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Molecular dynamics simulations of CH$_3$ sticking on carbon surfaces

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Employing both quantum mechanical and empirical force models, we use molecular dynamics simulations to obtain sticking cross sections for CH$_3$ radical chemisorption on unsaturated sites of carbon surfaces. Effects of the local atomic neighborhood on the chemisorption are examined for the comparison of the results with experiments. Our results show that the chemisorption of a CH$_3$ radical onto a dangling bond is highly affected by the neighborhood of the unsaturated carbon atom sites. Notably, sticking cross sections of totally bare dangling bond sites at the surface and sites partly shielded by neighboring methyl groups are observed to differ by two orders of magnitude, (15.3 ± 1.7) Å^2 and (0.2 ± 0.1) Å^2, respectively. We describe a steering effect which explains the recent experimental observation that the sticking cross section can be larger than the average area per surface site. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1536012]

I. INTRODUCTION

Diamond and diamond-like materials are important in many technological applications due to their unique mechanical, chemical, and optical properties.[1,2] Diamond-like hydrocarbon films are especially important for the performance and design of present and next-generation fusion devices.[3–5] When the deuterium and tritium ions and neutrals which have escaped from the fusion core plasma interact with carbon-based first walls, hydrocarbon species are released via physical and chemical sputtering. These species can either be redeposited on divertor tiles or deposited in other regions of the vacuum chamber which are not in direct contact with the fusion plasma.[6]

A major issue in fusion devices is how to achieve good control over the tritium inventory bound in deposited hydrocarbon films, as tritium is highly radioactive and cannot easily be recycled. With a better knowledge about the drifting of the hydrocarbon molecules in the vacuum chamber and growth of the hydrocarbon films, a better control of the tritium inventory can be achieved.

Using molecular dynamics (MD) simulations we now study the sticking process of methyl radicals on carbon dangling bonds. We examine several different dangling bond configurations lying on a hydrogen-terminated diamond (111) surface to be able to deduce what kind of dangling bond environment underlies the experimentally observed sticking coefficients.

II. BACKGROUND

In laboratories, diamond films are grown using techniques such as chemical vapor deposition, plasma assisted deposition, ion-beam deposition and sputtering, and laser ablation.[7–10] Models based on measurements, designed to estimate the concentration of gas-phase species present in a filament-assisted diamond growth, indicate that the two most important growth species are methyl (CH$_3$) and acetylene (C$_2$H$_2$) radicals.[11,12] Both experiments[13] and MD simulations[14,15] show that these radical species are among the most abundant sputtered species from fusion device plasma-facing carbon materials. This indicates that methyl and acetylene are important growth species of hydrocarbon films on the first wall.

Several models of diamond-like carbon film growth have been developed[16–21] but the precise reaction mechanisms are still unknown. It is generally accepted that the relative importance of methyl for C:H film growth depends not only on the high concentration in the feed gas and adsorption probability on unsaturated carbon sites (i.e., atoms with dangling bonds),[22,23] but also on the creation rate of new unsaturated carbon sites.[24] MD simulations by Alfonso and Ulloa[25] showed further that methyl radicals do not adsorb on fully hydrogen terminated carbon surfaces even at impact energies as high as 10 eV/molecule.

Since the growth of the carbon matrix by CH$_3$ proceeds only via chemisorption on carbon dangling bonds, we define the effective sticking cross section σ_c on these sites as an area on the surface to which the radical always chemisorbs upon impact. Clearly, factors contributing to σ_c are not only the feed gas and substrate surface temperature,[26] but also the local atomic neighborhood of the adsorption sites. Provided that the cross section is known, along with the concentration of adsorption sites n_{db}, the sticking coefficient of the growth species s and hence the overall growth of C:H films can be effectively predicted.

In recent studies by von Keudell *et al.*[24,27–29] surface processes on polymer-like hydrocarbon films were studied in radical beam experiments in an approach to isolate and quantify individual growth mechanisms. It was shown that an

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additional flux of atomic hydrogen, interacting simultaneously as methyl radicals with the surface, could enhance the sticking coefficient of CH$_3$ by two orders of magnitude. The hydrogen flux provides new adsorption sites via hydrogen abstraction in H$_2$ species and the results clearly show the importance of unsaturated carbon sites for the sticking of methyl radicals.

From simple rate equations, employing various experimentally determined parameters, von Keudell *et al.* obtained the cross section of a methyl radical chemisorption on an unsaturated carbon site to be $\sigma_c = 2.4$ Å^2. However, if elimination processes of the hydrogen incorporated to the substrate during methyl adsorptions are taken into account in the model, the cross section is higher, 5.9 Å^2. This latter approach, with $\sigma_c = 5.9$ Å^2, was done with methyl radicals in a 45° angle of incidence and was shown to be in excellent agreement with the experiments. When the experiment was done with incoming methyl radicals at normal angle of incidence the cross section obtained was much higher, 10–15 Å^2.[30] This is more than the average size for a surface site, 7.4 Å^2.[30] Thus a simple geometric argument is not enough to explain the large cross section. In this article we use computer simulations to shed light on the origin on this puzzling result.

III. SIMULATION METHOD

For simulating the chemisorption of a methyl radical on a diamond (111) surface, we used both tight binding (TB)[31,32] and empirical[33] hydrocarbon force models. Both of the models describe well the chemistry in C–H systems, the former giving a more rigorous, quantum mechanical representation, based on a second order expansion of the Kohn–Sham total energy in density functional theory with respect to charge density fluctuations. On the other hand, the empirical Brenner potential[33] is computationally less intensive while still describing bond formation and breaking correctly. This allows one to achieve more comprehensive statistics in MD simulations. It is worth noting that the two models have essentially nothing in common in the way the inter atomic forces are obtained. The main difference between the TB and empirical potential methods is that the empirical potential energy is obtained from an analytical function of atom coordinates usually fitted to experimental data, whereas in the TB method the energy is calculated by solving the Schrödinger equation for electrons in the field of atom cores. Hence, comparison between the two models is also useful in the view of validating the simulation results.

The experiments we compare our results with were conducted at 320 K rather than the 0 K we use. However, our previous experience with impact simulations[34,35] indicates that this is not a problem, as the lattice vibrations in strongly bonded materials are typically so small below $\sim$600 K that they do not affect impact or surface reaction events significantly. For the present study we also tested this explicitly by repeating some of the central impact simulations with substrate temperatures of 0 and 320 K. The resulting sticking coefficients were in all cases the same within the statistical uncertainties (which were $\lesssim$10%).
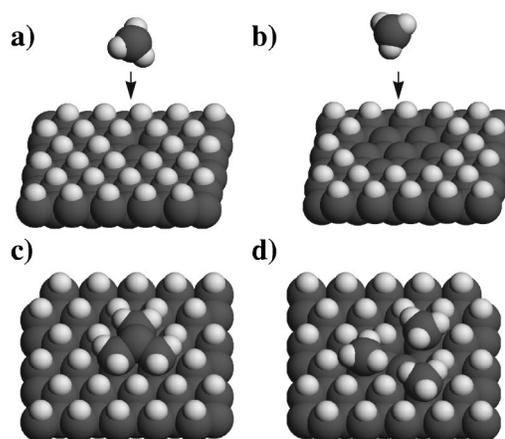
FIG. 1. Illustrations of four diamond (111) surfaces used in our modeling, with one (a) and seven (b) unsaturated carbon atoms, a four carbon atom cluster (c) on top of the surface (three of these carbon atoms being terminated by hydrogen) and finally with three methyl groups (d) neighboring the dangling bond seen in the middle of the surface. The dark spheres represent carbon atoms and the light ones hydrogen atoms. In total there were two layers of carbon atoms in the (111) direction. The incoming methyl radical is shown above the surface in the cases (a) and (b).

For the TB simulations we first created a diamond lattice consisting of two layers of carbon atoms, a total of 120 atoms. The lattice was equilibrated at 0 K using the temperature and pressure scaling methods of Berendsen *et al.*,[36] using a maximum time step of 0.25 fs which was found to be a small enough value to conserve the total energy well in systems of interest. The surface temperature was the same in all the sticking simulations. The carbon matrix was terminated with hydrogen at both (111) surfaces. One hydrogen atom was then removed from the surface thus resulting in an unsaturated carbon atom with one dangling bond [see Fig. 1(a)].

In order to study the effect of neighboring atoms we also created three other diamond surfaces. On the second lattice [cf. Fig. 1(b)] we had seven unsaturated carbon sites at the surface, namely the dangling bond used in the previous case and dangling bonds on the neighboring carbon atoms. The third lattice consisted of a cluster of four carbon atoms at the surface. Three of the carbon atoms were terminated by two hydrogen atoms, leaving a dangling bond site in the middle [see Fig. 1(c)]. Although this is clearly an artificial structure, it allowed us to study a completely bare dangling bond while still preserving the sp^3 bonding structure. The last surface was made by replacing 1, 2, or 3 hydrogen atoms neighboring the dangling bond with methyl groups, resulting in a partly shielded dangling bond site [see Fig. 1(d)].

The sticking simulations were begun by creating a CH$_3$ radical above the diamond surface [see Figs. 1(a) and (b)]. The distance between the radical and surface was larger than the cutoff (interaction) radius of the model. The radical was directed to the surface in the normal angle of incidence, with a translational velocity, rotation, and vibrational motion corresponding to a selected temperature. The simulation run for 500 fs, before the final bonding configuration was examined. Radicals bound to an unsaturated carbon atom by covalent bonds at the end of the simulation, were considered chemi-

sorbed. Tests with longer simulation times (2 ps) verified that 500 fs simulations were adequate to determine the chemisorption of an incoming radical.

The impact points were chosen randomly inside circular segments, centered on the dangling bond site, with a radial width $\Delta r = 0.1$ Å each. This is a stratified Monte Carlo (MC) strategy, which has been shown to give accurate results more efficiently than the conventional MC (i.e., completely arbitrary impact points on the whole surface).[37,38] The maximum distance of an impact point from the dangling bond site was 3.0 Å. By running series of impact simulations for each segment and integrating over the corresponding sticking probabilities, an effective sticking cross section was obtained for each surface configuration. In the case of seven dangling bonds only chemisorptions to the central unsaturated carbon site were taken into account. The total number of trajectories simulated for each temperature and surface configuration was typically 4000 in the classical potential simulations, and 100 for the TB simulations. The latter small value was necessitated by the high computational cost of TB calculations, but was still enough to give sufficient statistical accuracy for the comparison of different kinds of surfaces configurations.

Before initiating the actual sticking simulations, a number of tests for our models were carried out. First, we tested how the incoming molecule state, i.e., the rotational and vibrational motion, affects the sticking cross section. This was done in the following way. First, the CH_3 molecules were equilibrated in a heat bath at 2100 K for about 50 ps, resulting in translational, vibrational and rotational motions. As the thermal motion gave the radicals a random direction for the translational movement, the CH_3 molecules were then rotated so that their center-of-mass velocity vectors were parallel to the surface normal. The molecules were then brought above the substrate and the sticking simulations were performed, using the surface with seven dangling bonds and the carbon–carbon cutoff distance of 2.0 Å. By the use of the empirical potential we were able to gather comprehensive statistics. The results show that the cross section did not change significantly by adding vibrations and rotation to the motion of the CH_3 molecules, as the results were the same within the margins of error. Since this is a purely qualitative conclusion, the uncertainty with the potential cutoff radius (see Sec. IV B.) is not a problem here.

One physical effect which is not explicitly accounted for in our simulations are the zero-point vibrations of atoms.[39] In this case, there are two kinds of zero-point vibrations which might affect the results. The first kind is the zero-point vibrations of the H atoms in the CH_3. From the vibrational frequencies of the CH_3 molecule,[40] we found that the zero-point energy of the H atoms can correspond to temperatures of the order of 300 K. Since we have found (see above) that the sticking coefficients we obtain are the same for CH_3 internal temperatures between 0 and 2000 K, it is highly unlikely that the zero-point vibrations of the methyl radical would affect our results.

The second kind is the zero-point vibrations in the substrate. These can be substantial; the Debye model predicts a zero-point energy for diamond corresponding to a temperature of 2100 K.[39] This corresponds to a root-mean-square
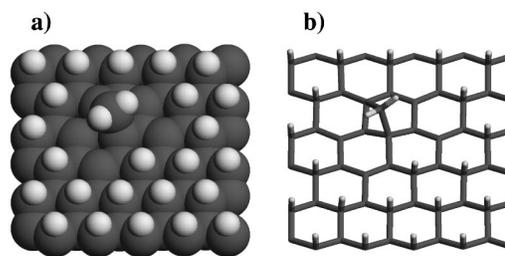
FIG. 2. Sphere (a) and simple stick (b) illustrations of one of the unusual bonding configurations for CH_3 chemisorption that we observed in the TB simulations for a surface with seven dangling bonds.

displacement of atoms from their lattice sites of about 0.040 Å in each dimension.[41] In our classical model, a lattice temperature of 700 K gives the same amplitude of vibrations for the C atoms. Hence we did test simulations of sticking coefficients for lattices at this temperature. The results were the same as those for the lower temperatures 0 and 320 K, indicating that zero-point vibrations do not have a significant effect on our results within the current statistical uncertainties of $\sim 10\%$.

We also examined whether the size of the lattice affects the sticking cross section. Since the tight-binding calculations are computationally very expensive it was preferable to work with a rather small lattice. The test simulations were performed by repeating the same series of simulations for two different hydrogen-terminated diamond (111) lattices, consisting of 173 and 233 atoms corresponding to two and three layers of carbon, respectively. The size of the lattice was not observed to have any effect on the sticking cross section within the margins of error.

The TB model employs a nonorthogonal, self-charge-consistent (SCC) parametrization.[31,32] Although charge fluctuations were not expected to be important for the present problem, we still tested the model with both SCC and non-SCC modifications. The results were roughly the same for both cases and the non-SCC modification was used in the sticking simulations, reducing the calculation time significantly.

In the following, we present results for methyl radicals impinging lattices consisting of one or two layers of carbon atoms. The radicals have rotational and vibrational motion corresponding to the classical distributions of the methyl gas temperature, since this is the case in most experiments.

IV. RESULTS

A. Tight-binding simulations

In the TB simulations, the most common behavior for the incoming methyl radical was to chemisorb onto a dangling bond site or to form a volatile CH_4 molecule by capturing a surface hydrogen and drifting away from the surface.

In addition to these two cases, the CH_3 radical sometimes adapted unusual (observed in $\sim 15\%$ of the sticking cases) bonding configurations at the surface with seven dangling bonds (see Fig. 2). These bonding configurations were probably intermediate and metastable, but the time scale of

the simulations did not allow us to determine the lifetime of these states.

In some cases the CH_3 group fragmented as one or two of its hydrogen atoms chemisorbed to dangling bond sites at the surface. The remaining CH_x group chemisorbed onto the surface, either onto another dangling bond site or by sticking to the surface between two dangling bond sites (Fig. 2). Another possibility was that one of the hydrogen atoms in CH_3 chemisorbed onto a dangling bond site, leaving a methylene (CH_2) radical which drifted away from the surface. However, since these unusual bonding configurations are rare, they have no significant effect on the sticking cross sections reported below within the current statistical uncertainties. However, if a better accuracy is achieved in the future in the simulations and modeling, special configurations like this will need to be taken into consideration in the analysis.

The sticking cross section obtained for the surface with one dangling bond was $\sigma_c = (10.4 \pm 1.2)$ Å^2. The quite large value, in comparison with the area per surface site ~ 5.7 Å^2, was obtained when CH_3 radicals impinging even at a rather large distance from the unsaturated carbon atom, were deflected from the surface hydrogen and, in some cases directing the methyl radical towards the dangling bond.

Repeating the simulations by the use of the surface with seven dangling bonds, σ_c obtained was about half of the value deduced for one dangling bond, (6 ± 2) Å^2. However, as previously mentioned, only chemisorptions to the central dangling bond were taken into account. As the CH_3 species chemisorbed in all of the simulations (i.e., the sticking probability was 1), the σ_c obtained was simply the area per one dangling bond site at the surface, namely 5.7 Å^2.

For the third surface [Fig. 1(c)] σ_c was even larger than for the surface with one dangling bond, (15.3 ± 1.7) Å^2. This is not a surprise, as there were no steric hindrances for the chemisorption. Any attractive interaction between the carbon atom in the CH_3 radical and the unsaturated carbon atom almost certainly resulted in chemisorption; one can consider this a kind of steering effect. Contrary to this, in the case where the chemisorption site had three neighboring methyl groups [cf. Fig. 1(d)], the cross section was dramatically smaller, $\sigma_c = (0.2 \pm 0.1)$ Å^2. Here the methyl groups shield the incoming radical from the dangling bond.

B. Classical simulations

Before we present the results of the classical simulations, we discuss one problem associated with them, namely the choice of the cutoff. Contrary to other parameters in the model, the carbon–carbon cutoff range is not optimized[33,42] and it is known that the model can be sensitive to modifications of this parameter.[43,44] To test this, we created two modified versions of the potential energy function with larger cutoff radii, $r_c = 2.25$ (Ref. 44) and 2.46 (Ref. 45) Å. Larger cutoffs than $r_c = 2.46$ Å cannot be used, since for $r_c > 2.46$ Å the equilibrium properties of C in the graphite and diamond phases start to change.

Several series of simulations were then run with the modified force models (cf. Fig. 3). The results show that the value of the interaction cutoff is significant for the sticking
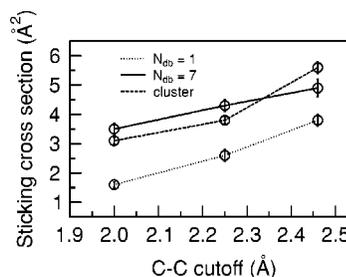
FIG. 3. Sticking cross sections obtained using the classical Brenner hydrocarbon potential for the cases with one dangling bond on the surface ($N_{db} = 1$), seven dangling bonds on the surface ($N_{db} = 7$), and one dangling bond on top of a cluster (cluster), consisting of four carbon atoms (three of these saturated). The methyl gas temperature was in all the cases 2100 K.

process in the classical model. For example, at a methyl gas temperature of 2100 K, the value of the sticking cross section on a surface with a single dangling bond varied from (1.6 ± 0.1) Å^2 (original cutoff of 2.0 Å) to (3.8 ± 0.2) Å^2 (cutoff of 2.46 Å). For a surface configuration with seven dangling bonds the effect was weaker, cross sections obtained with larger cutoff radii being only about 50% larger than for the original value. Since the value of 2.46 Å has been systematically optimized and provides sticking cross sections closest to the TB values, we use results obtained for this cutoff in the remainder of the article.

The results of the classical model were clearly different from those of the TB model. Chemisorptions were not as frequent as for the TB model for any of the surfaces, resulting in much smaller cross sections. Also, the cross sections obtained for surfaces with seven dangling bonds were roughly a factor of 2–3 larger than for the surface with only one dangling bond, remaining still smaller than the area per surface site. However, the largest cross sections were still observed for the case of the bare dangling bond site.

For examination of whether and how the sticking cross section of incoming radicals is affected by the number of neighboring methyl groups next to the dangling bond site at the surface, we used the classical force model and surfaces with one, two or three methyl groups next to the unsaturated carbon atom. The results are shown in Fig. 4. The cross section clearly increases with the decrease of the number of neighboring methyl groups, illustrating the dramatic effect of the local atomic neighborhood on the chemisorption process.
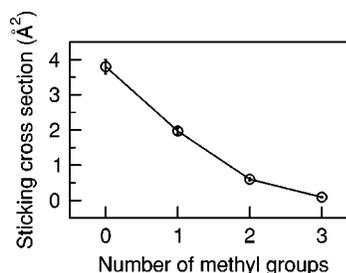
FIG. 4. Sticking cross sections obtained using the classical Brenner hydrocarbon potential and a surface with zero, one, two, and three methyl groups next to the unsaturated carbon atom. The methyl gas temperature in all the cases was 2100 K.

V. DISCUSSION

The cross sections obtained with the TB model were larger than the ones obtained with the empirical model in all the cases studied. While the original interaction range parametrization of the empirical model gave cross sections lower than the TB model by a factor of 2–7, the cross sections were observed to increase as the cutoff range was increased. We emphasize that the Brenner model was originally developed for the modeling of chemical vapor deposition of diamond.[33] However, our present comparison with TB shows that the probability for one of the most important growth reactions is probably too low. While the original reason for the optimization of the cutoff range were the structures obtained in carbon phase changes,[44] the chemical reactions between C:H networks and CH_3 radicals show now a significant dependence on the cutoff range. Even at the largest cutoff range, 2.46 Å, the sticking cross sections remained up to a factor of ~ 3 lower than for the TB model.

Our results show that there is a dramatic effect of the local atomic neighborhood of the dangling bond on the chemisorption probability. Depending on the surface configuration, the sticking cross sections were observed to vary by two orders of magnitude. Although the configuration of three methyl radicals surrounding an unsaturated carbon site is quite improbable, this study illustrates the importance of the hydrogen flux on the growth of the C:H network. Without the removal of the hydrogen atoms bound in the methyl groups, the probability of CH_3 adsorption remains low. Furthermore, the cross linking of the methyl groups cannot take place without hydrogen abstraction, as the typical C—H bond energy is higher than those of sp^2 and sp^3 C—C bonds.

Provided that the dangling bond coverage of the surface is low enough, each CH_3 impact near a dangling bond site can be described independently of the other dangling bond sites on the surface. The sticking probability of the CH_3 species is then simply the ratio of the sticking cross section and the total surface area multiplied with the number of dangling bond sites. However, if the dangling bond coverage is large, neighboring unsaturated carbon sites will affect the sticking cross section. This is seen in our modeling in the case of seven dangling bonds. For the TB model the cross section drops from 10.4 Å^2 of an isolated dangling bond site to 6 Å^2 for seven dangling bonds the latter is roughly the area per surface site, and corresponds to a sticking probability of one.

The values of sticking cross sections obtained in our simulations compare well with an experimentally determined cross section of 10–15 Å^2.[30] Since there are many types of surface sites, the experimental value is an average over all the cross sections. The sample used in the experiments was not diamond-like carbon but less dense, polymer like hydrogenated carbon. As the average number of neighboring carbon atoms in diamond is higher than in the polymer like films, where the H/C ratio is roughly one, it can be assumed that the shielding of the dangling bond sites was quite low. From the four cases studied in this work, the case of one dangling bond corresponds best to the case of polymer like C:H.

The internal motion (i.e., rotation and vibration) of the impinging radical was not observed to have significant effect on the sticking cross sections. The likely reason for this is that the chemisorption reaction of the CH_3 radical is much faster compared to the time scale of the internal motion of the radical.

Since von Keudell *et al.* obtained a different value, 10–15 Å^2,[30] for the sticking cross section at normal angle of incidence of the incoming methyl groups than for 45° angle of incidence, 5.9 Å^2,[29] the sticking cross section is probably angle dependent. This is a topic in our following simulation studies.

VI. CONCLUSIONS

In conclusion, using both tight binding and empirical force models, cross sections for CH_3 radical chemisorption on unsaturated carbon sites on various carbon surfaces were determined. Although the results for the two models were qualitatively similar, the TB simulations gave cross sections about a factor of 3 higher than the empirical potential with the optimized cutoff. This indicates that the Brenner potential has significant problems in the quantitative description of hydrocarbon reactions with carbon surfaces, one of the very situations it was originally designed to handle.

For the TB model, the cross sections ranged from 15.3 ± 1.7 Å^2 (for the case of completely bare dangling bond) to 0.2 ± 0.1 Å^2 (an unsaturated carbon site shielded by three neighboring methyl groups). Thus, the local atomic neighborhood of the dangling bond can lead to variation of the sticking cross section within two orders of magnitude. The cross sections observed for the bare dangling bond configurations are larger than the area per surface site. This is explained by the fact that a long-range attraction steers the radical to the dangling bond. This explains the surprisingly large sticking cross section of 10–15 Å^2 observed in experiments.

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