Thermal Conduction in a Single Polyethylene Chain Using Molecular Dynamics Simulations *

HU Guo-Jie(胡国杰), CAO Bing-Yang(曹炳阳)**, LI Yuan-Wei(李元伟)

Key Laboratory for Thermal Science and Power Engineering of Ministry of Education,
Department of Engineering Mechanics, Tsinghua University, Beijing 100084

(Received 11 June 2014)

Research on the thermal conduction in a single polymer chain is significant for the improvement of the thermal property of bulk polymer materials. We calculate the thermal conductivity of a single polyethylene (PE) chain by using both the Green–Kubo approach and a nonequilibrium molecular dynamics simulation method. The results suggest that the thermal conductivity of an individual polymer chain is very high although bulk PE is a thermal insulator, even divergent in our case. Moreover, the thermal conductivity of PE chains is observed to increase with the chain length.

PACS: 65.80.–g, 66.30.hk, 61.41.+c DOI: 10.1088/0256-307X/31/8/086501

Polymer materials, both natural and synthetic, play an essential and ubiquitous role in everyday life due to their unique properties including toughness, viscoelasticity, and a tendency to form glasses and semicrystalline structures rather than crystals. In recent years, with the progress in nanofluidics and nanotechnology, polymer nanostructures have drawn increasing attention for their wide potential applications in areas such as photonics,[1,2] mechatronics,[3,4] medicine and fluidic nanodevices.[5,6] However, polymer materials are generally regarded as thermal insulators due to the fact that they have very low thermal conductivity on the order of 0.1–1 W/(m·K), at room temperature.[7,8] By performing an ab initio calculation, it was also observed that the thermal conductivity can reach a high value of about 310 W/(m·K) in a 100 nm PE chain at room temperature.[9] What is more, the high thermal conductivity of a single PE chain or oriented PE chains has been recently confirmed by experimental measurements. Shen et al.[10] measured the thermal conductivity of ultradrawn PE nanofibers to be about 104 W/(m·K). Cao et al.[11] discovered that the thermal conductivity of PE nanowire arrays with a high orientation of chains was 26.5 W/(m·K), about 300 times that of the bulk counterpart. Considering that PE is one of the non-conducting polymers which have extremely low electrical conductivities, a PE chain will be a possible candidate of the materials with high thermal conductivities while having the low electrical conductivities that are desired for engineers in an integrated circuit. The enhancement of the thermal conductivity of a single polymer chain or oriented polymer chains, which is believed to be attributed to a better alignment of polymer chains, implies a more efficient way to enhance the thermal conductivity of polymer products, and thus it is meaningful to investigate thermal conduction in a single polymer chain.

The related studies have been carried out as mentioned above, while some inconsistent conclusions should be noted. Herry et al.[12,13] found the divergence of the thermal conductivity of an individual PE chain when the simulation domain was longer than 10 nm, while Jiang et al.[14] predicted the up-

*Supported by the National Natural Science Foundation of China under Grant Nos 51322603, 51338001 and 51335001, the Program for New Century Excellent Talents in University, the Science Fund for Creative Research Groups under Grant No 51321002, and the Initiative Scientific Research Program of Tsinghua University.

**Corresponding author. Email: caoby@tsinghua.edu.cn
© 2014 Chinese Physical Society and IOP Publishing Ltd
per limit of the thermal conductivity in a 100 nm PE chain. Moreover, the influence of the chain length on the thermal conductivity has not been clarified. The underlying mechanisms of the thermal transport remain obscure. In our work, both the limiting thermal conductivity of PE chains and the dependence of the thermal conductivity of finitely long PE chains on the chain length are studied.

In our simulations, a simplified model of a PE chain where methylene (CH₂) groups are regarded as united atoms is applied as shown in Fig. 1. The model ignores the motion of the hydrogen atoms by attaching them rigidly to the carbon atoms on the backbone. The atomic interactions are described by the Kirkwood model,\(^{[19]}\) which has a smaller computational demand and can accurately describe the heat conduction of PE chains,\(^{[20]}\)

\[
\Phi = \sum_i \left[ \frac{\gamma_r}{2} (\Delta r_i)^2 + \frac{\mu_r}{3} (\Delta r_i)^3 + \frac{\nu_r}{4} (\Delta r_i)^4 + \frac{\gamma_\theta}{2} (\Delta \theta_i)^2 - \frac{\mu_\theta}{3} (\Delta \theta_i)^3 + \frac{\nu_\theta}{4} (\Delta \theta_i)^4 \right],
\]

where

\[
\Delta r_i = |\mathbf{r}_i - \mathbf{r}_{i-1}| - r_0, \quad \Delta \theta_i = \frac{(\mathbf{r}_i - \mathbf{r}_{i-1}) \cdot (\mathbf{r}_{i+1} - \mathbf{r}_i)}{|\mathbf{r}_i - \mathbf{r}_{i-1}||\mathbf{r}_{i+1} - \mathbf{r}_i|} + \cos \theta_0.
\]

Here \(\mathbf{r}_i\) denotes the position of the \(i\)th united atom, \(\gamma_r, \mu_r, \text{ and } \nu_r\) denote the force constants for stretching the carbon-carbon bond, while \(\gamma_\theta, \mu_\theta, \text{ and } \nu_\theta\) are the force constants for bending the bond. The equilibrium carbon-carbon distance is denoted by \(r_0 = 0.154\) nm and \(\theta_0\), which is roughly equal to the tetrahedral angle where \(\cos \theta_0 = -1/3\).

![Fig. 1. Schematic diagram of the actual structure and simplified model of a PE chain.](image)

The Green–Kubo approach,\(^{[21]}\) where the thermal conductivity is given by

\[
\lambda = \frac{V}{k_BT^2} \int_0^\infty \langle J(0)J(t) \rangle dt,
\]

which is used here to determine the limiting thermal conductivity of PE chains. In the above equation, \(\langle J(0)J(t) \rangle\) is the heat flux autocorrelation function (HAF) where \(J(t)\) denotes the heat flux directed along the carbon backbone of the chain at time \(t\), \(T\) is the temperature, and \(V\) is the chain’s volume. Here the volume is taken as the chain length \(L\) multiplied by a cross-sectional area \(A\) of 18 Å², which is based on the unit cell dimensions of PE’s idealized bulk lattice structure. The periodic boundary conditions are applied. Considering the chosen equilibrium simulation method (i.e., the Green–Kubo approach) and periodic boundary conditions, the boundary scattering would not conceal any divergent behaviors and the phonon modes would be allowed to propagate on an infinite chain, uninhibited by the boundaries. Thus our Green–Kubo results can explore the limiting thermal conductivity. The mean temperature of the system is set to be 300 K. The motion equations for the molecules are integrated by using the Leap-Frog algorithm with a time step of \(dt = 0.5\) fs. Moreover, since the initial condition would significantly influence the results of the Green–Kubo thermal conductivity, 32 cases under various initial velocity conditions are simulated to obtain the ensemble average of the HAF. The HAF integration that is the Green–Kubo thermal conductivity integral is presented in Fig. 2, while the dependence of the thermal conductivity on the case number is given in the inset. As shown in Fig. 2, the Green–Kubo thermal conductivity increases with the integration time strikingly within the first 250 ps and continues increasing in the integration limit of 3 ns, which indicates that the thermal conductivity exhibits diverging behavior in our simulation since for the three-dimensional bulk crystalline materials studied by the Green–Kubo method, the HAF integration typically converges within the first 500 ps.\(^{[22]}\)

![Fig. 2. Green–Kubo thermal conductivity integral and (inset) dependence of the thermal conductivity on the case number.](image)

The divergence of the thermal conductivity has also been observed in previous studies.\(^{[12,13]}\) However, the behavior was believed to be related to the feature of the initial velocity conditions. As mentioned before, the above results are the ensemble average of 32 cases under various initial velocity conditions, thus the influence of the initial conditions is excluded. To illustrate this phenomenon more clearly, the depen-
dence of the thermal conductivity on the case number is also obtained, as shown in the inset in Fig. 2. It can be seen that the thermal conductivity converges with the case number when the number is larger than 20. Thus the diverging behavior of the thermal conductivity observed in our simulations is not attributed to the initial conditions. It is believed that the divergent phenomenon is likely due to the specific feature of one-dimensional polymer chains where some nondecaying phonon modes are observed. Moreover, the values of our results are smaller than those obtained by Henry et al.\cite{12,13} due to the fact that the group velocities estimated by the Kirkwood model are lower than those calculated from the AIREBO potential employed by them.

Except for the limit of the thermal conductivity, the result for a finitely long PE chain and its dependence on the chain length are also meaningful for understanding the heat conduction. The nonequilibrium molecular dynamics simulation method is used here to investigate the dependence of the thermal conductivity on the chain length. A temperature gradient is built in the system by using the particle velocity exchange algorithm,\cite{23} where the heat flux is calculated by

\[ J = \frac{\sum_{\text{transfers}} m (v_{h}^{2} - v_{c}^{2})}{tA}, \]

where \( m \) is the mass of the unit atom (CH\(_{2}\)), \( t \) is the simulation time, and \( v_{h} \) and \( v_{c} \) are the velocities of the hot and cold particles, respectively, which are interchanged. Then, the thermal conductivity can be very easily extracted by using Fourier’s heat conduction law. In addition, a fixed boundary condition is applied. In the simulation, the motion equations for the molecules are also integrated by using the Leap-Frog algorithm with a time step of \( dt = 0.5 \) fs. The mean temperature of the system is maintained at 300 K by the Nose–Hoover thermostat method.\cite{24,25} The temperature difference between the hot and cold slabs is set to be 20 K. Each case is run for 5 ns to stabilize the heat conduction and then for 5 ns to average the local slab temperatures and heat flux. The heat flux evolution over the statistics time for a 65 nm long PE chain is presented in Fig. 3(a). It can be seen that the result of the heat flux has already converged, which indicates that the simulation time length is sufficient to obtain converged results. Figure 3(b) shows the temperature distribution for a 65 nm long PE chain. The temperature jumps near the boundaries. The jumps can be attributed to the existence of localized edge modes (LEM) and the accumulation of LEM caused by the velocity exchange. The LEM attenuates fast along the direction of heat conduction and affects the conduction at the section less. Thus the temperature is approximately linear in the middle section and the temperature gradient is obtained by a linear fitting of the temperature distribution in the section.

![](image)

Fig. 3. Heat flux evolution over the statistics time (a) and temperature distribution (b) for a 65 nm long PE chain.

Figure 4 shows the simulation thermal conductivities of the PE chains with various lengths. The results agree well with the previous values calculated by Ni et al.\cite{20} It is shown that the thermal conductivity increases with the chain length while the trend is weakened with the increasing length. When the length is shorter than 70 nm, the increase is approximately linear, while the increase becomes slower as the chain length keeps increasing. This indicates that the phonon transport in the PF chains is in the ballistic-diffusive regime, and transits from ballistic to diffusive with the increase in the chain length. Furthermore, model analysis is used to determine the intrinsic thermal conductivity. Based on Matthiessen’s rule, considering phonon-phonon and phonon-boundary scattering, the phonon mean free path can be expressed as \( l^{-1} = l_{p-p}^{-1} + L^{-1} \), where \( l_{p-p} \) is the phonon mean free path due to phonon-phonon scattering. Then, the thermal conductivity can be determined as

\[ \lambda = C \nu_{g} l = C \nu_{g} \frac{L}{L + l_{p-p}} = \lambda_{p-p} \frac{L}{L + l_{p-p}}, \]

where \( C \) is the specific heat per unit volume of the chain, \( \nu_{g} \) is the phonon group velocity, and \( \lambda_{p-p} \) is the intrinsic thermal conductivity. We can obtain the parameters of \( \lambda_{p-p} \) and \( l_{p-p} \) by two-parameter fitting of the simulation results. The fitting curve is presented in Fig. 4. It can be seen that the curve fits the MD results very well. The obtained two parameters are determined to be \( \lambda_{p-p} = 314.5 \, \text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1} \) and \( l_{p-p} = 324 \, \text{nm} \). Different from the divergence of the limiting thermal conductivity calculated by the Green–Kubo method, the obtained intrinsic thermal conductivity is a finite value. The departure is likely
to be attributed to the nonequilibrium approach that would have concealed any potentially nonattenuating modes.

![Graph](image)

**Fig. 4.** Dependence of the thermal conductivity of PE chains on the length.

In summary, the thermal conduction in a single polymer chain is studied by using MD simulations. The Green–Kubo approach is used to simulate the limiting thermal conductivity of PE chains at room temperature. It is observed that the thermal conductivity of a single PE chain diverges. Meanwhile, the dependence of the thermal conductivity of finitely long PE chains on the chain length is studied by using the nonequilibrium molecular dynamics simulation method. The results show that the thermal conductivity increases with the chain length while the trend is weakened with increasing the length, which indicates that the phonon transport in the PF chains is in the ballistic-diffusive regime, and transits from ballistic to diffusive with the increase of the chain length.

**References**

[10] Padgett C W and Brenner C W 2004 *Nano Lett.* 4 1051