i*th particle, respectively. The symbol \otimes indicates a tensor product. The potential energy of the *j*th particle, $\phi_j = \phi_j$ ($\mathbf{r}_1, \ldots, \mathbf{r}_N$), only depends on atom positions. The notation ($\mathbf{r}_i - \mathbf{r}_j$)^{*} means the part of the vector $\mathbf{r}_i - \mathbf{r}_j$ included in the control volume. The *zz* component of the stress tensor was calculated within the control volume located at the center of the chain with a *z*-width of 50 Å for $N_{\rm C}$ = 85 and 100 Å for $N_{\rm C}$ = 165 with the



FIG. 1. Simulation model of a single polyethylene chain. The distance between terminal carbon atoms is the chain length L of polyethylene.



FIG. 2. Temperature distribution along a polyethylene chain composed of 165 hydrocarbon units, where the length is 20.6 nm, calculated using AIREBO potential. The cross marker represents the average temperature of a single carbon site, while the black line shows the linear fitting. The vertical dashed gray lines indicate the control volume.

xy cross-sectional area of S = 18 Å². This value of *S* is an approximate cross section of a single polyethylene chain,⁴ and here, it was assumed to be constant regardless of the degree of chain elongation and $N_{\rm C}$.

The thermal conductivity κ was obtained via Fourier's law,

$$\kappa = \frac{-J}{(dT/dz)},\tag{4}$$

where *J* is the heat flux, and dT/dz is the temperature gradient. The heat flux was calculated from the energy input into the heat source atoms, $E_+ > 0$, and that into the heat sink atoms, $E_- < 0$, by the Langevin thermostats during the production simulation with a time duration of t = 8 ns,

$$J = \frac{(E_{+} - E_{-})}{2St}.$$
 (5)

The temperature gradient was calculated via linear fitting to the temperature distribution along the z direction as shown in Fig. 2, where the temperature of each carbon atom is plotted against the time-averaged z coordinate of the atom. The fitting was performed over the control volume. We note that since the statistical error in the thermal conductivity calculated by a single 10 ns NEMD simulation was relatively large compared with those in other properties, the 10 ns NEMD simulation was performed 10 times in total using different random seeds of the Langevin thermostats. The thermal conductivity was calculated as the average over these ten trajectories, where the data in the first 2 ns for each run corresponding to the relaxation were not used.

III. RESULTS AND DISCUSSION

A. Thermal conductivity-strain relation

The calculated thermal conductivity is shown in Fig. 3 as a function of strain. The strain for a chain with length L was defined as $\varepsilon = (L-L_0)/L_0$ from the reference chain length L_0 in Table I. In the case of the NERD potential, the thermal conductivity always increases with increasing strain for both $N_C = 85$ and 165. Similar results have been obtained in other MD studies of polyethylene

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FIG. 3. Thermal conductivity of a single polyethylene chain composed of (a) 85 and (b) 165 carbon atoms as a function of strain.

chains and other one dimensional materials^{32,33} using non-reactive potential models based on harmonic potentials for covalent bonds, such as COMPASS,¹⁷ PCFF,¹⁸ and TraPPE.²⁰ As Rieder et al.³⁴ reported on the basis of a stationary solution of the generalized Liouville equation, the thermal conductivity of a one-dimensional harmonic chain is known to diverge in proportion to the chain length. As the bonds in the chain cannot be broken, the thermal conductivity of the chain will continue to increase with strain. It is, therefore, considered that the diverging trend of thermal conductivity is a common feature of non-reactive potential models. In contrast, when the AIREBO potential is used, the thermal conductivity exhibits a maximum at $\varepsilon \sim 0.03$. This result seems more reasonable than that of the NERD potential because the strength of an actual covalent bond is weakened as the bond breaking distance is approached. However, it is worth noting that the curves for the AIREBO potential discontinuously jump at $\varepsilon \sim 0.1$. The reason for this jump will be discussed in Secs. III C and III D. Thus, the thermal conductivity values computed from the two potentials are close to each other only when the strain is smaller than ~0.03, but as the strain increases, the two potentials show a large difference. There is a possibility that the leveling-off of the AIREBO curve at high strain is due to the explicit hydrogen atoms, since these atoms, which are not present in the NERD potential, can be a scattering source for phonons propagating in the carbon backbone. Although we did not examine non-reactive potentials with explicit hydrogens in the present

study, other MD studies^{17–19} have shown that the thermal conductivity of a single polyethylene chain calculated with such a model continues to increase to the order of 10^2 W/(m K) with increasing strain to the order of 0.1, as the NERD curves in Fig. 3. Therefore, the existence of explicit hydrogens is not the main reason for the leveling-off.

In addition, to briefly see the effect of temperature, we have performed an additional simulation for each potential at 400 K with $\varepsilon = 0.05$ and $N_{\rm C} = 85$. The calculated values of thermal conductivity at 400 K were $\kappa = 18.3 \pm 0.8$ W/(m K) for AIREBO and $\kappa = 96.6 \pm 9.6$ W/(m K) for NERD. These values are lower than those at 300 K for the same ε and $N_{\rm C}$, $\kappa = 22.5 \pm 1.4$ W/(m K) for AIREBO, and $\kappa = 155.9 \pm 6.8$ W/(m K) for NERD. This reduction of thermal conductivity is presumably because ballistic heat transfer along the chain is more scattered by enhanced thermal motion. On the other hand, the two potentials still exhibit a large difference in thermal conductivity at 400 K, indicating that the qualitative difference in strain-dependent thermal conductivity between the two potentials is not peculiar to 300 K.

B. Stress-strain relation

The *zz* component of the stress tensor, σ_{zz} , in the polyethylene chain, as defined by Eq. (3), was also calculated as a function of strain, and the result is shown in Fig. 4(a). For all curves in Fig. 4(a),



FIG. 4. (a) Stress–strain curve for a single polyethylene chain represented by either the AIREBO or NERD potentials at different chain lengths L. (b) Apparent Young's modulus E of a single polyethylene chain as a function of strain, calculated with the AIREBO and NERD potentials.

the stress is not completely zero even when the strain is zero, i.e., $L = L_0$, because the stress values were calculated at a finite temperature, whereas L_0 was obtained at 0 K. As mentioned in Sec. II, we adopted this definition of strain because it was difficult to determine the chain length of zero stress at 300 K from Fig. 4(a) without ambiguity. It can be seen that the curves for $N_{\rm C}$ = 85 and 165 are almost identical as long as the same potential model is used, meaning that the effect of the number of carbon atoms is not significant. The difference between the AIREBO and NERD potentials is small when $\varepsilon < 0$, but when $\varepsilon > 0$, the stress values calculated by the two potential models are significantly different. For $\varepsilon > 0$, AIREBO has larger stress values than NERD, contrasting with the fact that the latter produces higher thermal conductivity in Fig. 3. The exact reason for this reversal of the relationship between stress and thermal conductivity is not clear, but one possibility is that in the AIREBO case, the motions of explicit hydrogen atoms enhance the scattering of the phonons traveling through the carbon backbone, which results in a significant reduction in thermal conductivity. A similar mechanism has been used to explain the reduced thermal conductivity of hydrogenated graphenes.³⁵ The stress curve in Fig. 4(a) was numerically differentiated with respect to strain ε by the central difference method, and the resultant curve is shown in Fig. 4(b). The vertical axis $E = d\sigma_{zz}/d\varepsilon$ can be regarded as Young's modulus, but it might be called apparent Young's modulus because it is strain-dependent and not a material constant. From Fig. 4(b), the apparent Young's modulus E of the NERD potential roughly remains unchanged after $\varepsilon \sim 0$. This indicates that the elastic energy is expressed as a quadratic function of strain, consistent with the fact that the harmonic bond stretching potential is used in the NERD potential. In the case of the AIREBO potential, *E* decreases after $\varepsilon \sim 0.03$, which corresponds to the weakening of the interaction as the dissociation of the C–C bonds approach. The peak position $\varepsilon \sim 0.03$ is close to that in the curve of thermal conductivity for the AIREBO in Fig. 3, indicating a clear correlation between thermal conductivity and elastic property. Thus, the difference in the modeling of covalent bond interactions between the NERD and AIREBO potentials resulted in qualitatively different stress–strain relations under large strain conditions.

C. Vibrational density of states analysis

In order to analyze the difference in the heat transfer mechanism between the NERD and AIREBO cases, VDOS was calculated by Fourier transforming the carbon atom's velocity autocorrelation function for the chain with $N_{\rm C}$ = 165. This analysis was performed for the zero (ε = 0) and the largest strain states (ε = 0.13 and ε = 0.15 for the NERD and AIREBO potentials, respectively) to examine the effect of the strain. As can be seen by comparing Figs. 5(a) and 5(b), in the case of the NERD potential, the change in VDOS by the application of strain was relatively small, indicating that the vibrational modes available for heat conduction do not change significantly with strain, although their intensities can change. This result suggests that the heat transfer mechanism is maintained to some extent regardless of strain.

In contrast, in the case of AIREBO potential in Figs. 5(c) and 5(d), there was a clear difference between the VDOS profiles for the two strain values. When the strain is zero, the overall shape of the VDOS is similar to that of the NERD in Fig. 5(a), although each peak is slightly less sharp and is located at a much higher frequency.



FIG. 5. VDOS of a single polyethylene chain under different strain ε . (a) and (b) show the results for the NERD potential at zero and the largest strain examined in the present study, respectively. Similarly, (c) and (d) are the results at zero and the largest strain for the AIREBO potential, respectively.

The reason for the different peak locations can be explained by the larger spring coefficient in AIREBO than in NERD, as shown in Fig. 4(b). That is to say, at zero strain, the vibration modes in the two potential models are approximately similar except for their frequencies. The calculated peak positions for the AIREBO potential at $\varepsilon = 0$ [Fig. 5(c)] are in good agreement with those in other studies.^{4,36} However, at $\varepsilon = 0.15$, the peak at 18 THz was shifted toward the lower frequency side, and the peak at 28-35 THz became a rather broad peak at the high frequency range. This change is considered to reflect the fact that the periodic potentials for phonon vibrations are more anharmonic. This increased phonon scattering and the decrease in the apparent Young's modulus in Fig. 4(b)may explain the suppression of thermal conductivity calculated by the AIREBO potential at high strain states in Fig. 3. However, it should be noted that a similar change in VDOS has been obtained by Yang et al. when they applied a strong strain to graphene nanoribbons modeled with the AIREBO potential.³⁷ They concluded that an inaccurate behavior of the switching function for representing the formation and breaking of covalent bonds, shown in Eq. (2), is responsible for these changes in the peak shapes. This inaccuracy at the same time causes an overestimation of Young's modulus, thereby leading to an overestimation of thermal conductivity. It has also been shown that Young's modulus of graphene cannot be correctly evaluated under high strain when the ReaxFF force field, a reactive potential, is used.³⁸ Thus, in the case of reactive potentials, where the use of a switching function is inevitable, it is considered that thermal conductivity cannot be calculated accurately under high strain.

We can conclude that when the distance *r* between covalently bonded carbon atoms does not exceed r^{\min} , the AIREBO potential reasonably describes the heat transfer between them, but when covalent bonds whose distance is in the switching region at $r^{\min} < r < r^{\max}$ exist, such covalent bonds make the thermal conductivity calculation inaccurate. This can be observed in Fig. 3, where the thermal conductivity for the AIREBO potential decreases with increasing strain after $\varepsilon \sim 0.03$, but it increases again at $\varepsilon = \sim 0.1$ discontinuously and does not decrease for higher strain values. As will be shown in Sec. III D, this inconsistent behavior for $\varepsilon > 0.1$ is due to the overestimation associated with the inaccuracy in the switching function.

D. Bond distribution analysis

In order to examine the effect of the switching function, we calculated the probability distribution of C–C bond distance for the $N_{\rm C}$ = 165 chain with the AIREBO potential. The calculation results for a low strain case with ε = 0.03 (7 GPa) and a high strain case with ε = 0.15 (24 GPa) are shown in Figs. 6(a) and 6(b), respectively. Since the distribution might be affected by the fixed ends of the chain, we also calculated the same distribution function from simulations under constant tensile force conditions. In this simulation, for the right side, the fixed boundary condition was removed,



FIG. 6. Probability distribution of C–C bond distance in a single polyethylene chain composed of 165 hydrocarbon units and modeled by the AIREBO potential. In (a) and (b), the hydrocarbons at both ends were fixed; in (c) and (d), only the left end was fixed, and a constant tensile force was applied to the right side. The average tensile force in (c) and (d) are equal to those in (a) and (b), respectively.

and a constant tensile force was applied on the terminal carbon atom, while for the left side, the terminal atoms were kept fixed. The results of the constant tensile force simulations for the same values of applied tensile force as those in Figs. 6(a) and 6(b) are shown in Figs. 6(c) and 6(d), respectively. The inner cutoff distance $r^{\min} = 1.7$ Å, which indicates the start of the switching region, is shown by the vertical dashed line in Fig. 6.

In the low strain case [Fig. 6(a)], the number of bonds exceeding r^{\min} was almost zero. In contrast, in the high strain case [Fig. 6(b)], the C–C bond distance exceeded r^{\min} with a high probability. It is also noted that the distribution for the larger interatomic distances rapidly drops to zero. Since we confirmed that there was no breaking of C-C bonds, this sudden change of bond distance distribution may indicate that the molecule is in an unphysical state. The switching function for the C–C distance r_{CC} changes steeply from 1 to 0 in the narrow range $r^{\min} = 1.7$ Å $\leq r_{CC} \leq r^{\max} = 2.0$ Å, which is likely to cause the sudden change in the bond distribution. Brenner et al. pointed out²⁵ that the range of the switching region must be restricted to 1.54 Å $\leq r_{CC} \leq 2.2$ Å in view of the reproduction of C–C bond distances in real materials. It is, therefore, difficult to significantly enlarge the switching region by decreasing r^{\min} and increasing r^{max} to mitigate the steep switching. As shown in Figs. 6(c) and 6(d), similar results were obtained for the constant tensile force simulations, indicating that this seemingly unphysical state is not due to specific boundary conditions. This analysis suggests that for $\varepsilon > 0.1$, the system is significantly affected by the switching function, which might result in thermal conductivity being overestimated. Therefore, the thermal conductivity calculated with the AIREBO potential is only reliable up to $\varepsilon = 0.1$. Although it appears that this threshold of ε can be increased by increasing r^{\min} , the increased amount of r^{\min} is quite limited by the condition $r^{\min} < r^{\max}$ and the above restriction for the range of the switching region. In addition, if r^{max} is fixed, the switching function becomes steeper as r^{\min} increases, thereby making the numerical integration of the equation of motion more unstable.

E. Discussion

In the case of the NERD potential, the high thermal conductivity values at the high strain states in Fig. 3 are likely due to the harmonic nature of the covalent bond potentials. In actual molecules, as the bond distance increases, the corresponding interatomic interactions should become weaker and more anharmonic until the bond finally breaks under a sufficiently large strain. Therefore, a non-reactive potential, especially a harmonic potential, is not suitable to represent covalent bonds where polymer chains are greatly stretched, and the resulting high thermal conductivity values obtained in this work under such high strain for the NERD potential are likely an artifact of this. Therefore, while the use of non-reactive potentials produces apparently valid thermal conductivity values in polymer chains, reactive potentials such as the AIREBO potential would be preferable to investigate thermal transport in materials under strain. However, as previously suggested by Ref. 37, the range of strain should be carefully chosen so that the bond distance does not fall within the switching region of the potential function used. In this study, thermal conductivity calculated with the AIREBO potential is reliable for ε < 0.1. In more practical materials, such as hydrogels,³⁹ thermal conductivity and stress are cross-coupled with many other properties, including diffusivity and electric conductivity. Care must be taken when one investigates these properties under high strain using classical potentials since similar errors might also exist in these properties.

IV. CONCLUSION

In this study, MD simulations were used to calculate the thermal conductivity of a single polyethylene chain under strain using a non-reactive (NERD) and a reactive (AIREBO) potential model.

We found that the two potential models give similar thermal conductivity values under near zero strain, but they lead to qualitatively different results at higher strain values. The difference in the thermal conductivity values calculated by the two models amounted to more than tenfold when compared at $\varepsilon = 0.1$. Under high strain, the thermal conductivity in polyethylene modeled by a non-reactive potential can be very high, but this is likely due to the unrealistic non-reactive nature of the harmonic potential representing covalent bonds. The use of a reactive potential is, therefore, recommended when one investigates the thermal conductivity of polyethylene and other polymer chains under strain. However, in order to fully prove the superiority of reactive potentials for high strain states, it would be necessary to actually measure the strain-dependent thermal conductivity of a single polyethylene chain by experiments or to evaluate it by ab initio molecular dynamics simulations. In addition, even with reactive force fields, the thermal conductivity cannot be reliably determined under very large strain, $\varepsilon > 0.1$ in this work, due to the effect of switching functions used to change between bond formation and dissociation. Therefore, the development of a new force field is necessary in order to investigate thermal transport properties in materials under high stress using classical MD simulation.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

T.I. and H.M. have contributed equally to this work.

Tsuyoshi Ito: Data curation (lead); Investigation (lead); Writing – original draft (lead). Hiroki Matsubara: Methodology (lead); Supervision (lead); Writing – review & editing (lead). Donatas Surblys: Supervision (lead); Writing – review & editing (lead). Taku Ohara: Funding acquisition (lead); Project administration (lead); Supervision (lead); Writing – review & editing (lead).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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