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

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Sticking cross sections for CH$_3$ radicals at different angles of incidence and different energies were calculated using molecular dynamics simulations, employing both quantum-mechanical and empirical force models. At 2100 K, the chemisorption of a CH$_3$ radical onto a dangling bond is seen to be highly dependent on the angle of incidence of the incoming radical, as the sticking cross section decreases from (10.4 ± 1.2) Å^2 to (1.4 ± 0.3) Å^2 when the angle of incidence of the methyl radical increases from $0°$ to $67.5°$. A simple geometrical model is presented to explain the angular dependence. In the sticking process of CH$_3$ radicals with higher kinetic energies (1, 5, and 10 eV), both a fully hydrogen terminated surface and a surface with one unsaturated carbon site were used. The sticking probability is observed to be enhanced with increasing radical energy. We also observed sticking onto the fully hydrogen terminated surface for all cases except for the case when the methyl radicals had energies corresponding to a temperature of 2100 K.

I. INTRODUCTION

The selection of plasma facing materials for present and next-generation fusion devices is still an open question. Diamond and materials with diamond-like structures are important in many technological applications because of their unique mechanical, chemical and optical properties [1,2]. They are especially important for future fusion devices [3–5] since carbon is a major candidate as a plasma-facing material. The plasma-facing component lifetime and the contamination of the plasma will be determined by the erosion mechanisms and their rates, but also by the transport and re-deposition of eroded material. Hydrocarbon species are released via physical and chemical sputtering when deuterium- and tritium ions and neutrals which have escaped from the fusion core plasma interact with carbon-based first walls. These radicals may later redeposit onto the divertor tiles but also in other regions of the vacuum chamber which are not in direct contact with the fusion plasma [6,7]. Due to the fact that tritium is bound in these hydrocarbon films, is highly radioactive and can not easily be recycled, the achievement of a good control over these deposited hydrocarbon films is of great importance. In experiments carried out at the ASDEX Upgrade [7], both soft polymer-like C:H films (H/C $\sim$ 1) and hard C:H films (H/C $\sim$ 0.4) were formed. Hence detailed knowledge about such film growth, especially about the fundamental erosion and redeposition processes of hydrocarbon species, is needed in order to successfully model and predict the performance of the next-step device.

The C:T film formation in fusion devices might be controlled by using a liner in the divertor pump duct [8] where neutral hydrocarbon radicals will be trapped or transformed before they can deposit in remote areas of the vacuum vessel. One of the most abundant sputtered radical species is the CH$_3$ radical [9,10]. It is also known to be an important growth species in chemical vapour deposition growth of carbon films [11,12]. Experimental investigations on surface processes between polymer-like C:H films and simultaneous methyl and atomic hydrogen beams, done by von Keudell *et al.* [13,14], have provided valuable information on the individual film growth mechanisms. Since the chemisorption of the impinging methyl radicals predominantly takes place on unsaturated carbon sites, the film growth can be characterized with a CH$_3$ sticking cross section to these sites. The sticking cross section can be thought of as the effective area to which the CH$_3$ radical always chemisorbs upon impact.

Using molecular dynamics (MD) simulations we have examined the sticking process of methyl radicals impinging onto a surface with one carbon dangling bond. The angle of incidence of the incoming radical was varied. By using both a fully hydrogen terminated surface and a surface with one unsaturated carbon site, we have also examined how the sticking probability is affected by incoming radicals at higher kinetic energies.

II. SIMULATION METHOD

Both tight-binding (TB) [15,16] and empirical [17] hydrocarbon force models have been employed in our simulations, where methyl radicals imping onto diamond (111) surfaces. The chemistry in C–H systems is well described in both of these models. The empirical Brenner potential [17], with a cutoff 2.46, is computationally less intensive which allows one to achieve more comprehensive

statistics in MD simulations, while still describing bond formation and breaking correctly. TB is based on a second order expansion of the Kohn-Sham total energy in density functional theory with respect to charge density fluctuations. This method gives a quantum mechanical representation.

As a chemisorption substrate in our simulations, we have used a diamond lattice with two layers of carbon atoms, a total of 120 atoms. Both (111) surfaces were hydrogen terminated and a carbon atom site was created by removing one hydrogen atom from the surface, see Fig. 1. In the study of CH_3 radicals impinging at normal angle of incidence and having larger energies, we used both a fully hydrogen terminated surface and a surface with one unsaturated carbon site. The surface temperature prior to the radical bombardment was 0 K in all our simulations. For a more detailed description, see Ref. [18].

A CH_3 radical was created above the diamond surface with a distance between the radical and surface larger than the effective interaction range in the model. The radical, having translational velocity, rotational and vibrational motion corresponding to a selected temperature, was directed at a certain angle of incidence to a randomly chosen point on the surface. According to a stratified Monte Carlo (MC) strategy, the impact points on the surface were chosen randomly inside circular segments with a radial width of $\Delta r = 0.1$ Å each and centered on the dangling bond site, see Fig. 2. This has been shown to give accurate results more efficiently than conventional MC (i.e., completely arbitrary impact points on the whole surface) [19,20]. The impact points were chosen on a distance of 0.6 Å from the surface, since test simulations revealed that with this distance the obtained sticking cross sections were the largest when the radical impinged towards the dangling bond and decreased with growing distance from the dangling bond.
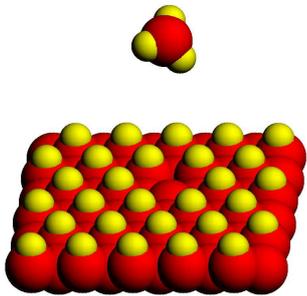

FIG. 1. Surface with one dangling bond used in the modelling. The CH_3 radical is seen above the surface.

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, the sticking cross section was obtained.
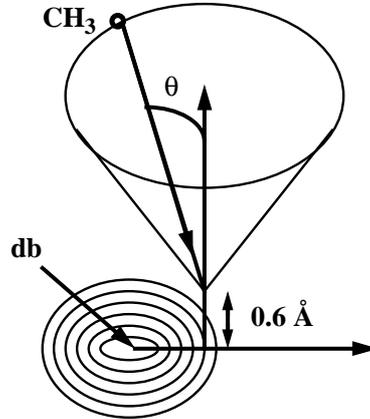

FIG. 2. Determination of the randomly chosen impact point for the CH_3 radical with angle of incidence θ. The impact point is chosen randomly inside a circular segment centered on the dangling bond site, with a radial width $\Delta r = 0.1$ Å.

Radicals which were bound to an unsaturated carbon atom by covalent bonds at the end of the simulation were considered chemisorbed. The simulations were followed for 500 fs (since tests with longer simulation times verified that 500 fs simulations were adequate to determine the chemisorbtion of an incoming radical), after which the final bonding configuration was examined.

III. RESULTS

A. Tight-binding simulations

In the simulations with varying angle of incidence of the incoming CH_3 radical, the most common reaction process for the radical was to 1) chemisorb onto the unsaturated carbon site, 2) form a volatile CH_4 molecule by capturing a surface hydrogen and drifting away from the surface and 3) form a bonding configuration, where the carbon atom in the incoming CH_3 radical bonded to two carbon atoms or one or two hydrogen atoms got stuck to one or two carbon atoms. The bonding configurations (3) were probably intermediate and metastable, but the time scale of the simulations did not allow us to determine the lifetime of these states. Since these 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 simulations or numerical modeling of experiments, special configurations like this will need to be taken into consideration in the analysis.

The sticking cross sections obtained varies from (10.4 ± 1.2) Å^2 to (1.4 ± 0.3) Å^2 for normal and 67.5° angle of incidence respectively, see Fig. 3. In these simulations the incoming methyl radical had an energy corresponding to 2100 K. The reason for this angular dependence can partly be explained by simple geometry, since the dangling bond is more exposed to methyl radicals at normal angle of incidence than to radicals at larger angle of incidence. The hydrogen atoms in the methyl radical, when impinging at a large angle of incidence, will react with the surface hydrogen more probably and form a volatile CH_4 molecule than for a radical at normal angle of incidence.
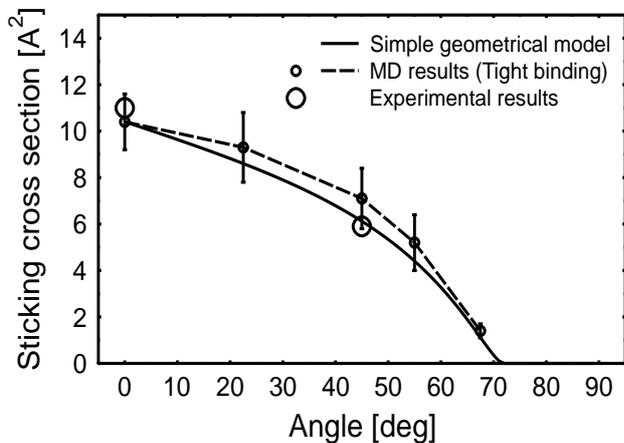

FIG. 3. Sticking cross sections obtained when employing the tight-binding model in the simulations for the case with one dangling bond at the surface and different angles of incidence of the incoming methyl radical. The methyl gas temperature was 2100 K in all cases. The results are compared with sticking cross sections obtained with the simple geometrical model, and with results obtained experimentally [13,14,21,22].

B. Classical simulations

The results of the classical model differ from those obtained with TB. The values obtained are a factor of 2-7 smaller depending on the angle. With the classical model we could analyse the sticking profiles in more detail since although the absolute values differ, better statistics could be achieved. These are plotted in Fig. 4.

For CH_3 radicals with higher energies, 1, 5, and 10 eV, we observed sticking even when we used the fully hydrogen terminated surface. The sticking probability is generally enhanced with higher energy. For radicals with

energies corresponding to 2100 K we observed no sticking when using the fully hydrogen terminated surface. Fig. 5 shows the sticking events obtained for a fully hydrogen terminated surface and methyl radicals with energies of 10 eV.
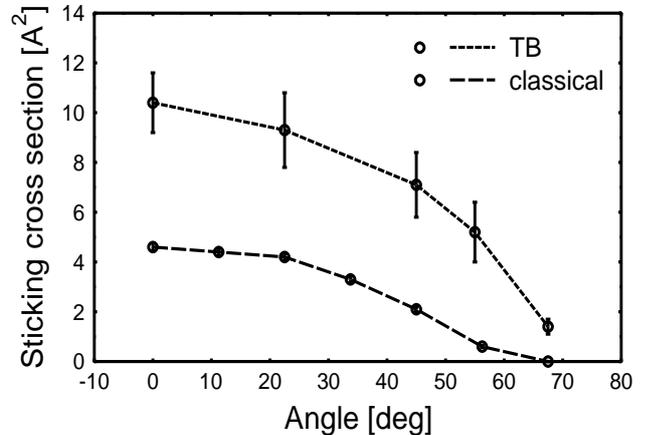

FIG. 4. Profiles of sticking probabilities obtained with the classical Brenner hydrocarbon potential for the case with one dangling bond at the surface and different angles of incidence for the incoming methyl radical. The methyl gas temperature was 2100 K in all cases.
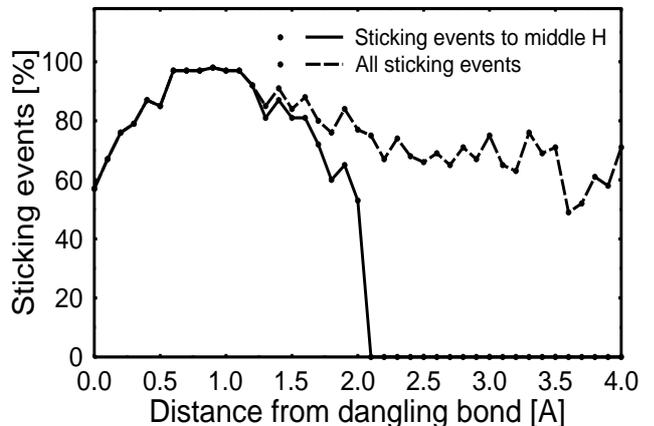

FIG. 5. Sticking events obtained with the classical Brenner hydrocarbon potential when using a fully hydrogen terminated surface and methyl radicals with energies of 10 eV. The line represents sticking events onto the middle hydrogen atom on the surface, while the dashed line represents all sticking events on the fully hydrogen terminated surface.

IV. DISCUSSION

Our results show that the angle of incidence of the incoming methyl radical has a dramatic effect on the chemisorption probability. Depending on the angle of

incidence, the sticking cross section was observed to decrease from (10.4 ± 1.2) Å^2 to (1.4 ± 0.3) Å^2 when the angle of incidence increased from $0°$ to $67.5°$. This angular dependence can be explained by a simple radially symmetric geometrical model, where the dangling bond can be approximated by a cylinder with surrounding hydrogen atoms at the edges. The incoming radical is assumed to move in a straight path, and the only change in the direction it can have takes place in the scattering off the surface. Radicals which reach the bottom of the cylinder are assumed to always stick. The area of the bottom of this cylinder, where the incoming radical is able to chemisorb onto the dangling bond, will decrease with increasing angle of incidence. But at oblique angles radicals scatter from the surface, shadowing part of the cylinder.
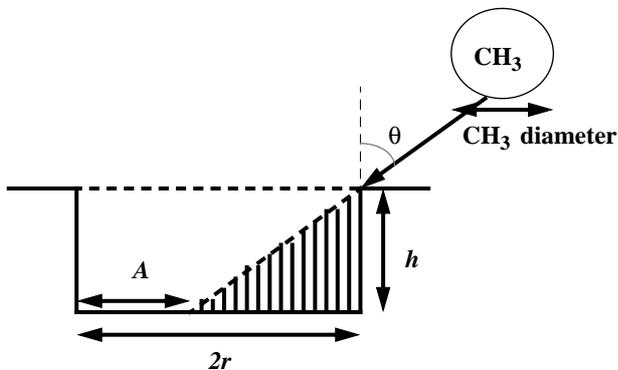

FIG. 6. Simple geometrical model for the sticking cross section at a certain angle θ of incidence of the CH$_3$ radical. The cross section is calculated as the total area A at the bottom of the cylinder, where the incoming radical is able to chemisorb onto the dangling bond. The dangling bond is approximated to be surrounded by a cylinder with radius r and height h.
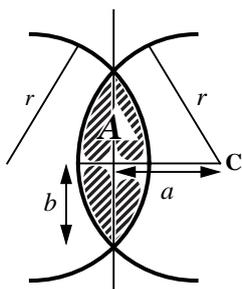

FIG. 7. Calculation of the total area A (shaded) at the bottom of the dangling bond cylinder, in which radicals are able to chemisorb onto the unsaturated carbon atom. This area consists of two segments of two circles. a is defined as the distance from the center of the cylinder, C to the point of intersection in the middle of the two circle segmets. b is defined as the distance from this intersection to the point of intersection between the two circles.

The sticking cross section $\sigma(\theta)$ is thus the total area, A,

that the radical can reach at the bottom of the dangling bond cylinder. This area, $A(r, h, \theta)$, will due to simple geometry become (see Fig 6 and 7),

$$A(r, h, \theta) = 2\nu r^2 - 2ab, \qquad (1)$$

where

$$\nu = \tan^{-1}\left(\frac{b}{a}\right), \qquad (2)$$

$$a = r - \frac{2r - h\tan(90 - \theta)}{2}, \qquad (3)$$

and

$$b = \sqrt{r^2 - a^2}. \qquad (4)$$

The height, h, and radius, r, of the dangling bond cylinder (see Fig. 6) are chosen as follows. We first calculate an effective covalent radius for the CH$_3$ radical by calculating the total volume of one C and three H atoms from their covalent radii (0.77 Å for C and 0.35 Å for H), and then calculating the radius of a sphere with this volume. [1] The parameter h is then chosen as the sum of the covalent radii of the CH$_3$ radical (≈ 0.85 Å) and a H atom (0.35 Å). This choice has a physically reasonable motivation: if the C atom in the methyl gets down to the same level as the H atoms surrounding the C radical, there is nothing which prevents it from sticking. Otherwise it is assumed to be reflected. d is simply a fit to the sticking value for $\theta = 0$. This gives $r = 1.82$ Å, and $h = 1.20$ Å, respectively.

This geometrical model gives excellent agreement with the sticking coefficients observed in our TB MD simulation, see Fig. 3. In particular, it gives a natural explanation to why the sticking coefficient drops to zero below $90°$ angle of incidence.

We note that there are several processes related to the sticking which our simple geometrical model does not account for. First, the angle of rotation of the radical with respect to the surface will be of importance for the sticking probability. The reason is that radicals with a rotation where the hydrogen atoms face the surface before the carbon atom, will react more easily with the surface, and form a CH$_4$ molecule. In the opposite case the methyl radical will more probably stick to the dangling bond. Second, some of the radicals that in the simple geometrical model would react with the dangling bond, can also react with the surface before this.

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[1] While the exact values of the covalent radii used are somewhat arbitrary, we note that the quality of the fit is still good within the uncertainties even for values of the radii differing by some tens of percents.

For example, they can react with a surface hydrogen, resulting in the formation of a CH_4 molecule. Third, radicals have also been observed to chemisorb onto the unsaturated carbon atom when impinging at a rather large distance from the dangling bond due to a steering effect [18], contributing to a larger sticking cross section. However, the fact that our radially symmetric model fits well the θ dependence shows that all these complications can be averaged out to first approximation.

The values of sticking cross sections obtained in our simulations compare well with experimentally determined values. In experiments by von Keudell *et al.* [13,14,21,22], sticking cross sections of $\sigma = 11$ Å^2 for normal angle of incidence, and 5.9 Å^2 for $45°$ angle of incidence were obtained from complex rate equations, employing various experimentally determined parameters. In these experiments the sample was not diamond-like carbon but polymer-like hydrogenated carbon, where the average number of neighboring carbon atoms is smaller and the shielding of the unsaturated carbon atom site can therefore be assumed as quite low. Both of the experimental values agree well with our results for normal and $45°$ angle of incidence, (10.4 $\pm$ 1.2) Å^2 and (7.1 $\pm$ 1.3) Å^2 respectively. Thus our findings strongly support the experimental evidence that the sticking process is angle dependent.

In the simulations with different kinetic energies of the incoming radical, we observed an increasing sticking cross section for increasing energy of the CH_3 radical. Even at a fully hydrogen terminated surface, 1 eV radicals got stuck to the surface. When radicals had the initial energy corresponding to a temperature of 2100 K, no sticking was observed. In Ref. [23] no sticking was observed for fully hydrogen terminated surfaces even when the incoming radical had energies of 1, 5, and 10 eV. The surface was diamond (100). One explanation for the increased sticking probability for radicals with higher energies is that the original molecule can break up, allowing the fragments to stick to the surface more readily. Hydrogens at the surface are more likely to be sputtered away when the radicals are impinging onto these with higher energies than with lower energies, which also makes it easier for the radicals to chemisorb to the surface. These results imply that even for different coordination of the surface one may have to use different values for the sticking cross section.

One single value for the sticking cross section is often used in the litterature [24,25]. Our results suggest that several different values should be taken into account due to different angle of incidence and energy of the incoming radical.

V. CONCLUSIONS

In the modelling of erosion and redeposition for future fusion devices, the angle with which particles are impinging, and reflected at, is of great importance. Methyl radical chemisorptions on an unsaturated carbon atom site on a diamond (111) surface were studied employing both tight-binding and empirical hydrocarbon force models in molecular dynamics simulations. Our results show that the CH_3 radical chemisorption is affected by the angle of incidence of the radical and that the sticking of CH_3 with higher energies (1, 5, and 10 eV) occurs also at a fully hydrogen terminated (111) surface. The dependence of the angle of incidence on the sticking cross section can be described by a simple geometrical model.

ACKNOWLEDGMENTS

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