Desorption Process of an Atom from a Vibrating Graphene Surface

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We theoretically investigate the desorption process of an argon atom from a vibrating nanographene sheet. A high eigenfrequency of a graphene membrane owing to a small mass density per area and a large Young’s modulus of graphene enable increasing the velocity of an atom enough to escape from the attractive interaction between the atom and graphene in a short time by accelerating the graphene sheet. We present the dependence of the velocity of ejected atom on the frequency and amplitude of the graphene membrane and consider an application to heating gas in small cavity. [DOI: 10.1380/ejssnt.2018.400]

Keywords: Molecular dynamics; Computer simulations; Atomistic dynamics; Nano-films, stacks, and other nano materials; Graphite

I. INTRODUCTION

Heating of gas molecules usually arises from the interaction with solid surfaces, and many engineering applications such as combustion engine and heat pump are based on heating of gas molecules. The main purpose of heating is increasing the velocity of molecules. Among various methods for heating, adiabatic compressing is the most well-known method of heating of gas molecules. From the microscopic viewpoint, adiabatic compressing is realized by collision of molecules with an accelerating surface. The increasing rate of velocity is proportional to the relative velocity of a gas molecule to the surface. Thus, the mean velocity of gas, which is regarded as temperature, increases with the velocity of the surface.

The acceleration of the solid surface is limited mainly by its mass and strength. More power is needed for accelerating a heavier solid surface. In addition, the surface must be strong to withstand huge acceleration. To realize quick heating with small energy consumption, a nanographene may be a good candidate for the movable surface. Because the mass density of graphene is very low but the stiffness is very large [1–3]. These implies that the eigenfrequency of a graphene sheet can be very high [4]. These excellent properties of a graphene sheet have already been used in sensors [5–7]. In addition, graphene sheets have the potential to be used as actuators. However, little is known about the applications of graphene sheets to actuators [8]. For this reason, we investigate the acceleration of a gas molecule by vibration of a nanographene sheet, which realizes quick heating of gas trapped in a small cavity.

The desorption process of considered acceleration is as follows. A single atom is initially adsorbed at the center of a nanographene sheet with the Lennard-Jones interaction [9]. Next, the graphene membrane is deformed by applying an external force, such as electrostatic force [10], and the external force is decreased instantaneously to zero. The gas is accelerated by the restoring force of the nanographene sheet and desorbed from the graphene surface if the gas atom acquires a sufficient velocity to escape from the Lennard-Jones potential well. We focus on the dependence of the injection velocity on the displacement at the center and the eigenfrequency of the nanographene sheet, which is primarily determined by the size of the graphene membrane.

This paper is structured as follows. In Sec. II, we consider the Lennard-Jones interaction between a graphene membrane and a noble gas atom. A gas atom near the graphene membrane interacts with some carbon atoms. If the minimum distance between the gas atom and the graphene membrane is small, the carbon atoms just below the gas atom dominantly contribute to the force caused by the Lennard-Jones interaction. As the minimum distance between the gas atom and the graphene membrane increases, the number of carbon atoms that contributes to the Lennard-Jones interactions increases. The separation dependence of the Lennard-Jones potential between an argon atom and the graphene membrane is presented. In Sec. III, molecular dynamics (MD) simulations of argon gas ejected from the graphene membrane are described. In this simulation, it is shown that the velocity of an injected argon atom exceeds 2 km/s, which corresponds to the root-mean-square speed of argon atom at 6400 K. In Sec. IV, we show that the motion of the argon atom obtained from the MD simulation can be approximately represented by solving the Newtonian equation of motion of a one degree of freedom system, in which the force depends on time. In Sec. V, the velocity of the argon atom ejected from a nanographene sheet is calculated by varying the initial displacement and frequency of the graphene membrane using the model introduced in Sec. IV. It is shown that the dependence of the desorption velocity on these conditions of the graphene membrane becomes complicated when multiple collisions occur between the argon atom and the graphene membrane. In Sec. VI, we present the conclusions of this study and comment on the application to nanotechnology.

II. LENNARD-POTENTIAL BETWEEN A GAS ATOM AND GRAPHENE

When an atom approaches a graphene membrane from afar, the atom is attracted at the beginning. As the separation between the atom and graphene decreases, the atom is pushed back from the graphene surface. The interaction between a noble gas atom and the graphene surface is often described by the summation of the Lennard-Jones potential. In this study, we consider the interaction between an argon atom and the graphene membrane as an
example. The Lennard-Jones potential between an argon atom and a carbon atom is usually expressed as

\[ V_{\text{Ar-C}}(r) = 4\epsilon \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6}, \]

where \( \epsilon = 9.683 \times 10^{-22} \) J and \( \sigma = 3.446 \) Å [9]. To calculate the force acting on the argon atom, the distances between the argon atom and each carbon atom in the graphene membrane should be known. We assume that the argon atom is located along the \( z \)-axis, which is vertical to the graphene membrane and passes through the center of a six-membered ring. Figure 1 shows the honeycomb structure of an unreformed graphene membrane, where the origin is set at the center of the six-membered ring.

Multiple atoms exist on a concentric circle. We define the distance between the origin and carbon atoms on the \( n \)-th concentric circle with the radius \( R_n \) and the number of carbon atoms on the \( n \)-th circle with radius \( R_n \) as \( N_n \). Integer \( n \) is labeled in ascending order of the radius. The first ring exists on a circle of the radius \( R_1 = l_c \), which is equal to the distance between adjacent carbon atoms, and \( N_1 = 6 \). For small \( n \), \( R_n \) and \( N_n \) are shown in Table I.

In order to calculate \( R_n \) and \( N_n \), we used the following algebraic relationship. The radius \( (R_n/l_c)^2 \) is an element of the following set [12]: \[ S = \{3(i^2 + ij + j^2 + i + j) + 1| i, j \in \mathbb{Z} \}. \]

The number of carbon atoms can be expressed as the coefficient of \( q(R_n/l_c)^2 \) in the following function:

\[ F(q) = \sum_{i,j \in \mathbb{Z}} q^{i^2+ij+j^2}. \]

If the argon atom exists on the \( z \)-axis, the potential energy between the argon atom and the graphene membrane is given by

\[ V(z, n_{\text{max}}) = \sum_{n=1}^{n_{\text{max}}} N_n V_{\text{Ar-C}} \left( \sqrt{R_n^2 + z^2} \right). \]

Figure 2 shows the potential energy between the argon atom and the graphene membrane for \( n_{\text{max}} = 1 \) and 15. As \( n_{\text{max}} \) increases, the depth of the potential well increases and the equilibrium distance decreases. The depth of the potential at \( n_{\text{max}} = 15 \) is 0.104 eV and the equilibrium distance is 3.40 Å. Accordingly, the argon atom at rest on the graphene surface must acquire the kinetic energy greater than 0.104 eV to escape from the graphene surface.

### III. MD SIMULATION

We investigate the change in the velocity of an argon atom that is ejected from a quadrate nanographene sheet using MD. The graphene membrane consists of 322 carbon atoms and the size is \( L_x = 2.8 \) nm and \( L_y = 2.9 \) nm. The argon atom at rest is located above the center of the deformed graphene membrane at time \( t = 0 \) as shown in Fig. 3. All carbon atoms along the edge of the graphene membrane are fixed, and the initial shape of the graphene membrane is given by

![Graphene Membrane Initial Configuration](image_url)
\[ \zeta(x, y) = -\frac{A}{16L_x^2L_y^2} \left( x - \frac{L_x}{2} \right) \left( x + \frac{L_x}{2} \right) \left( y - \frac{L_y}{2} \right) \left( y + \frac{L_y}{2} \right), \]

where \( A \) is the displacement at the origin of the graphene membrane. The initial velocities of all carbon atoms are zero.

We used the Tersoff potential [11] to express the potential energy between carbon atoms, and the Newtonian equation was solved keeping the conservation of energy. Figure 4 shows the snapshots of the cross section of the graphene membrane taken at 0.1 ps intervals with the initial displacement \( A = 4 \text{ Å} \) represented by dots.

The graphene membrane moves from the bottom to top in approximately 0.7 ps. Thus, the frequency of the graphene membrane is significantly large and in the terahertz range. However, since the mass density of graphene is very small, the maximum kinetic energy of the graphene membrane is approximately 50 eV.

The velocity of an ejected argon atom, whose initial position is the center of the graphene sheet, as a function of the cross section of the graphene membrane is approximately expressed as

\[ \zeta(t) = \frac{1}{\sqrt{2\pi}} e^{-\frac{t^2}{2}}, \]

where \( \zeta(t) \) is the vertical displacement of carbon atoms obtained by the MD simulation, and the solid lines represent the fitting to \( \zeta(t, x, y) \) defined in Eq. (8).

FIG. 4. Temporal change in the cross section of the graphene membrane taken at intervals of 0.1 ps. The dots represent the positions of carbon atoms obtained by the MD simulation, and the solid lines represent the fitting to \( \zeta(t, x, y) \) defined in Eq. (8).

IV. ANALYSIS USING A ONE DEGREE OF FREEDOM SYSTEM

When sufficient energy is transferred from the nanographene sheet to molecules on it, molecules can escape from the nanographene sheet. The transferred energy depends mainly on the initial displacement \( A \) and the frequency of the graphene membrane \( \omega \). Thus, we consider the dependence of the final velocity of the ejected atom on \( A \) and \( \omega \). Using the MD simulation, the final velocity of the ejected atom can be calculated for any initial conditions of the graphene membrane. However, much computational time is necessary especially for large graphene membranes. We examine whether the desorption process from the nanographene sheet can be approximately described by a one degree of freedom system that is characterized by the separation distance between the argon atom and the graphene membrane. Thus, we consider the dependence of the final velocity of the ejected atom on \( A \) and \( \omega \).

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FIG. 5. Temporal change in the velocity of the argon atom obtained by MD is shown by dots. The solid line shows the solution of the Newtonian Equation of motion for a one degree of freedom system, in which the position of graphene obtained by MD is used. The dashed line is obtained by assuming that the graphene membrane is a harmonic oscillator.
differential equation Eq. (7), where $\zeta_\alpha(t)$ in Eq. (6) is the vertical displacement obtained from MD. Although the final velocity is slightly smaller than the value obtained by MD, the temporal change is well reproduced. To solve Eq. (7) without using the results of MD, we need to express the displacement of the graphene membrane as a function of time. We assume that the vertical displacement of the graphene membrane is expressed as

$$
\zeta_\alpha(t, x, y) = \frac{-A \cos(\omega t) + c}{16L_xL_y} \left( x - \frac{L_x}{2} \right) \left( y - \frac{L_y}{2} \right) \left( y - \frac{L_y}{2} \right).
$$

In Fig. 6, the dots shows the vertical displacement of the center six-membered ring obtained by MD, and the solid line shows the fitted values of $-A \cos(\omega t) + c$ with $A = 3.79$ Å, $\omega = 4.9$ THz and $c = -0.25$ Å that is obtained by the least square method. The cross sections of the graphene membrane calculated using the fitted function are shown as solid lines in Fig. 4. Using the fitting function, the temporal change in the velocity obtained by solving Eq. (7) is shown as a broken line in Fig. 6. The final velocity obtained using the fitting function is larger than that obtained by MD because the displacement near $t = 0.5$ ps is overestimated. Although accurate prediction of the injection velocity using the one degree of freedom system is difficult, the acceleration performance of various nanographene sheets can be qualitatively examined.

To simplify the calculation, we employed the fixed boundary condition for a graphene membrane. This edge effect can harden the graphene membrane and lead to a higher eigenfrequency. We therefore examine a more realistic model that implements a graphene membrane with a higher eigenfrequency without fixed boundary condition, as shown in Fig. 7. The graphene membrane is sandwiched between silicon plates with square holes. Figure 8 shows the vertical displacement of a square graphene membrane with $L_x = 5.3$ nm and $L_y = 4.2$ nm obtained by MD simulation, in which the interaction between a carbon atom and a silicon atom is represented by the Lennard-Jones potential with $\epsilon = 8.012 \times 10^{-22}$ J and $\sigma = 3.629$ Å. The dimension of the square hole and the separation distance between the silicon plates are $L_{H} = 2.2$ nm and $d = 0.6$ nm, respectively. Although the maximum displacement of the graphene membrane stabilized between the silicon plates decreases compared to that at a fixed boundary condition, the time duration for the displacement to reach the maximum decreases. The eigenfrequency of the graphene membrane decreases as the size of the square hole increases.

V. DEPENDENCE OF THE DESORPTION VELOCITY ON DYNAMICAL PROPERTIES OF THE NANOGRAFHE SHEET

Using the one degree of freedom system introduced in Sec. IV, we consider the dependence of the desorption velocity on the amplitude $A$ and the angular frequency $\omega$ of the graphene membrane. Figure 9 shows the contour plot of the velocity of the argon atom at 100 ps obtained by solving differential equation Eq. (7) with the fitting function defined in Eq. (8), in which $L_x$ and $L_y$ are the same as the values used in MD and $c = 0$. 

FIG. 6. Vertical displacement of the six-membered ring at the center of the graphene membrane obtained by MD is indicated by dots. The fitting function with cosine is shown by a solid line.

FIG. 7. Schematic of a graphene membrane sandwiched between silicon plates.

FIG. 8. Comparison of vertical displacements of the graphene sheet with the fixed boundary and when clamped between silicon plates.

J-Stage: https://www.jstage.jst.go.jp/browse/ejssnt/
FIG. 9. Contour plot of the velocity of the argon atom at 100 ps versus the angular frequency and the amplitude. The borderline, where the velocity is zero, is indicated by a white dashed line.

Brighter regions indicate the region where the velocity is large. Figure 10 shows the dependence of the velocity on the angular frequency at $A = 2$ Å. When the angular frequency is decreased from 4 THz, the velocity approaches zero near $\omega_c = 3.48$ THz. Figure 11 shows the change in the position of the argon atom and the center of the graphene membrane at $A = 2$ Å and $\omega_c$. In addition, the force acting on the argon atom is shown as a dashed line.

Initially, the velocity of the argon atom is smaller than that of the graphene membrane. Accordingly, the distance between the argon atom and the graphene membrane decreases. It follows that the repulsive force acting on the argon atom increases. The argon atom is accelerated, and its velocity exceeds that of the graphene membrane because the mass of argon atom is much smaller than that of the graphene membrane. Then, the distance between the argon atom and the graphene membrane increases and the character of the force acting on the argon atom changes from repulsive and attractive. The work done by the repulsive force is almost equal to that by the negative force at $\omega_c$. Thus, the velocity of the ejected atom is almost zero. As the angular frequency is increased above $\omega_c$, the work done by the repulsive force increases and the final velocity also increases. In Fig. 10, a complicated change in the velocity is observed between $\omega = 3.3$ THz and $\omega_c$. Furthermore, large peaks in the injection velocities are observed. Figure 12 shows the change in the position of the argon atom at $\omega = 3.2$, 3.3, and 3.6 THz.

Below $\omega_c$, the argon atom is not ejected by the first launching. The work done by the repulsive force is smaller than that by the negative force. The bounced argon atom returns to the graphene membrane and recoils. The relative velocity of the argon atom to the graphene membrane depends on the time. If the argon atom collides with the rising graphene membrane, the velocity of the recoiled argon atom becomes large. Near $\omega_c$ the velocity of the bounded argon atom is small. Thus, it takes long time to return to the graphene membrane. This means that the relative velocity changes greatly with a slight difference of $\omega$. As a result, the velocity changes in a complex manner. The boundary where the velocity is zero near $\omega_c$ is indicated by a white dashed line in Fig. 9. If the size of the graphene membrane is large, the molecules move with the graphene membrane, and the adsorption state

FIG. 10. Velocity of the argon atom versus the angular frequency at $A = 2.0$ Å.

FIG. 11. Position of the ejected argon atom (blue) and graphene membrane (red) versus time. The force acting on the argon atom is shown by a dashed line.

FIG. 12. Relative position relation between the positions of the argon atom and graphene membrane (red) for different angular frequencies.
continues. Although we could not exactly determine the boundary, the relationship between $A$ and $\omega$ at the boundary is approximately expressed as $A \omega^2 = \text{constant}$ within the limits of the considered parameter spaces.

VI. CONCLUSION

Gas usually consists of numerous atoms, and its temperature represents the mean velocity of a gas atom. Thus, the temperature of gas can be controlled by changing the velocity of a gas atom. For instance, laser cooling enables lowering the temperature of neutral gas near absolute zero by decreasing the velocity of an atom with radiation pressure. We showed that an argon atom could be accelerated by using the restoring force of a nanographene sheet and proposed methods of simple calculation of the injection velocity. The motion of adsorbed atoms on a vibrating graphene membrane is very complicated. Thus, we introduced some assumptions. We assumed that an argon atom is located at the center of the graphene membrane. If the location of the atom is not central, the atom is not ejected completely vertically. In addition, thermal fluctuations of graphene were neglected. Furthermore, if two or more atoms adsorb on the graphene membrane, the interaction between atoms must also be taken into account. However, the essential properties of the acceleration by vibration of the graphene membrane were investigated in the presented system, and it is shown that the relationship of the dynamical response of the ejected atom near the equilibrium position between and the graphene membrane is crucially important.

We showed that the motion of the argon atom which is initially trapped at the minimum of the Lennard-Jones potential can be approximately analyzed using a mass-spring system. The spring constant between the argon atom and the graphene membrane near the equilibrium position is $5.5 \text{ N/m}$. Recalling that the mass of the argon atom is $6.634 \times 10^{-26} \text{ kg}$, the angular frequency $\omega_s = \sqrt{k/m}$ is $9.1 \text{ THz}$: the trapped argon atom can respond to the motion of the graphene membrane very quickly. Thus, if the eigenfrequency of the graphene membrane is much smaller than $\omega_s$, the interaction time becomes small, and the argon atom is not sufficiently accelerated. The potential depth of the Lennard-Jones potential considered in this study is $0.104 \text{ eV}$. Accordingly, if the graphene membrane is at rest, the necessary velocity starting from the equilibrium point to escape is approximately $500 \text{ m/s}$. The maximum velocity of the harmonic oscillator with amplitude $A$ and $\omega$ is $\mathcal{A} \omega$. If the amplitude is $1 \mathcal{A}$, the necessary angular frequency is approximately $5 \text{ THz}$. Since the angular frequency of the membrane is proportional to the square root of the Lamé parameters and mass density of the membrane, graphene, which has large Lamé parameters and a small mass density, is a good candidate for molecular accelerators. If the size of graphene membrane is large, molecules moves with the graphene membrane and the adsorption state continues.

Conversion from mechanical energy to heat is the main subject of thermodynamics, and it was developed by introducing simple models such as the Carnot cycle. Recently, thermodynamics in systems including nanomachines such as Feynman-Smoluchowski ratchet [16] has attracted our attention. In these systems, determining the maximum efficiency of nanomachines is important. Since the motion of an atom accelerated by a nanographene sheet can be expressed by a simple differential equation, the system presented in this study may be also a good model to consider the efficiency of the transfer from work to heat using nano-electro-mechanical systems.

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