<u>修士論文</u>

Molecular Dynamics Simulation of Thermal Boundary Conductance between SWNT and Surrounding Fluid 単層 CNT と周囲流体の界面熱コンダクタンスの分子動力学解析

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Chapter 1

Introduction

1.1 Background

Dimensionally, carbon can take many forms: 3D-diamond and graphite, 2D-graphene – one layer of graphite, 1D-carbon nanotube (CNT) and 0D-fullerene (See Fig 1.1). The Fullerene was discovered in 1985 by Robert F. Curl, Sir Horold W. Kroto, and Richard E. Smalley [1], who were awarded the Nobel prize in chemistry in 1996.

In 1991, Iijima *et al.* discovered multi-walled carbon nanotubes (MWNT) when they made fullerenes by arc-discharge. Two years later, they could make a single-layer rolled up carbon tube, and they named it "single-walled carbon nanotube (SWNT)" [2,3]. Due to its nano-structural outstanding electronic, thermal and mechanical properties, it has been one of the most focused topics in nano-technology research.



Figure 1.1 (a) A single-walled carbon nanotube (1D) and (b) C_{60} or the "buckyball", known as a quantum dot.

1.2 The structure of SWNT

An SWNT structure is formed as if it is rolled up from a graphene sheet, and its diameter ranges from 1 nm to 5 nm, but its length from μ m to mm. Due to the high aspect ratio of SWNTs, it is treated as a quasi-one-dimensional material. The form it takes depends on which chiral vector is chosen for rolling up from graphene. This chiral vector mainly decides the diameter and chiral angle of SWNTs, and they are key factors for physical properties.

The structure of the sp² carbon network of a two-dimensional (2D) graphene sheet is described as a hexagonal lattice in Fig. 1.2(a). The unit cell shown in Fig. 1.2(a) contains two non-equivalent C atoms. Vectors a_1 and a_2 represent the unit vectors of the cell. The Brillouin zone of the graphene is shown in Fig. 1.2(b). This is the momentum space reciprocal lattice, and spanned by the reciprocal space basis vectors b_1 and b_2 . These are expressed as

$$a_1 = \left(\frac{\sqrt{3}}{2}a, \frac{a}{2}\right), \quad a_2 = \left(\frac{\sqrt{3}}{2}a, -\frac{a}{2}\right)$$
 (1.1)

and

$$\boldsymbol{b}_1 = \left(\frac{2\pi}{\sqrt{3}a}, \frac{2\pi}{a}\right), \quad \boldsymbol{b}_2 = \left(\frac{2\pi}{\sqrt{3}a}, -\frac{2\pi}{a}\right) \tag{1.2}$$

where $|a_1|=|a_2|=a=\sqrt{3} a_{c-c}$, where $a_{c-c}=1.452$ Å is the distance between neighboring carbon atoms. By contrast, high symmetry points at the center, corner, and the midpoint of the neighboring corners of the Brillouin zone are denoted as Γ , M, and K points, respectively.

The structure of a carbon nanotube is specified by the chiral vector C_h as shown in Fig. 1.3, which defines the direction of rolling up the graphene sheet in to a tube. The chiral vector C_h is expressed in terms of real-space unit vectors a_1 and a_2 and two positive integers n and m as



Figure 1.2 (a) The unit cell of graphene (enclosed by the dashed rhombus) contains two atoms A and B. (b) The Brillouin zone (green region), and high symmetry points Γ , M, and K. The real- and reciprocal-space unit vectors are shown by a_i and b_i (i=1, 2).



Figure 1.3 The chiral vector C_h for an (n,m) = (5,2) SWNT. The chiral angle is shown by θ .

$$\boldsymbol{C}_{h} = n\boldsymbol{a}_{1} + m\boldsymbol{a}_{2} \equiv (n,m) \tag{1.3}$$

Since the length of C_h indicates the circumferential length of the SWNT, the diameter of the SWNT, d_t is expressed as

$$d_{t} = \frac{|C_{h}|}{\pi} = \frac{\sqrt{C_{h} \cdot C_{h}}}{\pi} = \frac{a\sqrt{n^{2} + m^{2} + n}}{\pi}$$
(1.4)

The angle formed by C_h , and a_1 is termed the chiral angle θ , and its value is $0 \le \theta \le 30^\circ$ due to the hexagonal symmetry of the honeycomb lattice; specifically, expressed as

c
$$\theta c = \frac{C_{h_{c}} \cdot a_{1}}{|C_{h}||a_{1}|} = \frac{2n+m}{2\sqrt{n^{2}+m^{2}+n}}$$
 (1.5)

The translation vector T is defined as the unit vector of the SWNT, which is parallel to the SWNT axis. It is oriented parallel to the SWNT axis, and is perpendicular to C_h . The translation vector is defined as

$$T = t_1 a_1 + t_2 a_2 \equiv (t_1, t_2),$$
(1.6)
$$(t_1 = \frac{2m + n}{d_R}, \quad t_2 = -\frac{2n + m}{d_R})$$

where the value d_R is the greatest common divisor (gcd) of (2m+n) and (2n+m).

By Euclid's law, it turns out that

$$d_{R} = \begin{cases} d & \text{if } (n-m) \text{ is mutiple of } 3d \\ 3d & \text{if } (n-m) \text{ is not mutiple of } 3d \end{cases}$$
(1.7)

the vectors C_h and T define the rectangle *OAB B* in Fig. 1.3, which encloses the unit cell of the SWNT. The number of hexagons in the unit cell is N, where

$$N = \frac{|C_h \times T|}{|a_1 \times a_2|} = \frac{2(n^2 + m^2 + n)}{d_R}$$
(1.8)

The combinations of (n,m) give rise to many possible SWNT structures, which generally can be classified by chiral angle, and be described as achiral (zigzag and armchair) and chiral SWNTs (See Fig. 1.4).



Figure 1.4 Examples of the three different SWNT geometries, zigzag, armchair and chiral.

1.3 Thermal conductivity of SWNT

Since the SWNT was discovered, it has been investigated in various fields to take advantage of its outstanding electrical, optical, mechanical, and thermal properties. In particular, its very high thermal conductivity is believed to surpass even that of diamond, so numerous studies have so far investigated its thermal properties [4-6]. Since 1999, the number of experiments measuring the thermal properties of SWNTs has increased.

In the beginning, a mat type bundles of carbon nanotubes, so-called "nanotube mats" or "Bucky mats" was taken to measure the thermal conductivity of SWNTs by Hone *et al.* Through the above experiments, thermal conductivity of SWNTs was found to depend on the temperature [6]. Thermal conductivity of SWNTs simply increases in the range from 10 to 400 K, and it is about 200 W/mK at 300 K [7]. Moreover, they specified the contribution of electrons to thermal conductivity of SWNTs by comparing that to electrical conductivity. Shi *et al.* made it possible to measure the temperature of SWNTs using a scanning thermal microscope (SThM) which used a thin thermoelectric film as a cantilever. However, the thermal conductivity of SWNTs is not yet fully understood

On the other hand, many studies by molecular dynamics simulation have been reported about the thermal conductivity of SWNTs since around 2000 [8-10]. One of them indicated the thermal conductivity of SWNTs at 300 K is as much as 6600 W/mK [8], compare this to copper, a metal well-known for its good thermal conductivity, which transmits 410 W/mK. However, the value of thermal conductivity is not uniformly distributed so there is not yet a quantitatively reliable value. For these reasons, it is plausible that the means to determine temperature distribution of the system is not optimized (i.e., the stationary molecular dynamics simulation and non-stationary molecular dynamics simulation by Green-Kubo equation), or that the definition of cross-sectional area of SWNTs during measurement for heat flux is unreliable, or the system being simulated is so small that it is easy to be influenced by wobble of the nanotube.

Recently, it is not only the expectation of high thermal conductivity that has driven the many simulation studies of SWNT thermal conduction, but also a report about the analysis of thermal conductivity inside a solid by the approximation of phonons in the microscale [11]. Here, the analysis using molecular dynamics simulation is expected to obtain a group velocity of phonons which requires a qualitative understanding and quantitative estimation for the cradle of the phonons (Umklapp process by phonon deflection, interfacial dispersion) [12].

Maruyama *et al.* have so far made many studies about SWNT thermal conductivity using a simplified potential derived from the Brenner-Tersoff type potential between carbon atoms, used in fullerene structures and the process of SWNT synthesis [13-15]. In addition, they specified thermal conductivity dependence on length by simulation for SWNT with a length ranging 10 - 400 nm.

1.4 Purpose of this research

Since SWNTs were discovered, they have been one of the most anticipated new materials, and numerous studies have been conducted. In particular, there is a need to perform analysis from various perspectives in order to take advantage of the thermal properties of SWNTs, however, most studies so far focused only on the thermal conductivity inside SWNTs and not on the interfacial heat and mass transfer between the SWNT and surrounding materials.

The increase in thermal conductivity of SWNT-epoxy composites is much more than for larger-diameter carbon fibers [16], and SWNTs can lead to materials with reduced interfacial resistance and higher composite thermal conductivity [17]. Understanding of thermal boundary resistance (TBR), however, is essential to above cases, because the interfacial thermal resistance of carbon nanotubes-solid, carbon nanotubes-liquid and carbon nanotubes-gas, is not clarified yet, so it cannot be applied generally.

There have recently been extensive studies on the TBR between SWNTs and surrounding materials with strong motivation [16-27]. Maruyama and Kimura have reported a temperature jump resulting from thermal resistance exists at solid-liquid surface [26]. Ohara and Suzuki investigated interfacial thermal resistance at a solid-liquid surface with the concept based on intermolecular energy transfer [27]. Furthermore, Carlborg *et al.* investigated the TBR between an SWNT and Lennard-Jones molecules considering the contribution of inelastic transport [20]. Additionally, Hu *et al.* demonstrated the influence of binding energy on the TBR between an SWNT and air [23]. While these studies have revealed interfacial thermal transport of specific systems or parameters, the general law or model which is necessary to design thermal devices and simplify thermal management is not available to date.

In this study, as a thermal property of SWNT, I investigate the interfacial thermal transport between SWNT and various surrounding Lennard-Jones (LJ) fluids over wide density and temperature ranges using molecular dynamics (MD) simulation, adopting the lumped heat capacity method. Here, I qualify the interfacial thermal transport in terms of the thermal boundary conductance (TBC), the reciprocal of the TBR. My primary aim here is to identify the general scaling law, which would be important in predicting and designing thermal transport interfaces.

Chapter 2

Molecular Dynamics Simulation

2.1 Guidelines

Single-walled carbon nanotubes (SWNTs) are on the nanoscale, so it is hard to measure their thermal properties experimentally by generating a temperature difference. Therefore, many studies about thermal properties of SWNT have been investigated by numerical simulations.

The Maruyama laboratory where I belong has so far studied thermal properties of SWNT by using molecular dynamics (MD) simulation because it is appropriate for analysis on the required lengthand time-scales. In addition, I investigated the thermal boundary conductance between SWNT and surrounding fluids using MD simulation in this study. In this chapter, I describe potential between atoms, numerical integration, temperature control and boundary conditions which are needed for MD simulation.

2.2 Potential energy between atoms

2.2.1 Brenner Tersoff potential

The inter-atomic potential used for SWNT in these MD simulations is the Brenner potential used for synthesis progress simulation of diamond thin films [28], which is modified by adding a π -bond and adding hydrocarbon interaction from the poly-atomic potential proposed by Tersoff. For this potential, the force between carbon atoms which are separated by a long distance is neglected through use of a cut-off function f(r), and it is considered that the bonding energy depends on the coordination number of each carbon atom. These changes improve the model so that it can represent many structures such as a small hydrocarbon, graphite and diamond.

The potential energy of the system is shown as the sum of the energy of each bonding atom as

$$E_{b} = \sum_{i} \sum_{j(i>j)} [V_{R}(r_{i} - B_{i}^{*}V_{A}(r_{i})]$$
(2.1)

where $V_R(r_{ij})$ and $V_A(r_{ij})$ are repulsive force and attractive force, respectively. Those are represented by a Morse type exponential function including the cut-off function f(r) and are described by

$$V_R(r) = f(r) \frac{D_e}{S-1} e \qquad \Rightarrow \beta \sqrt{2\mathfrak{S}}(r - R_e)$$
(2.2)

$$V_A(r) = f(r) \frac{D_e}{S-1} e \qquad \Rightarrow \beta \sqrt{2Sp}(r - R_e)$$
(2.3)

$$f(r) = \begin{cases} 1 & (r < R) \\ \frac{1}{2} \left(1 + c \ o \frac{r - R_1}{R_2 - R_1} \right) \pi & (R_1 < r < R_2) \\ 0 & (r > R_2) \end{cases}$$
(2.4)

 B^* is given in terms of a coefficient of repulsive force for the function, and θ_{ijk} is the angle of neighboring bonds between *i*-*j* and *j*-*k*.

$$B_{i}^{*} = \frac{B_{i}^{*} + B_{j}^{*}}{2} + F_{i} \left(N_{i}, N_{j}, N_{i}^{c} \right)$$
(2.5)

$$B_{i} = \left(1 + \sum_{k(\neq i,j)} \left[G_{c}\left(\theta_{i}\right)f_{c}\left(r_{i}\right)\right]\right)^{-\delta}$$
(2.6)

$$G_{c}(\theta) = a_{0} \left(1 + \frac{c_{0}^{2}}{d_{0}^{2}} - \frac{c_{0}^{2}}{d_{0}^{2} + (1 + c - \theta)^{2}} \right)$$
(2.7)

where $F_{ij}(N_i, N_j, N_{ij}^{conj})$ is given in terms of a substituted term for π covalent bond as

1

$$N_i = \sum_{k(\neq j)} f(r_{i\,k}) \tag{2.8}$$

$$N_{i}^{c}{}_{j} \stackrel{o}{=} 1 + \sum_{k(\neq i,j)} f(r_{i})_{k} F(r_{i})_{k} + \sum_{l(\neq i,j)} f(r_{j})_{l} F(r_{j})_{l}$$
(2.9)

$$F_{ij} = \begin{cases} \frac{1}{1+c} & (x_{ik} \le 2) \\ \frac{1+c}{2} & (2 \le x_{ik} \le 3) \\ 0 & (3 \le x_{ik}) \end{cases}$$
(2.10)

$$x_{ik} = \sum_{m(\neq k)} f(r_m)$$
(2.11)

The above values are the optimized values for π covalent bonds, such as those among hydrocarbon molecules, which is added to make the structure of a diamond stable. This study does not concern about tracing for the progress of a cluster, so the substituted term was omitted for load reduction. Constants used in equations (2.1) to (2.11) are shown in Table 2.1.

There are two parameters for the Brenner potential: Parameter I optimized for the formation of cluster focusing on the distance between carbon atoms, and parameter II optimized for the measurement of physical properties of the force between carbon atoms [28]. The primary aim of this study is to investigate the interfacial thermal property, so the parameter II is employed for focusing on the force.

Table 2.1 Carbon-Carbon potential parameters.

2.2.2 Lennard-Jones potential

I employed the Lennard-Jones (LJ) potential between carbon atoms of SWNT and Lennard-Jones molecules of the surrounding fluid, which represent the Van Der Waals force which is usually used for MD simulation. The Lennard-Jones potential is a function of the inter-atomic distance r as

$$\phi(r) = 4\varepsilon \left\{ \left(\frac{\sigma}{r}\right)^1 - \left(\frac{\sigma}{r}\right)^6 \right\}$$
(2.12)

where ε and σ are the energy and length scales, and they represent the depth of potential and the radius of the molecule, respectively. Figure 2.1 shows the shape of the Lennard-Jones potential.

 ε , σ and *m* of Lennard-Jones molecules can be non-dimensionalized so that it is possible to indicate the generality, independently of the kind of materials. In chapter 3, I discuss and verify the non-dimensionalized generality. The equations of dimensionless temperature and density are described by

$$\rho^* = \frac{\rho \sigma^3}{m} , \qquad (2.13)$$

$$T^* = \frac{k_B T}{\epsilon} \qquad (2.14)$$

where *m* and k_B are mass and the Boltzmann constant, respectively. The parameters employed in this study are shown in Table 2.2. By equation (2.12), the Lennard-Jones potential is in inverse proportion to six times the molecular distance, so it decreases. On the other hand, a molecule from the distance *r* to $r+\Delta r$, which is existed in a sphere, is proportional to the *r* square in a case of isotropic system. Therefore, the sum of the force by Lennard-Jones potential converges with an increase in distance. It is necessary to determine the cut-off distance r_c for the Lennard-Jones potential for load reduction of calculation, so if the atom is out of r_c then it is not included in the force calculation.

The error of the calculation would be increased due to the cut-off distance, so it is usually set up $2.5\sigma - 5.5\sigma$ for consideration of practical condition such as calculation time. In this study, I set up the cut-off distance ranging $3.0\sigma - 3.5\sigma$, and nullify the force of distant atom.



Figure 2.1 Lennard-Jones potential.

Table 2.2 Parameters of Lennard-Joned fluid

	ε (meV)	$\sigma(\text{\AA})$
C – C	2.12	3.37
Ar – Ar	10.33	3.40
$H_2\!-H_2$	3.18	2.93
$N_2\!-N_2$	8.54	3.59
Ar-C	4.67	3.38
$H_2 - C$	2.59	3.15
$N_2 - C$	4.25	3.48

2.3 Temperature calculation and control

The temperature of molecules defined in a system firstly requires that a sum of kinetic energy is obtained

$$E_{k} = \sum_{i} \frac{1}{2} m_{i} v_{i}^{2}$$
(2.15)

And, E_k which is proportional to T is defined as

$$\frac{v_f}{2}k_B T = E_k \tag{2.16}$$

where k_B =1.380662x10⁻²³ J/K is Boltzmann constant, and v_f is degree of freedom. Because one atom has 3 degree of freedom, its value is 3 times the number of atoms. The temperature calculation in the simulation is employed for carbon atoms which consist of SWNT and Lennard-Jones molecules.

On the other hand, the velocity scaling method was used to control temperature which is commonly used in molecular dynamics simulations. By controlling the velocity of each molecule, the objective temperature was obtained.

$$v' = v \times \sqrt{\frac{r_{c} T_{o} + (1 - r)T}{T}}$$
(2.17)

where v', v, r, $T_{control}$ and T are the velocity controlled, velocity of molecule, parameter to decide degree of strength, temperature before control and objective temperature, respectively. As using pulse-type heating to measure thermal conductance, I employed r=0.6 to avoid the unnaturally made system by drastic temperature control.

2.4 Numerical integration

Molecular dynamics simulation assumes a potential energy function depending on the position of each molecule and defines a potential energy E of the entire system as a sum of the energy of the atoms, and treats the movement of each molecule as the motion of a particle following the Newton's law of motion. The law of motion for molecule *i* is defined as

$$F_i = -\frac{\partial E}{\partial r_i} = m_i \frac{d^2 r_i}{d^2 t}$$
(2.18)

A difference expansion takes the Verlet method [29] which approximates to the second term of Taylor expansion. The algorithm of the Verlet method is below.

As the finite time Δt approximates second-order derivative of Newton's law of motion to the centeral difference of the second-order precision, it becomes

$$r_{i}(t + \Delta t) = 2r_{i}(t) - r_{i}(t - \Delta t) + (\Delta t)^{2} \frac{F_{i}(t)}{m_{i}}$$
(2.19)

Velocity is obtained by the equation that approximates differential of position of time as the centeral difference.

$$v_i(t) = \frac{1}{2\Delta t} \left\{ r_i \left(t + \Delta t \right) - r_i \left(t - \Delta t \right) \right\}$$
(2.20)

It is able to trace the position of material point by a given initial value $r_i(0)$ and $r_i(\Delta t)$, which is the algorithm of Verlet method. Not only that, but with given initial condition of the position of material point $r_i(0)$ and velocity $v_i(0)$, it is possible to begin simulation. By eliminating $r_i(t-\Delta t)$ from the Equation (2.19) and (2.20),

$$r_{i}(t + \Delta t) = r_{i}(t) + \Delta t_{i}(t) + (\Delta t)^{2} \frac{F_{i}(t)}{2m_{i}}$$
(2.21)

Once t =0, $r_i(\Delta t)$ is obtained.

The main step of calculation algorithm is below.

- 1. Give initial position $r_i(0)$ and $v_i(0)$
- 2. Calculate $r_i(\Delta t)$
- 3. Calculate the force $F_i(n\Delta t)$ at time step n.
- 4. Calculate $r_i((n+1) \Delta t)$ at time step (n+1)
- 5. Repeat from the step 3 with (n+1) as n

One of characteristic of the Verlet algorithm is that it replaces the material point without velocity except setting up initial condition, so that it is impossible to apply velocity scaling method. Velocity is obtained by the equation (2.20), but as the equation is calculates the difference of position of finite time interval, one must be cautious about the cancellation of significant digits.

In this study, the modified Verlet algorithm which improves the Verlet algorithm in order to evaluate velocity and position at same time steps is employed. By the Taylor series expansion, position of material point and velocity is nullified, and first-order differential is approximated with a forward finite difference. The following equation is obtained.

$$r_i(t + \Delta t) = r_i(t) + \Delta t \cdot v_i + (\Delta t)^2 \frac{F_i(t)}{2m}$$
(2.22)

$$v_i(t+\Delta t) = v_i(t) + \frac{\Delta t}{2m} \left\{ F_i(t+\Delta t) + F_i(t) \right\}$$
(2.23)

The main step of calculation algorithm is below.

- 1. Give initial position $r_i(0)$ and $v_i(0)$
- 2. Calculate force $F_i(0)$
- 3. Calculate $r_i((n+1)\Delta t)$ at time step (n+1)
- 4. Calculate $F_i((n+1)\Delta t)$ at time step (n+1)
- 5. Calculate $v_i((n+1)\Delta t)$ at time step (n+1)
- 6. Repeat from the step 3 with (n+1) as n

Using the above modified Verlet algorithm restrained the problem by tracing the motion of material point with velocity such as the cancellation of significant digits mentioned with the equation (2.20).

2.5 Time step

There are two kind of error by differentiating. One of them is local error which is generated during each step of calculation. Another is accumulated error which is accumulated by local error during all steps (proportional to $1/\Delta t$), so it depends on all steps. Therefore, it is hard to simply say that that shorter Δt is always better. Considering time scale in the simulation, which is proportional to Δt , and the possibility to generate error by the cancellation of significant digits, Δt needed to be decided as long as possible in the range satisfying the law of energy conservation. When potential is described $\varepsilon \cdot \Phi(r/\sigma)$ by the scale of energy ε and length σ , the 1-dimensional equation of motion is described as

$$-\varepsilon \frac{\partial \Phi(r/\sigma)}{\partial r} = m \frac{d^2 r}{d^2 t}$$
(2.24)

using dimensionless distance $r'=r/\sigma$ and $t'=t/\tau_l$,

$$-\frac{\partial \Phi(r')}{\partial r'} = \frac{m\sigma^2}{\varepsilon_I^2 \tau} \frac{d^2 r'}{d'^2 t}$$
(2.25)

Comparing the order to differentiated term of both sides as 1,

$$\frac{m\sigma^2}{\varepsilon\tau_I^2} = 1, \ \tau_I = \sqrt{m\sigma^2/\varepsilon}$$
(2.26)

By above, time scale difference τ_l is obtained. Because τ_l is needed as a order of time of length σ moving at r'=1, Δt should be set up that there is not generated difference to τ_l . In this study, τ_l is 20 fs by $\varepsilon=R_e=6.325$ eV and $\sigma=D_e=1.315$ Å. In addition, Δt should be set up much less than thermal periodic frequency. Vibration frequency of carbon-carbon bond is about 1800 cm⁻¹ (5.4×10¹³ Hz), so vibration period becomes 2×10¹⁴ seconds. Therefore, Δt should be the order of 10⁻¹⁶. Considering above, I employed here $\Delta t=0.5$ fs.

2.6 Periodic boundary condition

Once you consider properties of materials, at least more than 10^{23} molecules are needed to possess macro properties of materials. However, it is not practically possible to simulate such a system, so it is necessary to set up boundary conditions in that some of the molecules are placed in a cube as a unit cell. If I simulate the inside properties out of the influence of surface, I have to consider how many molecules are needed to nullify the effect of the surface because the properties of surface and inside the bulk are different. By using periodic boundary conditions, it is possible that fewer molecules than 10^{23} molecules can represent the bulk properties away from the influence of surfaces compared to macro-scale systems. All the regions next to calculation region, which are completely the same as the calculation region, are placed as image cells with periodic boundary conditions (Figure 2.2 shows the case of 2-dimensional plane).

A molecule which is goes out of one side of the calculation region comes in again from the opposite side, and the effect of force of the molecules from the image cell is considered. By the above considerations, I can suppose the system is as a bulk state of unlimited arrays of system nullifying surface effects. When the force added to molecule i is calculated, the force by molecule j which is from far away is nullified to reduce the calculation time and to realize the isotropy. The force by the targeted molecule is employed the only from the molecule which is placed in a cube with a length lv of a side in calculation region. If the component of a position vector of molecule j which is influenced by molecule i is longer than lv/2, then it is represented by translating lv. Figure 2.2 shows that the molecule j which influences to molecule i and the molecules i which influences to molecule j plays as a molecule j' and a molecule i' in the image cell, respectively.

For the cut-off distance defined by the cut-off function such as the Brenner potential, it is fine if lv is taken 2 times more than the distance.

In the isotropic system, because a molecule from the distance r to $r+\Delta r$, which exists in a sphere, is proportional to the r square in a case of isotropic system, if the interaction between molecules decreased more than r^{-3} , it would be fine. However, if the interaction between molecules by such as the Coulomb force is proportion to less than r^{-3} , the cut-off distance has to be carefully considered.

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Figure 2.2 Periodic boundary condition.

Chapter 3

Thermal Boundary Conductance between Single-walled Carbon Nanotube and Surrounding Fluids

3.1 Guidelines

In this study, I calculate thermal boundary conductance K between a single-walled carbon nanotube (SWNT) and Lennard-Jones (LJ) molecules as a targeted surrounding fluids using non-stationary molecular dynamics simulation.

Chapter 3.2 indicates calculated results that thermal boundary conductance depends on the dimensionless density of surrounding fluids. Here, I employed the Lennard-Jones potential, which is able for each physical property to be non-dimensionalized.

In chapter 3.3, the thermal boundary conductance of SWNT was normalized in some degree by adsorption layer on the outer surface of an SWNT and parameters of surrounding fluids. Through above studies, I obtained a phenomenological description of the thermal boundary conductance between an SWNT and the surrounding LJ fluid.

3.2 Thermal boundary conductance between SWNT-Lennard-Jones molecules

3.2.1 Simulation method

A 25.1 nm long SWNT consisting of 2000 carbon atoms was placed in the center of a cubic cell and surrounded by a fluid of 1280 molecules, as seen in Fig. 1. The primary aim here is to identify the general scaling law of thermal boundary conductance K between the SWNT and surrounding fluids. Therefore, I simulate the SWNT and surrounding Lennard-Jones (LJ) fluid group—such as argon, hydrogen, and nitrogen—as a target. Here, the diatomic molecule of hydrogen and nitrogen are regarded as a monoatomic molecule. To simplify phenomena, there are arranged one SWNT and LJ fluids in a supercritical state with various densities, which does not undergo a phase transition according to the Lennard-Jones molecules phase diagram shown in Fig. 3.2 [30]. The axes of density and temperature are non-dimensionalized as described in equations (2.13) and (2.14).

$$\rho^* = \frac{\rho \sigma^3}{m} \tag{3.1}$$

$$T^* = \frac{k_B I}{\varepsilon} \tag{3.2}$$

The temperature T^* of all simulations is between 3 and 4.5 in order to ensure that all the fluids are in a supercritical state. With that, I changed the density ρ^* from 0.001 to 0.3 by adjusting the cross-sectional



Figure 3.1 Initial arrangement of SWNT and surrounding LJ molecules.



Figure 3.2 Lennard-Jones molecules phase diagram

size of the unit cell. Figure 3.3 shows snapshots of a wide density range in simulation.

I employed the Brenner potential [28] in a simplified form [31] to describe the carbon-carbon interactions within the SWNT as the total potential energy of the system, and for the interaction between carbon and the surrounding fluid, I adopted the 12-6 Lennard-Jones (LJ) potential based on Van der Waals forces between surrounding fluids molecules. Simulations were conducted for armchair SWNTs with chirality (5,5), which have a radius of 0.69 nm. The cross-sectional area of the simulation cell was varied from 2.3×2.3 nm to 46×46 nm, and periodic boundary conditions were applied in all directions. The space in which LJ molecules are arranged is only the space surrounding the SWNT, so that the density is represented as

$$\rho = \frac{N_{Fluid}}{l_x \{ l_y l_z - \pi (d + \sigma_{C-fluid})^4 / 4 \}}$$
(3.3)

where, N_{fluid} , l_x , l_y , l_z , d and $\sigma_{C-Fluid}$ are the number of fluid molecules, axial length representing the length of SWNT, two cross-sectional sides, diameter of SWNT and equilibrium distance between carbon and LJ fluid, respectively.

In each case, the first step was to keep the SWNT and surrounding fluid at a fixed temperature for 10 ps. The system was then relaxed for 990 ps without temperature control. After 1000 ps, the SWNT was heated instantaneously, and variations in the SWNT and surrounding fluid temperature were recorded. Values were ensemble-averaged from five individual simulations with different initial conditions.



Figure 3.3 Snapshots of simulations over a wide density range (0.001, 0.006, 0.02, 0.06, 0.1 and 0.3 clockwise from upper left).

3.2.2 Lumped-Heat capacity

In the case of thermal transport between two different materials, one needs to calculate the temperature change in both materials, which can be complicated. However, if the ratio of thermal conductivity λ [W/mK] inside the materials and the thermal boundary conductance *K* [W/m²K] between the materials is quite small, then it is possible that the temperature gradient inside both materials is nullified and they have equivalent temperature distributions inside. In this way, I regard the material neglected volume as a thermal point, which simplifies investigation of the interfacial thermal transport property to an extremely simple equation. This is the Lumped-Heat capacity.

As the ratio of thermal conductivity and thermal conductance is non-dimensionlized,

$$Bi = \frac{KL}{\lambda} \tag{3.4}$$

where Bi and L are the Biot number and a length of material, respectively. Once the Biot number is smaller than 0.01, the lumped-heat capacity can be employed neglecting temperature inside the material. Because a length L of some nanoscale materials ranges about 10⁻⁹, the Biot number is extremely small. Therefore, regarding a material as a thermal point with better precision is possible.

By applying the lumped-heat capacity to the system of calculation, it simply becomes that just two materials (hot and cold) are contacting. Using Newton's law, heat flux q is defined as

$$q = KS(T_{hot} - T_{cold})$$
(3.5)

where S is the contacted area between hot and cold materials. In addition, because the temperature of the material is also changed by thermal convection, equation (3.5) can be described as

$$\frac{dT_{hot}}{dt} = \frac{q}{\rho_{hot}c_{hot}V_{hot}}$$
(3.6)

$$\frac{dT_{cold}}{dt} = \frac{q}{\rho_{cold}c_{cold}V_{cold}}$$
(3.7)

Combining equations (3.6) and (3.7), the following relation can be deduced

$$\frac{d(T_{hot} - T_{cold})}{dt} = \left(\frac{1}{\rho_{hot}c_{hot}V_{hot}} + \frac{1}{\rho_{cold}c_{cold}V_{cold}}\right) KS(T_{hot} - T_{cold}) \quad (3.8)$$

$$T_{hot} - T_{cold} = A \exp\left\{ \left(\frac{1}{\rho_{hot} c_{hot} V_{hot}} + \frac{1}{\rho_{cold} c_{cold} V_{cold}} \right) KSt \right\}$$
(3.9)

The subscripts hot and cold refer to the SWNT and the surrounding LJ fluid, respectively.

3.2.3 Calculation of thermal boundary conductance

I calculated the thermal boundary conductance between a SWNT and surrounding LJ fluids employing the lumped-heat capacity. The right hand side of equation (3.9) is the temperature difference between the hot SWNT and the cold surrounding LJ fluid. Figure 3.4(a) shows the temperature profile of hot SWNT and cold surrounding LJ fluids, and Fig 3.4(b) shows their temperature difference fitted by an exponential function. As shown in Fig. 3.4 (b), due to the big oscillation generated by influence of the period of small temperature difference, I employed the least squares method to reduce the influence using the large period of temperature gradient from generating temperature difference. The approximated curve obtained by calculated results is represented by

$$T_{hot} - T_{cold} = A \exp(-\frac{t}{\tau})$$
(3.10)

where A and τ are obtained from the calculation conditions. Combining equations (3.9) and (3.10), I obtain

$$A\exp(-\frac{t}{\tau}) = A\exp\left\{-\left(\frac{1}{\rho_{hot}c_{hot}V_{hot}} + \frac{1}{\rho_{cold}c_{cold}V_{cold}}\right)KSt\right\}$$
(3.11)

A is the initial value of the temperature generated by heating, so it is not directly related to obtaining thermal conductance. Consequently, I obtain the equation of thermal boundary conductance as

$$K = \frac{1}{\left(\frac{1}{\rho_{hot}c_{hot}V_{hot}} + \frac{1}{\rho_{cold}c_{cold}V_{cold}}\right)\tau S}$$
(3.12)

The constants used in equation (3.12), which are invariant with calculation conditions, are shown in Table 3.1.

Figure 3.5 shows the contacted area defined in this system, which is a cylindrical area of SWNT and surrounding LJ molecules. The diameter of the cylinder is defined as the sum of the diameter of the



Figure 3.4 (a) Temperature profile, and (b) temperature difference SWNT and argon $\rho^*=0.04$.

S [nm ²]	<i>P</i> _{SWNT} V _{SWNT} [kg]	c_{SWNT} [J/K·kg]	$\rho_{LJ}V_{LJ}$ [kg]	c_{LJ} [J/K·kg]
81.1	3.98×10^{-23}	1039	depends on the number	312
01.1		1057	of LJ molecules	512

Table 3.1 Parameters used in the lumped-heat capacity.



Figure 3.5 The contacted area *S* defined in the system.

SWNT and the potential parameter $\sigma_{C-fliud}$ of the LJ potential, as follows,

$$S = \pi \left(d_{SWNT} + \sigma_{C-fluid} \right) \cdot l_{SWNT}$$
(3.13)

Through the above relation, the values of each thermal boundary conductance between SWNT and surrounding LJ fluids are arranged in Table 3.2 and Fig. 3.6.

ρ* Κ	Argon [MW/m ² K]	Nitrogen [MW/m ² K]	Hydrogen [MW/m ² K]
0.001	0.036	0.048	0.094
0.002	0.076	0.084	0.163
0.004	0.129	0.149	0.337
0.006	0.181	0.217	0.522
0.008	0.242	0.262	0.650
0.01	0.355	0.313	1.005
0.02	0.465	0.463	1.683
0.04	0.661	0.808	3.237
0.06	0.740	0.793	3.469
0.08	0.791	0.887	3.927
0.1	0.852	0.771	5.271
0.2	1.057	1.089	4.985
0.3	1.072	1.274	6.229

Table 3.2 Thermal boundary conductance *K* between SWNT and surrounding LJ fluids argon, nitrogen, and hydrogen.



Figure 3.6 Thermal boundary conductance between SWNT and surrounding LJ fluids argon, nitrogen, and hydrogen.

3.2.4 Dependence on dimensionless density of thermal boundary conductance

The thermal boundary conductance between SWNT and various surrounding LJ fluids was calculated over a wide density range. The density dependence of each fluid is shown in Fig. 3.6. Note that the data are plotted on a log-log scale. Hydrogen was found to have a higher thermal boundary conductance than other fluids for all calculated densities, whereas nitrogen and argon have almost the same thermal boundary conductance values, ranging from 0.037 to 1.274 MW/m²K. I found that the density dependence of the thermal boundary conductance of each fluid is almost linear for dimensionless densities less than 0.04, but becomes non-linear above 0.04 even though each simulation was performed in a supercritical state, thus does not undergo a phase transition.

3.3. Normalization of Thermal Boundary Conductance between SWNT and Lennard-Jones molecules

3.3.1 Adsorption layer on the outer surface of SWNT

Looking at the results from another perspective, I also considered the local density ρ_L , which is the density of molecules in the first layer surrounding the SWNT as seen in Fig. 3.7. For this, I have calculated the radial distribution function which verifies by counting the number of surrounding LJ molecules from the origin of SWNT axis to radial direction. The value of most molecules is here treated as



Figure 3.7 the first adsorption layer of surrounding molecules on the outer surface of SWNT.

the local density ρ_L .

Figure 3.8(a) shows the local density of argon on the outer surface of SWNT, and that at higher ρ^* for 30 ps after heating the SWNT is correlated to higher local density. This tends to converge with respect to increasing dimensionless density, as seen in Fig. 3.8(b). As seen in Fig. 3.8(c)-(d) and (e)-(f), other cases of nitrogen and hydrogen have the same tendency as argon. Here, the local density of the radial distribution function mentioned is the density of the number of surrounding LJ molecules, not their mass. Both the initial and maximum values of the local density, determined radially from this SWNT axis, depend on the value of the equilibrium distance σ of the carbon-surrounding molecule interaction found in Table 3.3. In addition, Figure 3.9 shows that the local density of each fluid is almost proportional to the dimensionless density.

	C - C	Ar – Ar	$H_2\!-H_2$	$N_2\!-N_2$	Ar – C	$H_2 - C$	$N_2\!-\!C$
ε (meV)	2.12	10.33	3.18	8.54	4.67	2.59	4.25
$\sigma({ m \AA})$	3.37	3.40	2.93	3.59	3.38	3.15	3.48

Table 3.3 Parameters of Lennard-Jones fluid.

I also investigated the influence of the second adsorption layer shown at higher ρ^* the outer layer, which is placed on the front and the rear of the distance from SWNT axis as seen in Fig. 3.8 (a), (c) and (e). The molecules exhibited no noticeable ordering beyond the second layer, and there was minor difference found by changing either the cell size or by increasing the number of fluid molecules, even if the contribution from the SWNT was ignored in determining the density. This shows that there was little influence of the second and outer layers on determining the thermal boundary conductance.



Figure 3.8 (a), (c) and (e) are radial distribution function of the fluids, argon, hydrogen and nitrogen, respectively. (b), (d) and (f) are relation between dimensionless density ρ^* and the local density ρ_L of each fulid.

Consequently, thermal boundary conductance depends on the local density of each fluid as seen in Fig. 3.9. The thermal boundary conductance is linearly proportional to ρ_L , and the hydrogen case is found to be much more sensitive to local density than argon or nitrogen. Comparing Figs. 3.8 and 3.9, I found that other factors must determine the thermal boundary conductance, because each fluid with the same local density had a different value of thermal boundary conductance. Therefore, I considered the



Figure 3.9 Thermal boundary conductance dependence on the local density of each fluid.

other factors to determine the thermal boundary conductance, such as the parameters of each Lennard-Jones fluid.

3.3.2 Fluid effect of thermal boundary conductance

The parameters used in these simulations were binding energy, equilibrium distance, and mass, as shown in Tables 3.3 and 3.4. For nitrogen and hydrogen regarded as monoatomic molecules in this study, it was necessary to define the boundary parameters between the SWNT and the surrounding LJ fluid. These parameters were determined by the Lorentz-Berthelot mixing rules as

$$\sigma_{C-LJ fluid} = \frac{\sigma_C + \sigma_{LJ fluid}}{2}$$
(3.14)

$$\varepsilon_{C-LJ\,fluid} = \left(\varepsilon_C \cdot \varepsilon_{LJ\,fluid}\right)^{1/2} \tag{3.15}$$

where $\sigma_{C-LJ fluid}$ and $\varepsilon_{C-LJ fluid}$ are equilibrium distance and binding energy on the interfacial surface between SWNT surrounding LJ fluid, respectively.

In order to determine the effect of each parameter on the thermal boundary conductance, I assumed hypothetical fluids and used parameters of argon as standard values. Each parameter was varied while keeping the other two constant, and all cases were performed with ρ *=0.04

Firstly, Figure 3.10(a) shows that the binding energy ε is proportional to thermal boundary conductance. In these five cases, as seen in Fig. 3.10(a), the thermal boundary conductance increases from 0.186 to 0.537 MW/m²K as binding energy ε increases from 3.18 to 10.34 meV. The dependence on binding energy ε was approximated by the equation $K \propto \varepsilon^{-0.9}$. In addition, as seen in Fig. 3.10(b), there is a minor difference of local density in the changes of the binding energy ε .

Secondly, I investigated the equilibrium distance σ . As seen in Fig. 3.10 (c), the change in thermal boundary conductance, which ranges from 0.54 to 0.72 MW/m²K, is smaller than in the case of binding energy (Fig. 3.10(a)). The dependence on equilibrium distance σ was approximated by the equation $K \propto \sigma^{-1.34}$. Additionally, Figure 3.10 (d) shows that—as with the binding energy ε —there is also a minor difference of local density in the changes of the equilibrium distance σ .

Lastly, I evaluated the mass. As above, all parameters except mass used the values of argon. As seen in Fig. 3.10(e), I found by comparing to above two cases that the thermal boundary conductance increased exponentially from 2.12 to 4.93 MW/m²K with decreasing mass from 131.3 to 2.02 amu. The mass dependence was approximated by the equation $K \propto m^{-0.76}$. Moreover, I investigated the relation between local density and the effect of mass, as seen in Fig. 3.10(f). Even though every hypothetical fluid has almost the same local density, the TBC is totally different.

Each parameter I employed in the study of the parameter effect is individually distributed in a different range. The maximized and minimized values of binding energy ε and equilibrium distance σ are ranging from the value of hydrogen and of argon. Mass values range from that of hydrogen to xenon. I found the

	Carbon	Argon	Hydrogen	Nitrogen
m (amu)	12.01	39.95	2.02	28.01

Table 3.4 Mass of Lennard-Jones fluids molecule.



reason why hydrogen cases have a higher thermal boundary conductance than other fluids through the above effect of each parameter.

Figure 3.10 The effect of each parameter, (a) binding energy ε , (c) equilibrium distance σ and (e) mass *m* on determining the thermal boundary conductance. In addition, (b), (d), and (e) indicate that each parameter is independent on local density. All cases are performed in $\rho^*=0.04$.

3.3.3 Generalized equation for TBC

Through the above parametric studies, I obtained a phenomenological description of the thermal boundary conductance between an SWNT and a surrounding LJ fluid. This is described by

$$K_{model} = a \cdot \frac{\rho_L \cdot \varepsilon}{m} \tag{3.16}$$

where *a* is equal to 1.67×10^{-23} kg nm⁻³s⁻¹K⁻¹. The effects of binding energy and mass of thermal boundary conductance are simplified from the approximated relations $\varepsilon^{0.9}$ and $m^{-0.76}$, as seen in Fig. 3.11. Here, I omitted the equilibrium distance σ from the equation because of recognition that there is little difference between the maximized and minimized equilibrium distance σ of the fluids.



Figure 3.11 Influence of the fluid parameters; (a) binding energy ε , and (b) mass *m* on the thermal boundary conductance.

I verified the accuracy of the equation by comparing values of the thermal boundary conductance obtained using equation (3.16) with those obtained from MD simulation (Fig. 3.12). Note that the data are plotted on a log-log scale.



Figure 3.12 Comparison of thermal boundary conductance values obtained from MD simulation and equation (3.16).

Chapter 4

Interfacial Energy Transfer Mechanism between Single-Walled Carbon Nanotube and Surrounding Lennard-Jones Fluids

4.1 Interfacial energy transfer between SWNT and surrounding LJ fluid

4.1.1 Interaction change by temperature between SWNT and surrounding LJ fluid

This study aims to clarify the mechanism of interfacial energy transfer. In particular, it is the most important to setup the state of interface in simulation. As mentioned in chapter 3.3, they are parameters such as the binding energy ε and equilibrium distance σ are determined by the Lorentz-Berthelot mixing rule usually used in MD simulation. This is described as

$$\sigma_{C-LJfluid} = \frac{\sigma_C + \sigma_{LJfluid}}{2}$$
(4.1)

$$\varepsilon_{C-LJ\,fluid} = \left(\varepsilon_C \cdot \varepsilon_{LJ\,fluid}\right)^{1/2} \tag{4.2}$$

There is minor difference between the equilibrium distance σ of extant Lennard-Jones fluids, so that I need not to be necessarily concerned by that about the influence to thermal boundary conductance. For the case of the binding energy ε , however, it influences directly to the thermal boundary conductance *K*, and that is why I need to determine that considerably. Once I make use of the Lorentz-Berthelot mixing rule defined in equations (4.1) and (4.2), the determined interfacial binding energy ε would be changed by the kind of LJ fluid which is surrounding the SWNT. Then it is hard to estimate which of the binding energies between the interface and fluid itself influences the interaction between SWNT and surrounding LJ fluid. Therefore, I assumed hypothetical fluids and used parameters of argon as standard values. The binding energy ε was varied from 0.5 to 10 times to the value determined by the Lorentz-Berthelot mixing rule, and all cases were performed with $\rho^*=0.04$. Here, the energy transfer is dependent on the binding energy ε so I investigated two cases, one of which has change of temperature corresponding to the binding energy ε , and the other which has constant temperature at the interface. Consequently, thermal boundary conductance of both cases is increased with increasing the interfacial binding energy, as shown in Fig. 4.1. Note that the



Figure 4.1 Ratio of thermal boundary conductance K to interfacial binding energy when temperature is changed vs. unchanged.

horizontal axis indicates the multiple of the binding energy determined by the Lorentz-Berthelot mixing rule, and the vertical axis is the ratio of thermal boundary conductance to that of standard value. As shown in Fig. 4.1, the interfacial binding energy becomes nonlinear when T is unchanged, indicating K is sensitive to the temperature.

4.1.2 Thermal boundary conductance change by increase of temperature

Dimensionless temperature was defined in equation (3.2) and used for comparing different Lennard-Jones fluids, as follows

$$T^* = \frac{k_B T}{\varepsilon} \tag{4.3}$$

All cases have been so far simulated with the dimensionless temperature changes from 3.0 to 4.5. The binding energy of LJ fluids depends on temperature, so it is meaningless to compare different LJ fluids using absolute temperature; this is why it is necessary to employ dimensionless density. $T^*=3.0$ of argon, nitrogen, and hydrogen are corresponding to T=162.58 K, 147.82 K, and 96.11 K, respectively. In addition, $T^*=4.5$ correspond to T=243.87, 221.73, and 144.17 K, respectively. Here, all cases are above $T^*=3.0$ in order to ensure that all the fluids are in a supercritical state without phase transition [30].

It is, however, hard to find the temperature influence of SWNT to surrounding LJ fluid as a fixing dimensionless temperature change from $T^*=3.0$ to 4.5. Therefore, I investigated the influence of dimensionless temperature to thermal boundary conductance by changing the dimensionless temperature of the SWNT up to 7.0 and 12.0, which correspond to 372.4 and 638.2 K of argon, respectively, as shown in Fig. 4.2(a).

Relaxation time decreased by increasing dimensionless temperature as seen in Fig. 4.2(b). Furthermore, Fig. 4.3(a) shows the distribution of the first layer of the above cases that the SWNT of the highest dimensionless temperature has the lowest density of the first layer, and that of the lowest dimensionless temperature has the highest density of it. I regard these as the desorption phenomenon on the surface of material. The general equation for the rate of desorption is defined as

$$R = rN^{x} \tag{4.4}$$

where r is the rate constant for desorption, N is the concentration of the adsorbed material, and x is the



Figure 4.2 (a) Temperature profiles of, and (b) temperature differences between SWNT and argon $\rho^*=0.04$ for different dimensionless temperatures.



Figure 4.3 (a) Radial distribution functions of the first adsorption layer and (b) thermal boundary conductance K values for different dimensionless temperatures.

kinetic order of desorption. Usually, the order of the desorption can be predicted by the number of elementary steps, and the rate constant r may be expressed in the form

$$r = Ae^{-E_a/k_B T} \tag{4.5}$$

where A is the chance of the adsorbed molecule overcoming its potential barrier to desorption, E_a is the activation energy of desorption, k_B is the Boltzmann constant, and T is the temperature.

Consequently, thermal boundary conductance between SWNT and surrounding LJ fluid was increased by dimensionless temperature changes, as seen in Fig. 4.3(b). In the case T>1000 K of SWNT, which is corresponding to T*>18.5, the SWNT becomes unstable, so I limited the dimensionless temperature up to T*=12.0.

4.1.3 Residence time on the outer surface of SWNT

In section 4.1.2, I show that thermal boundary conductance depends on the temperature. This tells us that temperature affects to energy transfer on the interface between SWNT and surrounding LJ fluid. Due to this, I investigate the change of energy transfer due to temperature. Before the evaluation, I have to define the concept of residence time, which is when a molecule comes into the first adsorption layer, and stays for a moment, and then leaves. The length of time a molecule exists in the adsorption layer is the residence time of a molecule on the surface of SWNT. To decide the first adsorption layer, the thickness and the distance of absorbed molecules from the SWNT have to be considered. Figure 4.4 shows the radial distribution function for a SWNT with chirality (5,5). It has a first adsorption layer with 5 Å thickness, and the value of peak is at 7.0 Å from the axis of SWNT. For this case, the point at 9.5 Å, where the thickness almost decreased, is defined as the boundary of the first adsorption layer.

Moreover, for using residence time to evaluate energy transfer, a start point and end point must be determined. Although molecules can stay on the surface for about 200 ps, if I decide the observation time is less than that it becomes hard to analyze energy transfer by the perspective of using residence time. Hence, it is necessary to decide the proper observation time through many times of simulations.

There are two special cases of molecules, one that was present before the beginning of observation and one that will remain after the end of observation. Both are not included in the calculation of residence time of molecules. Figure 4.5 shows that a molecule comes from somewhere in space into the adsorption layer at 144.5 ps and goes out at 178.5 ps, hence the residence time is determined as 34.0 ps. In this way, the residence times of the three cases where dimensionless temperature changed from $T^*=3.0$ to 4.5, 7.0, and 12.0 in section 4.1.2 are 92.38, 43.54, and 16.22 ps, respectively. Observation times of the above are determined from 1100 to 1300 ps because this was considered as the time of the most active moment for energy transfer. I found that residence time decreased with the increase of thermal boundary conductance and dimensionless temperature. However, it is hard to simply conclude that short residence



Figure 4.4 Definition of the first adsorption layer.

time make thermal boundary conductance high because the energy transfer with respect to residence time is not yet understood.



Figure 4.5 Snapshots of residence time in the first adsorption layer around a SWNT.

4.1.4 Energy balance between energy change of all argon and that of the interface

In order to evaluate energy transfer by residence time of molecules, it is necessary to consider the energy balance between energy change of all molecules in the surrounding fluid and that of the interface. To define the temperature of molecules in a system, one firstly needs to obtain a sum of kinetic energy

$$E_{k} = \sum_{i} \frac{1}{2} m_{i} v_{i}^{2}$$
(4.6)

 E_k , which is proportional to T, is defined as

$$\frac{v_f}{2}k_B T = E_k \tag{4.7}$$

where $k_B=1.380662 \times 10^{-23}$ J/K is the Boltzmann constant, and v_f is the number of degrees of freedom. Each atom has 3 degrees of freedom.

In sections 4.1.1 to 4.1.3, thermal boundary conductance has been changed by the change of interfacial temperature, so evaluating the energy balance between entire and interfacial molecules could be the standard of energy transfer, and could be extended to evaluate energy transfer by residence time.

In evaluating energy balance, there are more cases than what I considered about residence time in section 4.1.3. First, there have been molecules staying on the surface since before the beginning of observation. The initial energy $E_{i,in}$ of the molecule *i* is determined at the moment of beginning observation. Second, the *i*th molecule coming into the first adsorption layer during observation has initial energy $E_{i,in}$. Third, some molecules will stay until the end of observation time, and they have energy $E_{i,out}$ determined at the final moment of observation. Lastly, during observation, an outgoing molecule *i* has energy $E_{i,out}$ at the moment it leaves. Molecules in the first adsorption layer take balance between adsorption and desorption, even at the beginning and end moments during observation. So, I took $\Delta E_i = E_{i,out} \cdot E_{i,in}$ as the energy



Figure 4.6 Effect of dimensionless temperature on the energy balance between energy transfer of the entire fluid and by the interfacial molecules.

transfer.

Figure 4.6 shows energy balance between energy transfer of all molecules and the interfacial molecules at 9.5 Å from the SWNT axis, as seen in Fig. 4.5. In this case a SWNT with chirality (5,5) and diameter 0.69 nm. The result shows energy balances of 3.4/3.42 (99.4%), 9.29/10.9 (85%), and 21.4/25.6 (83.6%) when *T** was changed from 3.0 to 4.5, then to 7.0, and finally to 12.0. Therefore, I can conclude that interfacial energy transfer is the dominant energy transfer process in the entire fluid.

4.1.5 Distribution of interfacial transfer by changing SWNT temperature

Energy balance which indicates that interfacial energy transfer accounts for nearly all energy transfer of entire molecules was ensured in section 4.1.4, so I investigate difference of energy transfer using residence time of molecules by different heating temperature. In this study, I decide the observation time from 1100 to 1300 ps for the most active moment for energy transfer.

Figure 4.7 shows the distribution of molecules per residence time, which is shown as a percent of energy transfer because the number of residence molecules is not uniform for all cases during the observation. Heating the SWNT from $T^*=3.0$ up to $T^*=4.5$ is shown in Fig. 4.7(a), and there are 1140 molecules that enter and leave the first adsorption layer. Figure 4.7(b) shows the case of heating the SWNT up to $T^*=7.0$, which has 1156 transiting molecules. Comparing to the above case of heating the SWNT up to $T^*=4.5$, the distribution of molecules is increasing per shorter residence time and decreasing per longer



Figure 4.7 Percentage of molecules with different residence times. (a), (b), and (c) correspond to heating the SWNT to $T^*=4.5$, 7.0, and 12.0, respectively. Increase of dimensionless temperature decreases the residence time.



Figure 4.8 Energy transfer per atom for different residence times. SWNT was heated to (a) $T^*=4.5$, (b) 7.0, and (c) 12.0.

residence time. Figure 4.7(c) shows the distribution of molecules per residence time. Most molecules have a short residence time, and fewer have a longer residence time than the both above cases. In addition, the possibility of a long residence time is decreasing with the increase of dimensionless temperature.

Figure 4.8 shows energy transfer per atom with respect to the residence time of molecules. Here, I found that energy transferred more during long residence time than short. Moreover, comparing Figs. 4.8(a) and 4.8(b), the case of heating the SWNT up to $T^*=7.0$ transferred more energy than heating to $T^*=4.5$. The case of increasing dimensionless temperature up to $T^*=12.0$, as seen in Fig. 4.8(c), shows that residence times are shorter than in the two cases of lower dimensionless temperature, and more energy was transferred. Furthermore, Figure 4.8, as mentioned in section 4.1.1, is about the influence of temperature on thermal boundary conductance and binding energy ε , so I can expect that the binding energy ε plays a role as a energy capacity of molecule.

The Maxwell–Boltzmann distribution describes particle speeds in gases, where the particles do not constantly interact with each other but move freely between short collisions. It describes the probability of a particle's speed (the magnitude of its velocity vector) being near a given value as a

function of the temperature of the system, the mass of the particle, and that speed value. The Maxwell-Boltzmann distribution for the speed of molecule follows from the distribution of the velocity vector. Note that the speed is

$$v = \sqrt{v_x^2 + v_y^2 + v_z^2}$$
(4.8)

and the increment of volume is

$$dv_x dv_y dv_z = v^2 \sin\theta dv d\theta d\phi \tag{4.9}$$

where θ and φ are the course (azimuth of the velocity vector) and path angle (elevation angle of the velocity vector). Integration of the normal probability density function of the velocity over the course (0 to 2π) and path angles (from $-\pi/2$ to $\pi/2$), with substitution of the speed for the sum of the squares of the vector components, yields the probability density function



Figure 4.9 Total energy transfer in the first adsorption layer. (a), (b), and (c) correspond to heating the SWNT to $T^*=4.5$, 7.0, and 12.0, respectively.

$$f(v) = \sqrt{\frac{2}{\pi} \left(\frac{m}{k_B T}\right)} v^2 \exp\left(\frac{-mv^2}{2k_B T}\right)$$
(4.10)

for the speed. This equation is simply the Maxwell distribution with distribution parameter

$$a = \sqrt{\frac{k_B T}{m}} \tag{4.11}$$

where k_B =1.380662x10⁻²³ J/K is the Boltzmann constant, and *m* is the mass of a molecule. We are more interested in quantities such as the average speed of the particles rather than the actual distribution. The mean speed, most probable speed, and root-mean-square can be obtained from properties of the Maxwell distribution.

Figure 4.9 shows total energy transfer for each case of residence molecules during 200 ps from 1100 to 1300 ps. This is simply the product of Fig. 4.7 (the number of residence molecules per residence time) and Fig. 4.8 (the energy transfer per atom and residence time). As seen in Fig 4.9(a), the energy transfer by the molecules with short residence time (from 0 to 20 ps) is negative, which means possibility that molecules exited with higher temperature than that of the SWNT. Figure 4.9(b) and (c) are the cases of heating the SWNT to $T^*=7.0$ and 12.0, respectively. I found the elevation of temperature to influence energy transfer not only by decreasing the residence time per atom but also transferring more energy. Note that the molecules included in the calculation with residence time are only considered if they both come in and go out during the observation time.

4.2 Thermal boundary conductance of SWNTs with various diameters

4.2.1 Distribution difference of 1st adsorption layer by diameter of SWNT

I have so far investigated SWNT with a chirality (5,5), which has diameter d=0.69 nm. Here, I extend to SWNTs of various diameters, and investigate the dependence on the diameter. For that, the first adsorption layer has to be investigated because it plays a crucial role for thermal transfer between the SWNT and the surrounding LJ fluid.

I simulated two cases of SWNT with chirality (5,5) and (10,10), which have corresponding diameters d=0.69 and 1.38 nm. However, the number of molecules and thickness of the first adsorption layer are different. Figure 4.10 shows a comparison of the first adsorption layers on SWNTs with diameters d=0.69 and 1.38 nm. First, the first adsorption layer contains 310 and 423 molecules for d=0.69 and 1.38 nm SWNTs, respectively. The corresponding thicknesses are 3.5 and 1.5 Å, respectively. Through snapshots of simulations, I found the reason why each case has different thickness of the first adsorption layer as seen in Fig. 4.11. The SWNT with diameter d=0.69 nm is axially vibrating due to the interaction both to carbon and molecules of fluid, which has only 20 carbon atoms in the unit cell of SWNT. However, the SWNT of diameter d=1.38 nm is axially vibrating less than the SWNT of diameter d=0.69 nm, and that is why the thicknesses of the first adsorption layers are not equal. For the above reasons by comparison, it is hard to simply compare SWNTs with different diameter, and is necessary to consider the density of the first adsorption layer of SWNT to compare SWNTs which have different diameters.

Chirality of SWNT	(5,5)	(10,10)		
No. of carbon atoms	2000	4000		
No. of LJ molecules	1280	1280		
Diameter	0.69 nm	1.38 nm		
No. of molecules in 1 st adsorption layer	310	423		
Thickness of 1 st adsorption layer	3.5 Å	1.5 Å		

Table 4.1 Comparison between SWNTs of chiralities (5,5) and (10,10).



Figure 4.10 comparison of the first adsorption layers around SWNTs with chiralities (5,5) and (10,10), which have corresponding diameters d=0.69 and 1.38 nm.



Figure 4.11 Snapshots of SWNTs with chiralities (5,5) (left) and (10,10) (right).

4.2.2 Thermal boundary conductance of SWNTs with various diameters

In order to use SWNTs as thermal and electrical devices, they have to be controlled when they are synthesized. However, perfect control is not yet possible, so it is necessary to investigate SWNTs of different chirality with various diameters. Here, I studied the thermal boundary conductance of three different SWNTs with different diameters, considering the density of the first adsorption layer as mentioned in section 4.2.1.

Figure 4.12 shows a snapshot of SWNTs which have the chiralities (7,7), (12,12), and (18,18) corresponding to d=0.97, 1.66, and 2.5 nm, respectively. I considered the density of the first adsorption layer and indicate it shown in Table 4.2. The cross-sectional area of the simulation cell was 150.1×150.1 Å, and periodic boundary conditions were applied in all directions. Length of all SWNT were 25.1 nm, and the number of carbon atoms were 2800, 4800, and 7200 for diameters d=0.97, 1.66, and 2.5 nm, respectively. Densities of surrounding LJ molecules without absorbed molecules on the SWNT surface (ρ^*_{free}) were varied from 0.0064 to 0.0138.

Thermal boundary conductance increased with the increase in diameter, however, there is a minor difference between SWNT of d=1.66 and 2.5 nm. From that, I can conclude that thermal boundary conductance of SWNT with different diameters converges to some degree when the diameter becomes large, and it is possible to extend this for graphene, which is somewhat like a SWNT with $d=\infty$. There are no reports of thermal conductance measurements between graphene and the LJ fluids used here, however this value has been measured for graphene and CO₂ [32]. Although the systems are somewhat different, the reported value (corresponding to $d=\infty$) is of the same order of magnitude as this calculation for a SWNT with diameter d=2.5 nm.

Although SWNT with different diameters are under the same density (ρ^*_{free}), they did not have same thermal boundary conductance. Therefore, I investigated the difference of energy transfer in three cases. Here, I expect that the thermal boundary conductances are different because of the curvature of

Chirality	No. of carbon atoms	<i>d</i> (nm)	No. of LJ molecules	$ ho^{*_{free}}$	No. of molecules in 1 st adsorption layer	<i>K</i> (MW/m ² K)
			1000	0.0064	75	0.313
(7,7)	2800	0.97	1500	0.0097	93	0.358
			2000	0.0129	129	0.460
	4800	1.66	1200	0.0073	157	0.430
(12,12)			1700	0.0104	196	0.548
			2200	0.0134	270	0.743
			1400	0.0082	238	0.464
(18,18)	7200	2.5	1900	0.0113	286	0.581
			2400	0.0138	447	0.760

Table 4.2 SWNTs with various diameters and their corresponding first adsorption layers



Figure 4.12 snapshots of SWNTs with chirality (7,7), (12,12), and (18,18) (from left), corresponding to diameters d=0.97, 1.66, and 2.5 nm, respectively.



Figure 4.13 Diameter dependence of thermal boundary conductance for SWNTs under different densities (ρ^*_{free}).

SWNTs with different diameters. This could determine the easiness to absorb on the surface of SWNT, thus influence to the energy transfer by residence time.

However, in order to apply the evaluation of energy transfer per residence time as discussed in section 4.1.4, energy balance must be ensured that interfacial energy transfer accounts for the majority of the energy transfer in the system for SWNT with various different diameters. Figure 4.14 shows the energy balance of SWNTs with diameters d=0.97, 1.66, and 2.5 nm, indicating it is fine to investigate energy transfer by the perspective of using residence time.



Figure 4.14 Influence of SWNT diameter on energy balance.

4.2.3 Energy transfer of SWNTs with various diameters

Figure 4.15 shows that the number of molecules per residence time is dependent on diameter. First, residence times for SWNT of diameter d=0.97 nm tend to be shorter than other cases of SWNT with diameter d=1.66 and 2.5 nm. Distribution of residence time of SWNTs with diameter d=1.66 nm is a bit shorter than that for SWNTs with diameter d=2.5 nm, even though they are under almost the same density (ρ^*_{free}) and temperature, meaning the probability of adsorption on the surface of is essentially equal. Moreover, the number of molecules with short residence time on SWNTs with d=0.97 nm is higher than for SWNTs with diameter d=2.5 nm. Here, I conclude that molecules are more stable on a low-curvature surface, so they stay longer than on a high-curvature surface, and I expect that adsorption onto graphene is the most stable among the carbon network structures.

For energy transfer per atom and residence time by SWNT of different diameter, molecules with



Figure 4.15 Percentage of molecules with different residence times. (a), (b), and (c) are SWNTs with diameters d=0.97, 1.66, and 2.5 nm, respectively. Increase of diameter increases the residence time.



Figure 4.16 Energy transfer of atoms having different residence times. (a), (b), and (c) correspond to SWNTs with different diameters d=0.97, 1.66, and 2.5, respectively.

long residence time transferred energy more than those with short residence time. Figure 4.16 (a) shows the distribution of energy transfer per atom of SWNT diameter d=0.97 nm. Comparing to two other cases, the energy transfer tends to be mainly distributed around less than 100 ps. As shown in Fig. 4.16(b), energy per atom of SWNT with diameter d=1.66 nm was transferred more frequently between 80 and 100 ps than that with d=0.97 nm. Lastly, that of SWNT with d=2.5 nm transferred energy per atom more than over 100 ps. From the above, I can conclude that molecules with long residence time transfer more energy than those with short residence time.

Figure 4.17 shows total energy transfer per residence time during 200 ps from1100 to1300 ps. The meaning of total energy transfer is the number of residence molecules per residence time multiplied by the energy transfer per atom and residence time. I found the molecules that had higher speed than SWNT had residence times of 0 to 20 ps for all cases. Figure 4.17(a) shows for diameter d=0.97 nm that total energy per residence time was transferred little for residence times longer than 100 ps. For SWNT with diameter d=1.66 nm energy is transferred quite actively from 0 to 100 ps comparing to the d=0.97 nm case, as shown in Fig. 4.17(b). From Fig. 4.17(c), I found that the residence time is longer on SWNT with large



Figure 4.17 Total energy transfer in the first adsorption layer around SWNTs with diameters d= (a) 0.97, (b) 1.66, and (c) 2.5 nm.

diameters, and eventually, more energy at the interface between SWNT and surrounding LJ fluid was transferred.

Chapter 5

Conclusion

The thermal boundary conductance *K* between a single-walled carbon nanotube (SWNT) and various surrounding Lennard-Jones (LJ) fluids was investigated using non-stationary molecular dynamics simulations. I found that the density dependence on thermal boundary conductance relies on the local density of the molecules in the first adsorption layer, and there is little effect from outer layers. The hydrogen case is found to be much more sensitive to the local density than argon or nitrogen. For analyzing thermal boundary conductance, however, I needed to consider parameters of the surrounding fluid as well as the density dependence on thermal boundary conductance.

The molecular mass influences the thermal boundary conductance far more than other fluid parameters (i.e., binding energy and equilibrium distance), and the thermal boundary conductance increased exponentially with decreasing mass. For hypothetical fluids, where the mass was artificially changed, the thermal boundary conductance was found to be independent of local density. Furthermore, the local density and the mass of the LJ fluid have the most influence on the value for determining the thermal boundary conductance. Through the above studies, I obtained a phenomenological description of the thermal boundary conductance between a SWNT and a surrounding fluid and verified the accuracy of the equation.

I found that interfacial energy transfer accounts for the majority of the energy transfer occurring within the system, and an increase in temperature tends to increase the rate of energy transfer. This is why the thermal boundary conductance increases with temperature. In addition, the residence time of molecules on surfaces of SWNTs at high temperature was short, but the energy transfer was effective.

SWNTs with various diameters were simulated in order to verify the difference in thermal boundary conductance and energy transfer with respect to diameter under the same surrounding pressure. I found that the thermal boundary conductance is higher for large diameter SWNTs, but it is not simply proportional to diameter; I expect the value at larger diameters converges to that of graphene. I also found that surrounding LJ molecules could easily reside on the surface of SWNTs that have larger diameters because of the low-curvature of the surface. This leads to more transfer of energy than on SWNTs with highly curved surfaces.

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以上

Molecular Dynamics Simulation of Thermal Boundary Conductance between SWNT and Surrounding Fluid 単層 CNT と周囲流体の界面熱コンダクタンスの分子動力学解析

<u>1-60 ページ 完</u>

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