A molecular dynamics study of the carbon–catalyst interaction energy for multi-scale modelling of single wall carbon nanotube growth

Yasushi Shibuta a,*, James A Elliott b

a Department of Materials Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
b Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge CB2 3QZ, UK

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Abstract

The interaction energy between a graphene sheet and a catalytic substrate-supported metal cluster has been studied by classical molecular dynamics simulation, in the wider context of a multi-scale modelling investigation of the growth process of single wall carbon nanotubes (SWNTs). The contact angle of the metal cluster on the substrate is proportional to the binding energy of the potential function representing the interaction between the metal cluster and the substrate, and the total interaction energy between the metal cluster and the graphene sheet depends on contact angle. However, the interaction energy per unit area was found to be 1.0 eV Å⁻² (16.03 J m⁻²), independent of the contact angle, using Ni as catalyst.

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1. Introduction

The formation mechanism of single wall carbon nanotubes (SWNTs) [1] during synthesis using a chemical vapour deposition process has been widely discussed since their discovery [2]. Many different models have been proposed based on the atomic motion of catalytic metals [3] or the much larger carbon-saturated liquid metal clusters as a seed for SWNTs [4–11]. Since it is difficult to carry out experiments that can distinguish unambiguously between the different models, the molecular dynamics (MD) method can be used to provide more detailed information about the SWNT synthesis mechanism. However, it is difficult to reproduce the entire formation process of SWNTs due to computational limits on the system size and time scale. Therefore, most of the previously published numerical modelling works have focused only on a specific phase of the formation process, or on pure carbon systems [12,13].

On the other hand, one of us has previously described numerical modelling of the nucleation process of SWNTs, focusing on the role of the catalytic metal atoms [8,9] using novel many-body potential functions between carbon atoms and catalytic metal atoms constructed by fitting binding energies from Density Functional Theory (DFT) calculations [14,15]. This is an example of the first stage in the construction of a multi-scale modelling framework by the mapping of parameters from the ab initio calculations to the classical MD scale simulations. Ding et al. [10] have demonstrated a nucleation process that implicates the temperature gradient in the metal particle as a driving force for nucleation. Galli et al. [11] have shown explicitly the first stages of the nucleation of a fullerene cap on a metal particle by an ab initio MD simulation of several tens of picoseconds, but these results are limited by the extreme computational expense of the methods used. Therefore, the use of a more coarse-grained simulation methodology is essential for studying the growth process after the initial nucleation event.

Fig. 1 shows a schematic picture of our proposed multi-scale modelling framework for studying the growth of a SWNT. Firstly, information from ab initio quantum level is mapped onto the classical MD scale by constructing the empirical potential function from an ab initio energy calculation [14,15]. Secondly, the parameterization of a Metropolis Monte Carlo (MC) simulation is obtained using input from
MD simulation. That is, the interaction energy per unit area of the graphene sheet obtained by MD simulation is related to that for a coarse-grained triangular mesh element for further MC calculation. In this way, it is possible to establish a methodology for linking accurate quantum mechanical models of the atomistic interactions to a full-scale coarse-grained simulation of the SWNT growth process. In this Letter, we describe the results for contact angle of a metal particle on a substrate (Section 3.1), the effect of changing contact angle on the carbon–catalyst interaction energy (Section 3.2), and finally the parameterization of MC model (Section 3.3). The results from the MC calculation of the resulting growth process will be presented in a forthcoming publication [16].

2. Simulation methodology

A classical MD method was used to study the interactions between a metal cluster and a graphene sheet. A Brenner potential [17] was used to describe the covalent bonding between carbon atoms in the graphene. A many-body potential function [15] that was constructed originally for examining nucleation process of SWNTs [8,9] was used to describe the metal–metal and metal–carbon bonding. The parameter sets used for the simulations are listed in Tables 1 and 2.

In addition, the interaction between metal atoms in the cluster and the planar substrate was expressed using an one-dimensional averaged Lennard–Jones (1DLJ) potential [18]:

\[
F(z) = D_e \left\{ \frac{1}{5} \left( z - \frac{r}{\sigma} \right)^{-10} - \frac{1}{5} \left( z - \frac{r}{\sigma} \right)^{-4} \right\},
\]

where \( z \) is the coordinate normal to the substrate plane. This potential function represents the integrated interaction between a metal atom in the cluster and all atoms on the substrate by a standard 6–12 Lennard–Jones potential function. The parameter \( \sigma \) is set to 3.23 Å, determined from the van der Waals radius of a Si atom [19]. The parameter \( D_e \) was varied from 0.5 to 1.5 eV at 0.05 eV intervals in order to describe the variable affinity of the metal cluster for the substrate.

The velocity Verlet method was used to integrate the classical equations of motion with a time step of 0.5 fs. A Berendsen thermostat [20] was used for temperature control with a relaxation time of 0.17 ps.

3. Results and discussion

3.1. Contact angle of the metal cluster on the substrate

The interaction energy between a metal cluster on a substrate and a graphene sheet was calculated in a following way. Firstly, FCC crystal structures of Ni\(_{256}\), Ni\(_{500}\) and Ni\(_{864}\) were annealed for 2 ns at 2000 K. The clusters obtained were then annealed on the substrate for 100 ps...
at 1500 K. Finally, the binding energy of the 1DLJ potential was increased from 0.5 eV to 1.5 eV in 0.05 eV intervals. Fig. 2a shows the snapshots of Ni\textsubscript{256} clusters annealed on the substrate for three different values of \( D_e \). In general, a large binding energy tends to make the cluster wet the substrate more strongly. The contact angle, as defined in Fig. 2b, was estimated on the assumption that surface of the metal cluster was approximately spherical. It is then determined from the radius, \( R \) and the center of the fitted circle, \( h \):

\[
\cos \theta = -\frac{h}{R}. \tag{2}
\]

\( R \) and \( h \) were estimated by the top height of the cluster, \( x_1 \) and the radius of the sectional circle at the bottom of the cluster \( x_2 \) as follows:

\[
R = \frac{x_1^2 + x_2^2}{2x_1}, \quad h = \frac{x_1^2 - x_2^2}{2x_1}. \tag{3}
\]

Hence, the contact angle, \( \theta \) and the surface area of the cluster, \( A \) are known from \( x_1 \) and \( x_2 \):

\[
\theta = \cos^{-1}\left(\frac{x_1^2 - x_2^2}{x_1^2 + x_2^2}\right), \tag{4}
\]

\[
A = 2\pi R^2 (1 - \cos \theta) = 2\pi(x_1^2 + x_2^2). \tag{5}
\]

Fig. 2c shows the plot of contact angle, \( \theta \), against integrated depth of the 1DLJ potential function, \( D_e \). Two hundred and ten independent clusters were examined for each of the three different cluster sizes. The contact angle determined from MD simulations was reproducible, and negatively correlated with the integrated depth, \( D_e \). This is consistent with the behavior predicted by Young’s equation when the solid–vapor and liquid–vapour surface energies are constant:

\[
\cos \theta = \frac{(\gamma_{SV} - \gamma_{SL})}{\gamma_{LV}}, \tag{6}
\]

It is also in good accordance with the MD simulation of liquid droplets in contact with a solid surface [18]. The data were fitted to the linear function by least squares regression analysis, and the gradients of the fitted functions are \(-46.24, -35.13\) and \(-28.06 \) deg eV\(^{-1}\), respectively, in other words, the smaller the size of the cluster, the steeper the gradient becomes. This is consistent with the Young-Laplace equation, which says the internal pressure difference across the droplet interface, \( \Delta P \) becomes larger as its size decreases:

\[
\Delta P = -2\gamma/R \tag{7}
\]

3.2. Calculation of the interaction energy between a metal cluster and a graphene sheet

Next, the dependence of interaction energy between the metal cluster and a graphene sheet on the contact angle was examined. One of the equilibrated clusters obtained in Section 3.1 was placed on the bottom of a cubic cell, with dimensions 60, 80 and 100 Å for each of the three cluster sizes, respectively. The top and bottom boundaries had mirror boundary conditions and others had periodic boundary conditions. A graphene sheet was lowered from the center of the cell. The graphene sheet for the three different sizes of metal clusters contained 640, 1144 and 2560...
carbon atoms, respectively, in order to ensure that the sheet could cover the particle. In addition, the 1DLJ potential, with the parameters \( \sigma = 3.23 \) Å and \( D_\sigma = 0.5 \) eV, were used between the bottom boundary and a carbon atom in the graphene sheet for preventing it from becoming wrinkled, but the energy gain caused by this interaction was not counted towards the metal–graphene surface energy. After the graphene sheet came into contact with the metal cluster, it was annealed for 20 ps at 1500 K. During this time, the metal cluster was fixed (0 K) in order to maintain its structure.

Fig. 3a shows the initial condition and the annealed structure of a sample of a Ni\(_{500}\) cluster with the integrated depth of potential function, \( D_c = 1.25 \) eV. The surface of the metal cluster is coated by the graphene, although some large defects are observed in the 2D graphene lattice. Fig. 3b shows a time series of potential energy of carbon atoms and metal atoms from the same sample. Firstly, the potential energy of the graphene sheet becomes higher due to bending around the cluster. Soon after, it becomes stable by covering the entire surface of the metal cluster. The resulting energy gain of the graphene sheet is approximately 0.12 eV per carbon atom. Similarly, that of the metal cluster is approximately 1.21 eV per metal atom.

The total interaction energy between the metal particle and graphene sheet, \( E_{\text{int}} \), was estimated from the energy difference between the total energy of the metal cluster covered by the graphene sheet and the sum of the energies of individual metal cluster and graphene sheet:

\[
E_{\text{int}} = E_{\text{tot}} - (E_{\text{graphene}} + E_{\text{cluster}}),
\]

where \( E_{\text{tot}} \) is the total energy and \( E_{\text{graphene}} \) and \( E_{\text{cluster}} \) are the energies of the individual components. \( E_{\text{tot}} \) and \( E_{\text{cluster}} \) were obtained directly from the above MD calculations. \( E_{\text{graphene}} \) was obtained by calculating the potential energy of just the graphene sheet in the final structure in above MD calculation (i.e. having removed the substrate and cluster). For the sample shown in Fig. 3b, \( E_{\text{tot}} \), \( E_{\text{graphene}} \) and \( E_{\text{cluster}} \) were \(-9898.1\), \(-7774.5\) and \(-918.7\) eV, respectively. Therefore, the total catalyst–carbon interaction energy, \( E_{\text{int}} \) was \(-1204.86\) eV.

In the same way, 210 independent runs for Ni\(_{256}\), Ni\(_{500}\) and Ni\(_{864}\) were examined for all metal clusters obtained in Section 3.1. Fig. 4a shows the plot of interaction energy, \( E_{\text{int}} \) against the contact angle of metal cluster, \( \theta \). The interaction energy is negatively correlated with the contact angle in every case, although the variance in the data is large. The systematic trend is due to the finite bending stiffness of the graphene sheet. The plots were fitted to the linear function by using the least squares criterion, and the gradients of the fitted lines are \(-0.63\), \(-1.86\) and \(-2.55\) eV deg\(^{-1}\), respectively. This total energy gain can

Fig. 3. Calculation of the interaction energy between a Ni\(_{500}\) cluster and a graphene sheet with the integrated depth of potential function, \( D_c = 1.25 \) eV. (a) Schematic images. (b) Time series of the potential energy of the graphene per carbon atom (solid line) and of the Ni\(_{500}\) cluster per Ni atom (dashed line).
be converted into the interaction energy per unit area, with the effective surface area of the metal cluster given by Eq. (5). Fig. 4b shows the plot of interaction energy divided by the surface area of the metal cluster against the contact angle. The interaction energy per unit area (Å²) appears to be independent of the contact angle. The black lines in Fig. 4b represent the mean value of the interaction energy per unit area. The mean values were 1.01, 0.94 and 0.97 eV Å⁻², respectively, giving an overall average value of (0.97 ± 0.04) eV Å⁻².

3.3. Estimation of the interaction parameter for the Monte Carlo calculations

Parameters for the carbon–catalyst interaction energy for the further MC calculation can be calculated from the above MD results. In our MC simulation [16], the graphene sheet is modelled by a collection of nodes, each representing many carbon atoms, and triangular mesh (Fig. 5a). As shown in Fig. 5b, when the carbon bond length is 1.44 Å, the area of the smallest triangle is 2.69 Å². The areas of the second and third smallest triangles are 10.77 and 24.24 Å², with each triangle including 1, 4 and 9 carbon atoms, respectively. The number of the carbon atoms represented by a node is determined using the number of carbon atoms each triangle includes, \( n_C \), as \( 6n_C/3 \). Hence, a node has 2, 8 and 18 carbon atoms for the smallest, the second smallest and third smallest triangles, respectively. From the above MD calculation, the interaction energy per unit area is approximately 1 eV Å⁻², independent of the contact angle of the metal cluster. Therefore, the interaction energies for each triangular element are 2.69, 10.77 and 24.24 eV, respectively.

In our MC simulation, the carbon–catalyst interaction energy, \( E_{ct} \) is assumed to be:

\[
E_{ct} = \begin{cases} 
\infty & (d < 0) \\
A_1^2E_{ct,1} & (0 < d < d_0) \\
0 & (d > d_0)
\end{cases}
\]

where \( A_1 \) is the area associated with the node, \( E_{ct,1} \) is the interaction energy per node of the graphene sheet being in contact with the catalyst particle, \( d \) is the distance of the node from the surface of the particle and \( d_0 \) is the cut-off distance of carbon–catalyst interaction. \( E_{ct,1} \) is determined by assigning the surface area \( A \) and the interaction energy from MD calculation. In case of the smallest triangle, \( E_{ct} \) and \( A_1 \) are \((2.69 \times 6)\) eV and \((2.69 \times 6)^2\) Å⁴. Hence, \( E_{ct,1} \) is 61.9 meV Å⁻⁴. Similarly, the values of \( E_{ct,1} \) for the second and third smallest triangles are 15.4 and 6.9 meV Å⁻⁴, respectively. In principle, such calculation can be repeated for any pure metal or alloy catalyst particle, provided suitable atomistic potentials for catalyst–carbon clusters can be constructed.

Fig. 4. Plot of (a) the total carbon–catalyst interaction energy and (b) the carbon–catalyst interaction energy per unit area (Å²), against contact angle.
4. Conclusion

The interaction energy between a substrate-supported catalytic metal cluster and a graphene sheet was studied by MD simulation. It was found that the contact angle of the metal cluster on the substrate is proportional to the integrated depth of potential energy of the 1DLJ potential representing the surface, and the dependence of contact angle on catalyst–surface interaction and particle size are in accordance with continuum theory predictions. The total energy gain of the interaction between the metal cluster and the graphene sheet depends on the contact angle, and tends to decrease with increasing contact angle. However, the interaction energy per unit area does not depend on the contact angle; the value is approximately 1.0 eV Å⁻², i.e. 16.03 J m⁻², using nickel as the catalyst metal.

Finally, the carbon–catalyst interaction energy for a coarse-grained triangular mesh is related to the hexagonal atomistic graphene sheet. Since the MC calculation is much less computationally intensive than either the ab initio or classical MD, it is able to reproduce the growth process of SWNT over much longer time scales and larger size scale.

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