Interaction Energy between Graphene and a Silicon Substrate Using Pairwise Summation of the Lennard-Jones Potential

Norio Inui* and Sho Iwasaki

Graduate School of Engineering, University of Hyogo, Shosha 2167, Himeji, Hyogo, 671-2201, Japan
(Received 27 December 2016; Accepted 13 March 2017; Published 8 April 2017)

We consider the computation of a long-range interaction energy between a single graphene sheet and a silicon substrate, which arises from vacuum fluctuations. The interaction energy obtained by summation of the Lennard-Jones potential between a carbon atom in a single graphene sheet and a silicon atom is compared with the dispersion energy (Casimir energy) obtained by combining the Lifshitz theory and the Dirac model for graphene. Deviation of the pairwise summation of the Lennard-Jones potential from the Casimir energy is corrected by adding a power-function term, whose coefficient depends on the distance between atoms. We also consider the interaction between a graphene sheet and a silicon dioxide substrate. [DOI: 10.1380/ejssnt.2017.40]

Keywords: Construction and use of effective interatomic interactions; Atom-solid interactions; Carbon; Silicon; Silicon oxides

I. INTRODUCTION

The excellent mechanical properties of graphene [1, 2] have led to many promising applications in nanoelectromechanical systems (NEMS), such as a nanoelectromechanical contact switch [3] and resonator [4–6]. These new devices may open a novel way to reduce energy consumption in information appliance [7] and realize highly sensitive sensors [8]. To understand the mechanical structure and dynamical properties of graphene-based NEMS, molecular dynamic (MD) simulations are often used. The accuracy of MD simulations mainly depends on the degree of accuracy of the force between molecules used in the MD simulations. In particular, since the adhesion between graphene and a substrate is a key issue in graphene-based NEMS [9], the modelling of the interaction between a graphene sheet and substrate is very important.

The Lennard-Jones (6,12) potential is frequently used to express the interaction energy between a graphene sheet and substrate [10–12], which originates from the fluctuation of an electromagnetic field in a vacuum. The greatest advantage of the Lennard-Jones potential over other interatomic potentials may be the simplicity of the expression, and this strong point is helpful to reduce the computation time. However, the accuracy of the Lennard-Jones potential usually decreases as the distance between atoms increases because of the finiteness of the speed of light. For large separations, a retardation effect must be taken into account. In addition, multibody effects must be taken into account. Recently, the interaction between a graphene sheet and a flat substrate using the Lifshitz theory has been studied [13–17], and a good agreement between the theoretical value calculated by the combination of the Lifshitz theory and Dirac model and the measurement using a dynamical atomic force microscope (AFM) was reported [18].

In order to consider the modelling of the graphene-based NEMS using the Lennard-Jones potential, we examine the difference between the interaction energy obtained by a pairwise summation of the Lennard-Jones potential [19, 20] and that obtained by the Lifshitz theory (Casimir energy) [21, 22]. The multi-scale simulation is one possible scheme to correctly simulate graphene-based NEMS. The interaction between carbon atoms in a graphene sheet is described by atomic interaction energies such as the Tersoff potential, and the local pressure between a graphene sheet and substrate is calculated by the Lifshitz theory. However, in this study, we consider another approach to improve the MD simulation. We generalize the Lennard-Jones potential to agree with the Casimir energy between a graphene sheet and a substrate arranged in parallel without significantly losing the simplicity of the Lennard-Jones potential.

This paper is structured as follows. In Sec. II, we explain briefly the Lennard-Jones potential. In Sec. III, the interaction energy between a graphene sheet and silicon substrate is calculated using the Lennard-Jones potential, and the asymptotic behavior for large separations is considered by employing the continuum approximation. In Sec. IV, to calculate the interaction energy between dielectric plates, the Lifshitz theory is introduced. In Sec. V, the interaction energy between two parallel silicon plates is calculated using the Lifshitz theory and compared with that calculated using Lennard-Jones potential. To characterize the difference between the results obtained by these methods, we introduce the local power exponent that represents the degree to which the interaction energy decreases by increasing the separation distance. In Sec. VI, the local power exponent of the interaction energy between a graphene sheet and a silicon substrate is calculated, and the generalization of the Lennard-Jones potential is considered. In Sec. VII, the representation of the interaction energy between a graphene sheet and silicon dioxide using the generalized Lennard-Jones interaction is described. In Sec. VIII, we summarize our results and present the method of improving the MD simulation for the graphene-based NEMS.

II. LENNARD-JONES POTENTIAL

To express the interaction energy between a pair of neutral atoms, we often employ the Lennard-Jones (6-12) potential:

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

where 

\[ r = |\mathbf{r}_1 - \mathbf{r}_2 |, \]

\[ \sigma, \epsilon \] are parameters, and \( \mathbf{r}_1, \mathbf{r}_2 \) are the positions of the interacting atoms.

\* Corresponding author: inui@eng.u-hyogo.ac.jp
TABLE I. Lennard-Jones parameters.

<table>
<thead>
<tr>
<th>elements</th>
<th>$\sigma$ (\AA)</th>
<th>$\epsilon$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–C</td>
<td>3.431</td>
<td>4.55</td>
</tr>
<tr>
<td>Si–Si</td>
<td>3.826</td>
<td>17.4</td>
</tr>
<tr>
<td>Si–C</td>
<td>3.629</td>
<td>8.91</td>
</tr>
<tr>
<td>O–C</td>
<td>3.275</td>
<td>3.44</td>
</tr>
</tbody>
</table>

where $r$ is a distance between atoms. The first term represents repulsive interactions for small separations, and the second term represents the van der Waals interaction. The Lennard-Jones parameters $\epsilon$ and $\sigma$ depend on the combination of elements. For the combination of identical atoms, Rappé et al. [23] presented a table of Lennard-Jones parameters for various elements. The Lennard-Jones parameters between different elements $A$ and $B$ can be approximately determined by the following relationship

$$
\sigma_{A-B} = \frac{\sigma_{A-A} + \sigma_{B-B}}{2},
$$

(2)

$$
\epsilon_{A-B} = \sqrt{\frac{\epsilon_{A-A} \epsilon_{B-B}}}{2},
$$

(3)

where $\sigma_{X-X}$ and $\epsilon_{X-X}$ are the Lennard-Jones parameters between a pair of element X. The Lennard-Jones parameters used in this study are given in Table I, where the parameters are calculated based on molecular mechanics force field given by Rappé et al. [23]. We note that $V(r)$ takes the minimum $-\epsilon$ at $r = \frac{2^{1/6}}{\sigma}$.

III. PAIRWISE SUMMATION OF THE LENNARD-JONES POTENTIAL

We consider the interaction energy between suspended graphene and a silicon substrate as shown in Fig. 1 using the Lennard-Jones potential. We assume that the suspended graphene is located parallel to the substrate with a separation gap $a$. The configuration of carbon and silicon atoms is shown in Fig. 2. Silicon atoms are arranged in a diamond cubic crystal structure with a lattice constant $d_{Si}$ of 5.431 \AA. The origin of our chosen coordinate system is located at a center of a six-membered ring, where the $z$-axis is parallel to the (0,0,1) axis of silicon. We set the $x$ and $y$-axes to be perpendicular to the $z$-axis. Carbon atoms are arranged in a honeycomb structure, and the minimum distance between carbon $d_{C}$ is 1.421 \AA. In general, the interaction energy between two bodies $A$ and $B$ is given by the summation of the Lennard-Jones potential over all possible combinations of atoms in two bodies. We assign positive integers $i$ and $j$ to atoms of bodies $A$ and $B$, respectively. Then, the interaction energy is given by

$$
U(a) = \sum_{i} \sum_{j>i} V(r_{ij}),
$$

(4)

where $r_{ij}$ is the distance between atoms labelled by $i$ and $j$.

Let us consider the interaction energy between a single carbon atom that is located at $(x, y, a)$ and a substrate. If the silicon substrate is semi-infinite, the interaction energy depends only on $a$ and the relative position of a carbon atom measured from the nearest silicon atom on the top surface of the substrate. When the position of the nearest atom is $(X, Y, 0)$, the relative position of the carbon atom on the $x-y$ plane is determined by $(\xi, \eta) \equiv (x - X, y - Y)$, where $-d_{Si}/2 \leq \xi, \eta \leq d_{Si}/2$. Thus, the interaction energy is written as $U(\xi, \eta, a)$. The number density function of carbon atoms observed at $(\xi, \eta)$ is uniform due to the lattice mismatch between graphene and the silicon substrate. Thus, the interaction energy...
between a graphene sheet and a silicon substrate can be expressed using the interaction energy between a carbon atom and a silicon substrate $U(\xi, \eta, a)$ as

$$U(a) = \frac{1}{d_{Si-Si}} \int \frac{d\xi}{2\pi} \int \frac{d\eta}{2\pi} U(\xi, \eta, a)d\xi d\eta. \quad (5)$$

In the practical computation of $U(\xi, \eta, a)$, the size of the substrate is limited. We introduce $l_{max}$ as a parameter that characterizes the size of the substrate and sum over all atoms in the substrate within a domain $-l_{max}/2 \leq x, y \leq l_{max}/2$ and $-l_{max} \leq z \leq 0$ in the calculation below.

If the separation distance between the graphene sheet and silicon substrate is much larger than the lattice constant of the crystal silicon, the distance between the carbon and silicon atoms changes almost continuously from $a$ to $\infty$. Thus, we may use the continuum approximation, and the potential between the graphene sheet and silicon substrate is given by

$$U_{cont}(a) = 4\epsilon_{Si-C}\rho_{Si}\rho_{C} \int \frac{d\mathbf{r}_1}{r_{12}} \int \frac{d\mathbf{r}_2}{r_{12}} \left[ \left( \frac{\sigma_{Si-C}}{R(\mathbf{r}_1, \mathbf{r}_2)} \right)^{12} - \left( \frac{\sigma_{Si-C}}{R(\mathbf{r}_1, \mathbf{r}_2)} \right)^6 \right]. \quad (6)$$

Here, $r_{1} \equiv \{x_1, y_1, z_1\}$ denotes the position in the silicon substrate, and the integral for $r_{1}$ is calculated over the domain $-\infty \leq x_1, y_1 \leq \infty$ and $z_1 \leq 0$. The position in the graphene sheet is denoted by $r_{2} \equiv \{x_2, y_2, a\}$, and the integral for $r_{2}$ is calculated over the area $-\infty \leq x_2, y_2 \leq \infty$. The distance between the carbon and silicon atoms $R(\mathbf{r}_1, \mathbf{r}_2)$ is expressed by

$$R(\mathbf{r}_1, \mathbf{r}_2) = \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - a)^2}. \quad (7)$$

We denote the number density of silicon and carbon atoms as $\rho_{Si} = 4.994 \times 10^{28}/m^3$ and $\rho_{C} = 5.246 \times 10^{28}/m^2$, respectively. By employing cylindrical coordinates, the integrals in (5) are analytically calculated, and the interaction energy is given by

$$U_{cont}(a) = 4\epsilon_{Si-C}\rho_{Si}\rho_{C} \int \frac{d\mathbf{r}_1}{r_{12}} \int \frac{d\mathbf{r}_2}{r_{12}} \left[ \left( \frac{\sigma_{Si-C}}{a} \right)^9 - \frac{1}{6} \left( \frac{\sigma_{Si-C}}{a} \right)^3 \right]. \quad (8)$$

For large separations, the interaction energy can be asymptotically expressed by

$$U_{a \gg \sigma}(a) \approx \frac{2\pi \epsilon_{Si-C}\rho_{Si}\rho_{C} \sigma_{Si-C}^6}{3a^3}. \quad (9)$$

Figure 3 shows $|U(a)|$ calculated by (5) on a log-log scale, where the integral is evaluated with a grid interval length of 0.01$d_{Si}$ for $l_{max}/d_{Si} = 100, 200, and 300$. The solid line shows $|U_{a \gg \sigma}(a)|$, whose slope is $-3$. We confirm that $U(a)$ approaches $U_{a \gg \sigma}(a)$ as $a$ increases. However, a low convergence is also observed. For a large separation, a large system size $l_{max}$ is necessary. The difference between $U(a)$ and $U_{a \gg \sigma}(a)$ for small separations is due to a lack of validity of the continuum approximation.

IV. LIFSHITZ THEORY

In graphene-based NEMS such as nanoelectromechanical contact switches, the separation distance between the graphene sheet and substrate is much larger than the length $\sigma$ characterizing the Lennard-Jones potential. If expression (1) was valid for an arbitrary distance $a$, and the interaction energy between the graphene sheet and substrate was given by the summation of the Lennard-Jones potential between a carbon atom and an atom in the substrate, $U_{a \gg \sigma}(a)$ gives a good approximate potential. However, in actuality, these condition are not satisfied. The retardation and many-body effects must be taken into account. The retardation effect due to dielectric bodies was studied by Casimir [21] and generalized by Lifshitz [13, 22]. According to Lifshitz theory, the interaction energy between dielectric plates at temperature $T$, which is the Casimir energy, is given by

$$U_c(a, T) = \frac{k_B T}{8\pi a^2} \sum_{l=0}^{\infty} \sum_{\sigma \in \{TM, TE\}} \int_{\zeta_l}^{\infty} \frac{dy}{y} \ln \left[ 1 - \frac{r_{\sigma}^{(1)}(i\zeta_l, y)r_{\sigma}^{(2)}(i\zeta_l, y)e^{-y}}{y^{\epsilon(n)}} \right]. \quad (10)$$

Here, the normalized Matsubara frequency $\zeta_l$ is defined by $4\pi k_B T a l/\hbar c$ where $c$ is the speed of light in vacuum, $k_B$ is the Boltzmann constant, and $h$ is the reduced Planck constant. The variable $y$ is defined by $\sqrt{(2ak_{1L})^2 + \zeta_l^2}$ where $k_{1L}$ is the modulus of the wave-vector projection of light on the plate. The summation is taken over two contributions of transverse magnetic (TM) and transverse electric (TE) modes, and the prime on the summation symbol denotes that 1/2 should be inserted if $l = 0$. The function $r_{\sigma}^{(n)}(i\zeta_l, y)$ in (10) is the reflection coefficient of the $n$-th plate defined by

$$r_{\sigma}^{(n)}(i\zeta_l, y) = \frac{\epsilon^{(n)}_l y - \sqrt{y^2 + \zeta_l^2(\epsilon^{(n)} - 1)}}{\epsilon^{(n)}_l y + \sqrt{y^2 + \zeta_l^2(\epsilon^{(n)} - 1)}}. \quad (11)$$

$$r_{TM}^{(n)}(i\zeta_l, y) = \frac{y - y^2 + \zeta_l^2\epsilon^{(n)} - 1}{y + y^2 + \zeta_l^2\epsilon^{(n)} - 1}, \quad (12)$$

$$r_{TE}^{(n)}(i\zeta_l, y) = \frac{\epsilon^{(n)}_l y - \sqrt{y^2 + \zeta_l^2(\epsilon^{(n)} - 1)}}{\epsilon^{(n)}_l y + \sqrt{y^2 + \zeta_l^2(\epsilon^{(n)} - 1)}}.$$
where \( \epsilon^{(n)} \equiv \epsilon^{(n)}(i\omega_0/(2a)) \) is the permittivity of the \( n \)-th plate along the imaginary axis. Using the Kramers-Kronig relation \([22]\), the permittivity along the imaginary axis is calculated from the imaginary component of the permittivity as

\[
\epsilon(i\zeta) = 1 + \frac{2}{\pi} \int_0^\infty \frac{\omega \text{Im}[\epsilon(\omega)]}{\omega^2 + \zeta^2} d\omega. \tag{13}
\]

The Casimir force per unit area \( P_c(a, T) \) is
determined through the permittivity along the imaginary frequency axis. We obtained the permittivity of silicon by substituting the

\[
P_c(a, T) = -\frac{k_B T}{4\pi a^3} \sum_{l=0}^{\infty} \sum_{\sigma \in \{\text{TM}, \text{TE}\}} \int_{i\zeta}^\infty y^2 dy \left[ \frac{e^{\nu}}{r_\sigma^{(1)}(i\zeta, y) r_\sigma^{(2)}(i\zeta, y)} - 1 \right]^{-1}. \tag{14}
\]

If the permittivities are one for arbitrary frequencies, which they are for perfectly conductive plates, the Casimir energy at absolute zero is given by

\[
U_\infty(a) = -\frac{\pi^2 h c}{720 a^3}. \tag{15}
\]

## V. CASIMIR ENERGY BETWEEN SILICON PLATES

The electric properties of graphene are very unique, and the expression of the reflection coefficient is complicated in comparison with other materials. Thus, we will begin by considering the Casimir energy between silicon plates. The material dependence of the Casimir energy is mainly determined through the permittivity along the imaginary frequency axis. We obtained the permittivity of silicon along the imaginary frequency axis by substituting the

\[
P(a, T) \approx -\frac{\hbar}{16\pi^2 a^3} \int_0^\infty dx \int_0^\infty \frac{x^2}{(e^{i\xi} + 1)^2 (e^{i\xi} - 1)^2} e^x - 1 \tag{16}
\]

\[
= -\frac{\hbar}{8\pi^2 a^3} \int_0^\infty \text{Li}_3 \left[ \frac{(e^{i\xi} - 1)^2}{(e^{i\xi} + 1)^2} \right] d\xi. \tag{17}
\]

![FIG. 3. Potential energy between a silicon plate and a single graphene sheet obtained by summation of the Lennard-Jones potential between a silicon and carbon atom for \( l_{\text{c/s}} = 100 \), 200, and 300. The solid line shows \( |U_{a = \sigma}(a)| \), whose slope is −3.](http://www.ssj.org/ejsnt)

![FIG. 4. (a) Potential energy and (b) force between silicon plates calculated by the Lifshitz formula. The dashed lines are the straight lines with a slope of −2 and −3 for the potential energy and the force, respectively.](http://www.jstage.jst.go.jp/browse/ejsnt/)
This formula is rewritten as

\[ P(a, T) \approx -\frac{H}{6\pi a^3}, \tag{18} \]

where \( H \) is the Hamaker constant \([20]\). Similarly, the Casimir energy for small separation distances is given by

\[ U(a, T) \approx -\frac{H}{12\pi a^2}. \tag{20} \]

The Hamaker constant for silicon plates is \( 2.634 \times 10^{-19} \) J.

Let us estimate the Hamaker constant for silicon plates using the Lennard-Jones potential. Using the continuum approximation, the interaction energy is given by

\[ U_{\text{LJ},\text{Si-Si}}(a) = 4\epsilon_{\text{Si-Si}}\pi\rho_{\text{Si}}^2\sigma_{\text{Si}}^6 \times \left[ \frac{1}{360} \left( \frac{\sigma_{\text{Si}}}{a} \right)^8 - \frac{1}{12} \left( \frac{\sigma_{\text{Si}}}{a} \right)^2 \right]. \tag{21} \]

Thus, the term representing the van der Waals interaction is

\[ U_{\text{attractive}}(a) = -\frac{4\epsilon_{\text{Si-Si}}\pi\rho_{\text{Si}}^2\sigma_{\text{Si}}^6}{12a^2}. \tag{22} \]

By comparing (20) and (22) both methods successfully predict that the interaction decays proportional to \( a^{-2} \) for small separation distances. Equation (22) yields the Hamaker constant for the interaction energy:

\[ H = 4\epsilon_{\text{Si-Si}}\pi\rho_{\text{Si}}^2\sigma_{\text{Si}}^6. \tag{23} \]

For silicon plates, the Hamaker constant obtained by the summation of Lennard-Jones interaction is \( 2.747 \times 10^{-19} \) J, and is slightly different from that obtained by the Lifshitz theory. In addition, it is found that the slope in Fig. 4(a) increases as the separation distance increases. To observe this change, we assume that the Casimir energy can be expressed in the following form:

\[ U_c(a, T) = C(a)a^{-\alpha(a)}. \tag{24} \]

Although the local power exponent \( \alpha \) and coefficient \( C(a) \) depend not only on the separation distance but also on the temperature, we omit the temperature dependence for simplicity and concentrate our attention on the dependence of the separation distance. The exponent \( \alpha \) is determined from the Casimir energy and force by

\[ \alpha(a) = \frac{a F(a, T)}{U(a, T)}. \tag{25} \]

Figure 5 shows the dependence of the local power exponent \( \alpha \) on the separation distance at 300 K. We note that the thermal radiation and permittivity of silicon substrate depend on temperature \([25]\). Thus, \( \alpha \) also depends on temperature. As expected, \( \alpha \) approaches 2 as the separation distance decreases. Conversely, as the separation distance increases, \( \alpha \) approaches 3 and decreases as the distance decreases further. This change in the power exponent is mainly due to the finiteness of the speed of light. As seen in (15), the Casimir energy between perfectly conductive plates decreases proportional to \( a^{-3} \) as the separation distance increases. This implies that the asymptotic behavior of the Casimir energy between silicon plates is similar to that between perfectly conductive plates at large separations.

To examine the deviation between the interaction energy between silicon plates by summing the Lennard-Jones potential from that obtained by the Lifshitz theory, we introduce the relative error defined by

\[ \Delta U_{\text{Si-Si}}(a, T) = \frac{U_c(a, T) - U_{\text{attractive}}(a)}{|U_c(a, T)|}. \tag{26} \]

Figure 6 shows the relative error of the potential energies between obtained based on the Lifshitz formula and the pairwise summation method. Since the Casimir energy depends on the temperature, the relative error also depends on temperature. Fig. 6 shows the relative error at 300 K. The deviation increases with the separation distance.

Here, we assume that the interaction energy between two atoms is expressed by the following power function

\[ V_\beta(r) = -C_\beta \left( \frac{a}{r} \right)^{\beta}, \tag{27} \]

where \( C_\beta > 0 \). For example, the van der Waals interaction can be expressed as a special case of \( \beta = 6 \). We consider...
the interaction energy between semi-infinite plates, whose atoms interact with the potential in (27). If $\beta > 4$, the interaction energy between the semi-infinite plates obtained by the continue approximation is given by

$$ U_\beta(a) = -\frac{2\pi\rho_1\rho_2\sigma^4C_\beta}{(\beta-4)(\beta^2-5\beta+6)} \left( \frac{\sigma}{a} \right)^{\beta-4}. \quad (28) $$

For $\beta = 6$ and 7, we have

$$ U_6(a) = -\frac{\pi\rho_1\rho_2\sigma^4C_6}{12} \left( \frac{\sigma}{a} \right)^2, \quad (29) $$

$$ U_7(a) = -\frac{\pi\rho_1\rho_2\sigma^4C_7}{30} \left( \frac{\sigma}{a} \right)^3. \quad (30) $$

The local exponent of $U_\beta(r)$ is $\beta - 4$, and that for silicon plates changes between 2 and 3. Accordingly, the local exponent $\beta$ in (27) changes between 6 and 7. Because the power function with an exponent of 7 is necessary to express the interaction energy for large distances, we generalize the term representing the attractive interaction in the Lennard-Jones potential between silicon plates separated with a gap $a$ in the following form:

$$ V_{\text{LJ}}(r) = -\tilde{C}_6(a) \left( \frac{\sigma}{r} \right)^6 - \tilde{C}_7(a) \left( \frac{\sigma}{r} \right)^7. \quad (31) $$

Using the generalized Lennard-Jones potential, the attractive interaction energy between two plates including atoms with number densities $\rho_1$ and $\rho_2$ is given by

$$ \tilde{U}(a) = -\pi\rho_1\rho_2\sigma^4 \left[ \frac{\tilde{C}_6(a)}{12} \left( \frac{\sigma}{a} \right)^2 + \frac{\tilde{C}_7(a)}{30} \left( \frac{\sigma}{a} \right)^3 \right]. \quad (32) $$

As our focus is on the interaction energy for $a \gg \sigma$, the repulsive term in the Lennard-Jones potential, which rapidly decreases as the distance between atoms increases can be neglected. The coefficients $\tilde{C}_6(a)$ and $\tilde{C}_7(a)$ are determined by the solution of the following simultaneous equations:

$$ \begin{cases} \tilde{U}(a) = U_{\text{LJ}}(a, T), \\ -\tilde{U}'(a) = P_{\text{LJ}}(a, T). \end{cases} \quad (33) $$

Figure 7 shows the coefficients $\tilde{C}_6$ and $\tilde{C}_7$ for silicon plates, which are normalized by $\epsilon_{Si}$. For small separation distances, $\tilde{C}_7$ is very small. This means that (1) is a good approximate expression for small separation distances. On the other hand, $\tilde{C}_7$ increases in comparison with $\tilde{C}_6$. This means that the retardation effect becomes more important as the separation distance increases.

VI. CASIMIR ENERGY BETWEEN A GRAPHENE SHEET AND SILICON SUBSTRATE

We consider the interaction between suspended graphene and a silicon substrate in the framework of the Lifshitz theory. The main task involving the calculation of the Casimir energy given by (10) is to express the reflection coefficient as a function of the frequency and the modulus of the wave-vector projection of light on the plate. The electric properties of graphene are quite different from ordinary materials, and quantum field theory is required to derive the reflection coefficient of graphene.

Using the Dirac model, Bordag et al. presented the reflection coefficient of graphene at a finite temperature. (see Appendix). Recently, the Casimir force gradient between a Si-SiO$_2$-graphene substrate and an Au-coated sphere was measured by a dynamic AFM, and it agreed with the theoretical predictions obtained from the combination of the Lifshitz theory and Dirac model.

The one of the important parameters characterizing the reflection coefficient of a two-dimensional material is a mass gap of quasiparticle excitations $\Delta$. This value for graphene is conjectured to be very small, and thus we assume that $\Delta = 0$. In addition, the temperature dependence is expected to be a small except term with $l = 0$. Thus, we used the reflection coefficient at absolute zero except for the term with $l = 0$.

If the interaction energy between a silicon and carbon atom in a graphene sheet is expressed by (27), the interaction energy between a graphene sheet and silicon substrate obtained by the continuum approximation is given by

$$ U_{G,\beta}(a) = \frac{2\pi\rho_{\text{c}}\rho_{\text{s}}\sigma_{G,\text{Si}}^2C_\beta}{(\beta - 3)(\beta - 2)} \left( \frac{\sigma_{G,\text{Si}}}{a} \right)^{\beta-3}. \quad (34) $$

By comparing with (28), we find the exponent of $a$ is decreased by one. This is because graphene is two-dimensional material. Figure 8 shows that the local exponent $\alpha(a)$, which is defined in the previous section, changes between 2 and 3, which is similar to Fig. 5. The remarkable difference between Fig. 5 and Fig. 8 is that the local exponent for the combination of a graphene sheet and silicon substrates is considerably larger than 2 at small separations, and it differs from the asymptotic behavior in (20). Figure 9 shows the relative error, which is defined similarly with (26). The relative error is small in comparison with that for the silicon plates. The reason is explained below.

The exponent obtained by the continuum approximation in (34) is $\beta - 3$. Thus, if we assume the form in (27) for the interaction between a carbon and silicon atom, the exponent $\beta$ must change between 5 and 6. Thus, we define the generalized Lennard-Jones potential between a carbon atom in graphene and a silicon atom by

$$ \tilde{V}_{G,C}(r) = -\tilde{C}_5(a) \left( \frac{\sigma}{r} \right)^5 - \tilde{C}_6(a) \left( \frac{\sigma}{r} \right)^6. \quad (35) $$
This artificial interatomic potential yields the interaction energy between a graphene sheet and silicon substrate:

\[ \hat{U}(a) = -\pi \rho\sigma^2 \times \left( \frac{\tilde{C}_5(a)}{3} \left( \frac{\sigma_{C-Si}}{a} \right)^2 + \frac{\tilde{C}_6(a)}{6} \left( \frac{\sigma_{C-Si}}{a} \right)^3 \right). \]  

(36)

Figure 10 shows the changes in \( \tilde{C}_5(a) \) and \( \tilde{C}_6(a) \) normalized by \( \epsilon_{Si} \). The coefficient \( \tilde{C}_5(a) \) decreases as the separation increases. Interestingly, the extinction of \( \tilde{C}_5(a) \) at large separations implies that the interaction energy between a graphene sheet and silicon substrate can be approximately expressed by modifying only \( \epsilon_{Si-C} \) in the Lennard-Jones potential (6,12). For instance, \( \tilde{C}_6(a) = 2.0 \epsilon_{Si-C} \) and \( \tilde{C}_5(a) = 3.8 \times 10^{-3} \epsilon_{Si-C} \) at \( a = 100 \) nm. Thus, the interaction energy at \( a = 100 \) nm and \( T = 300 \) K can be expressed as a summation over the Lennard-Jones (6,12) potential with \( 2\epsilon_{Si-C} \).

Suspended graphene is often fabricated above a silicon dioxide substrate. Thus, we consider the Casimir energy between a graphene sheet and silicon dioxide substrate. To calculate the Casimir energy based on the Lifshitz theory, the permittivity of silicon dioxide is necessary. The structure of a silicon dioxide layer on a silicon wafer produced by thermal oxidation is amorphous. Thus, we use the permittivity of fused quartz described by

\[ \epsilon(\xi) = 1 + \frac{C_{UV}\omega_{UV}^2}{\xi^2 + \omega_{UV}^2} + \frac{C_{IR}\omega_{IR}^2}{\xi^2 + \omega_{IR}^2}, \]  

(37)

where \( C_{UV} = 1.098, C_{IR} = 1.703, \omega_{UV} = 2.033 \times 10^{16} \text{ rad/s}, \) and \( \omega_{IR} = 1.88 \times 10^{14} \text{ rad/s} \) [22]. Figure 11 shows the local power exponent of the interaction energy between a graphene sheet and SiO$_2$ substrate.

When calculating the interaction energy between the graphene sheet and SiO$_2$ substrate as a pairwise summation of the Lennard-Jones potential, two interatomic interactions must be considered. The first is the interaction between a carbon atom in the graphene sheet and a
the number density of oxygen atoms is two times larger than silicon atoms. Here we note that the factor of two be-
tween a carbon and an oxygen atom. Thus, we express the general-
ized Lennard-Jones potential (attractive terms) for these interactions as

\[
V_{5,6}(r) = \tilde{C}_{5,6,C} \frac{(\sigma_{5,6,C})^5}{r^5} + \tilde{C}_{6,6,C} \frac{(\sigma_{6,6,C})^6}{r^6},
\]

(38)

\[
V_{5,0}(r) = \tilde{C}_{5,0,C} \frac{(\sigma_{5,0,C})^5}{r^5} + \tilde{C}_{6,0,C} \frac{(\sigma_{6,0,C})^6}{r^6}.
\]

(39)

Unlike the generalized Lennard-Jones potential between the graphene sheet and silicon substrate, there are four unknown parameters. These parameters can be determined by introducing higher derivatives of the Casimir energy. However, as an alternate method, we simply introduce the following constraint for \(\beta = 5\) and 6:

\[
\frac{\tilde{C}_{\beta,5,C}}{\tilde{C}_{\beta,6,C}} = \frac{\epsilon_{5,C}}{\epsilon_{6,C}}.
\]

(40)

By this constraint, the number of independent parameters decreases to 2. The interaction energy between the graphene sheet and a silicon dioxide substrate obtained by the continuum approximation is given by

\[
U_{\text{SiO}_2-C}(a) = -\pi \rho_{\text{Si}} \rho_{C} \sigma_{5,6,C}^3 \left\{ \frac{\tilde{C}_{5,5,C}(a)}{3} \left( \frac{\sigma_{5,C}}{a} \right)^2 + 2 \frac{\epsilon_{5,C}}{\epsilon_{6,C}} \left( \frac{\sigma_{5,C}}{a} \right)^2 \right\} + \frac{\tilde{C}_{6,6,C}(a)}{6} \left\{ \left( \frac{\sigma_{6,C}}{a} \right)^3 \right\} + 2 \frac{\epsilon_{6,C}}{\epsilon_{5,C}} \left( \frac{\sigma_{6,C}}{a} \right)^3 \right\}.
\]

(41)

where \(\rho_{\text{Si}} = 2.641 \times 10^{28}/m^3\) is the number density of silicon atoms. Here we note that the factor of two before \(\epsilon_{5,C}/\epsilon_{6,C} (= 0.386)\) originates in the assumption that the number density of oxygen atoms is two times larger than that of silicon atoms. Figure 12 shows \(\tilde{C}_{5,5,C}(a)\) and \(\tilde{C}_{6,6,C}(a)\) normalized by \(\epsilon_{5,C}\). By comparing with Fig. 10, similar dependences of \(\tilde{C}_{5,5,C}(a)\) and \(\tilde{C}_{6,6,C}(a)\) on the separation distance are observed.

VIII. CONCLUSION

We calculated the interaction energy between a graphene sheet and a flat substrate by two methods and examined the difference between them. In the first method, the interaction energy is calculated by summation of the Lennard-Jones potential over all possible combinations of carbon atoms in a graphene sheet and atoms in the substrate. In the second method, both the graphene sheet and substrate are regarded as dielectric bodies, and the Lifshitz formula is applied. For large separation distances between the graphene sheet and substrate, the second method yields a more accurate interaction energy. However, the first method is more simple and suitable for MD simulations.

To clarify the difference in the interaction energies obtained by the two methods, we introduced the local power exponent. The interaction energy obtained by the first method with continuum approximation decays, obeying a power law, as the separation distance increases, and its power exponent is independent of the separation distance. On the other hand, the interaction energy obtained by the second method cannot be expressed by a power func-

FIG. 12. Dependence of the coefficients \(\tilde{C}_5\) (solid line) and \(\tilde{C}_6\) (dashed line) normalized by \(\epsilon_{5,C}\) on the separation distance for the Lennard-Jones potential between a silicon dioxide plate and a single graphene sheet.
distances between atoms. The generalized Lennard-Jones potential presented here is an effective potential to express the macroscopic bodies. The procedure of calculating the interaction energy between graphene and a substrate is summarized as follows. First, interaction energy is calculated using Lifshitz theory and Dirac model as a function of the separation distance. Second, the coefficients of the generalized Lennard-Jones potential are determined. Finally, the pairwise summation is performed.

Although the Lennard-Jones potential is widely used to simulate graphene-based NEMS, the marginal interaction distance must be determined. It is well known that the Lennard-Jones (6,12) potential is inadequate for calculating the interaction energy at large separations. The pairwise summation method of the Lennard-Jones (6,12) potential between a graphene sheet and silicon substrate unexpectedly gave a good approximate interaction energy near $a \approx 100$ nm. However, it should be noted that the Lennard-Jones (6,12) potential is not the correct expression for the interaction of a carbon atom in graphene and a silicon atom in the substrate for large distances between them.

**ACKNOWLEDGMENTS**

This research was supported by the Ministry of Education, Culture, Sports, Science and Technology, through a Grant-in-Aid for Scientific Research(C), MEXT KAKENHI Grant Number 25390117.

**Appendix A: Reflection coefficients of graphene**

The reflection coefficients of graphene $r_{\alpha}(i\zeta, y)$, which were derived on the basis of the Dirac model are characterized by three parameters [14, 16, 17]. The first is a mass gap of the quasiparticle excitations $\Delta$. The second is the Fermi velocity $v_F$. The last is the temperature $T$.

For simplicity, we introduce the non-dimensional parameters $\tilde{\Delta} = 2\Delta a/(\hbar c)$, $\tilde{v}_F = v_F/c$, $\tau = 4\pi a k_B T/(\hbar c)$. The reflection coefficients of graphene are expressed using the polarization tensor $\tilde{\Pi}$ of graphene as

$$r_{c,\text{TM}}(i\zeta, y) = \frac{y\tilde{\Pi}_{00} - 2(y^2 - \zeta_1^2)}{y\tilde{\Pi}_{00} + 2(y^2 - \zeta_1^2)}, \quad (A1)$$

$$r_{a,\text{TM}}(i\zeta, y) = \frac{(y^2 - \zeta_1^2)\tilde{\Pi}_{00} - y^2\tilde{\Pi}_{00}}{(y^2 - \zeta_1^2)(\tilde{\Pi}_{11} + 2y) - y^2\tilde{\Pi}_{00}}. \quad (A2)$$

Here, the 00-component of the polarization tensor is given by

$$\tilde{\Pi}_{00}(i\zeta, y) = \frac{8\alpha(y^2 - \zeta_1^2)}{v_F^2} \int_0^1 \frac{x(1 - x)}{f_2(\zeta_1, y, x)} \, dx$$

$$+ \frac{8\alpha}{v_F^2} \int_0^1 \, dx \left\{ \frac{\tau}{2\pi} \ln[1 + 2\cos(2\pi l)x] e^{-f_3(\tau, \zeta_1, y)} + f_3(\tau, \zeta_1, y) \right\}.$$ \hspace{1cm} (A3)

where $\alpha \equiv e^2/(\hbar c)$ is the fine-structure constant. The functions $f_i (i=1,2,3,4)$ are defined as

$$f_1(\zeta_1, y, x) = v_F^2 y^2 + (1 - v_F^2)\zeta_1^2, \quad (A4)$$

$$f_2(\zeta_1, y, x) = \sqrt{\Delta^2 + x(1 - x)f_1(\zeta_1, y, x)}, \quad (A5)$$

$$f_3(\tau, \zeta_1, y, x) = \frac{2\tau}{\tau} f_2(\zeta_1, y, x), \quad (A6)$$

$$f_4(\zeta_1, y, x) = \cos g(\tau, \zeta_1, y) + \cos(2\pi l x). \quad (A7)$$

The trace of the polarization tensor is given by

$$\tilde{\Pi}_{11}(i\zeta_1, y) = 8\sqrt{f_1(\zeta_1, y)} \int_0^1 \frac{x(1 - x)}{\sqrt{\Delta^2 + x(1 - x)}} \, dx. \quad (A11)$$

At absolute zero, the 00-component and the trace of the polarization tensor is given by

$$\tilde{\Pi}_{00}(i\zeta_1, y) = \frac{y^2 - \zeta_1^2 \Phi_{00}(i\zeta_1, y)}{f_1(\zeta_1, y)}, \quad (A9)$$

$$\tilde{\Pi}_{11}(i\zeta_1, y) = \frac{y^2 + f_1(\zeta_1, y) \Phi_{00}(i\zeta_1, y)}{f_1(\zeta_1, y)}, \quad (A10)$$

where

$$\Phi_{00}(i\zeta_1, y) = 8\sqrt{f_1(\zeta_1, y)} \int_0^1 \frac{x(1 - x)}{\sqrt{\Delta^2 + x(1 - x)}}. \quad (A12)$$


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