

Atomistic simulations of plasma–wall interactions in fusion reactors

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Abstract

Atomistic computer simulations, especially molecular dynamics, but also kinetic Monte Carlo simulations and electronic structure calculations, have proven to be a valuable tool for studying radiation effects in fusion reactor materials. In this paper, I will first review a few cases where these methods have given additional insights into the interaction between a fusion plasma and the first wall of a reactor. Then I will, in the spirit of the workshop theme of ‘new directions in plasma–wall interactions’ discuss some possible future avenues of research.

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1. Introduction

Atomistic computer simulations are the primary theoretical tool for studying radiation effects [1]. Binary collision approximation (BCA) simulations of atomic collisions are still the most suitable method for simulating high-energy ion penetration depths and ballistic physical sputtering [2, 3]. Molecular dynamics (MD) simulations have proven invaluable in studying low-energy collisional effects where many-body interactions are important (such as collisional spikes), as well as the resulting melting and phase changes of a material [4–6]. Density-functional theory (DFT) calculations are useful in determining point defect energetics and migration properties [7]. The defect generation data from MD simulations and migration information from experiments or DFT can be fed into object kinetic Monte Carlo (KMC) codes which simulate the long-time scale motion of defects and impurities [8, 9]. Finally, in materials where dislocation activity dominates the long-term damage evolution, dislocation dynamics (DD) can be used to model the effect of radiation on the mechanical materials properties [10].

Although all of these methods have been used to examine the changes in materials properties induced by neutrons in fusion reactor structural materials, except for BCA simulations they have only recently started to be used in studies of plasma–wall interactions [11–16]. In this paper, I give an overview of the MD, KMC and DFT methods, briefly review some of our results in this field, and finally discuss

the limits of the methods and additional important questions which may be addressed with one of these approaches.

2. Overview of MD, KMC and DFT methods

MD simulations involve numerical solution of the Newton equations of motion to determine the time evolution of a system of particles interacting with each other, and possibly also some external force field [17, 18]. The simplest variety of MD, direct solution of the equations of motion, is ideally suited to study ion-induced radiation effects since this correctly accounts for the non-equilibrium ballistic motion of high-energy ions as well as the subsequent thermalization of the ion [19]. Efficient and realistic simulation of radiation effects often requires the basic MD methods [17] to be amended with a few solutions specific to radiation effects. These included inclusion of electronic stopping as a frictional force [20], realistic high-energy repulsive interactions [21], an adaptive time step [20], multiple time step schemes [22] and temperature scaling at the boundaries.

The reliability of MD simulations (if carried out otherwise correctly) depends on the choice of interaction model. Classical potentials or quantum mechanical tight-binding models, which still remain the only methods efficient enough for dynamical simulation of most radiation effects, are fitted to empirical and/or DFT data, and it is always questionable whether they describe properly effects not directly dependent on the original fitted data. MD simulations are usually most valuable in providing insight into qualitative

mechanisms which cannot be studied directly by experiments, but have sometimes proven to also be able to reproduce, e.g., sputtering yields [23], ion beam mixing [24], and ion implant depth profiles [25] correctly within the experimental uncertainty.

Even if the interaction model is realistic enough, direct comparison of MD data with experiments is often complicated by the limited timescale (typically of the order of nanoseconds) of MD simulations. Hence, most diffusion processes and long-term relaxation of molecular structures are not included in the MD, which at worst may completely hinder comparison of MD results with experiments. KMC simulations can sometimes solve this problem [26, 27]. They take as input the rates of relevant processes in a system, which typically are the defect migration rates and incoming ion flux, and simulate the time evolution of the objects. The algorithm selects the processes proportional to their rate, so no effort is wasted in time steps with no events occurring. Since only the objects of interest are simulated (e.g., the mobile defects but not the lattice atoms) this allows for simulation of large time and length scales.

DFT methods [28] are, despite some known shortcomings [29, 30], the primary tool for simulation of the electronic structure of bulk materials. They have been widely used to study defects in irradiated materials, and can nowadays sometimes also be used to do MD over a few picoseconds. Conventional DFT is a ground-state method, but time-dependent DFT (TDDFT) can also be used to simulate electronic excitations. Unfortunately, DFT methods are generally limited to simulations of a few hundred atoms, and time-dependent methods are still orders of magnitude slower than conventional DFT. Thus dynamic DFT-level simulation of plasma-wall effects would require major methodological breakthroughs.

3. Carbon erosion in fusion reactors

We initiated our work on plasma-wall interactions by studies of low-energy (1–30 eV) H, D and T ions or neutrals impinging on amorphous hydrogenated carbon. These ions are well known to produce sputtering of carbon from this class of materials, but until recently the mechanism was unclear [31, 32]. At high temperatures it is known that the H can enter the a-C:H and change the bonding structure, resulting in the formation of a weakly bound molecule which can migrate to the surface and desorb [33]. But this requires thermal activation and cannot explain the fact that desorption is observed between liquid nitrogen and room temperature with no temperature dependence [34].

Using MD simulations, we have described a new kind of chemical sputtering mechanism which can lead to instantaneous sputtering of C species from surfaces, but still is clearly distinct from physical sputtering [35–37]. The physical nature of the mechanism is easiest to understand by considering the model system of one H atom colliding with a C-C dimer. The most symmetric case possible is the one where the H comes in perpendicular to the chemical bond towards the middle of it, see figure 1. If the initial kinetic energy of the H atom is low, the H atom is reflected back, see figure 1(a). The impact also results in moving the dimer as a whole

Swift chemical sputtering bond breaking mechanism:

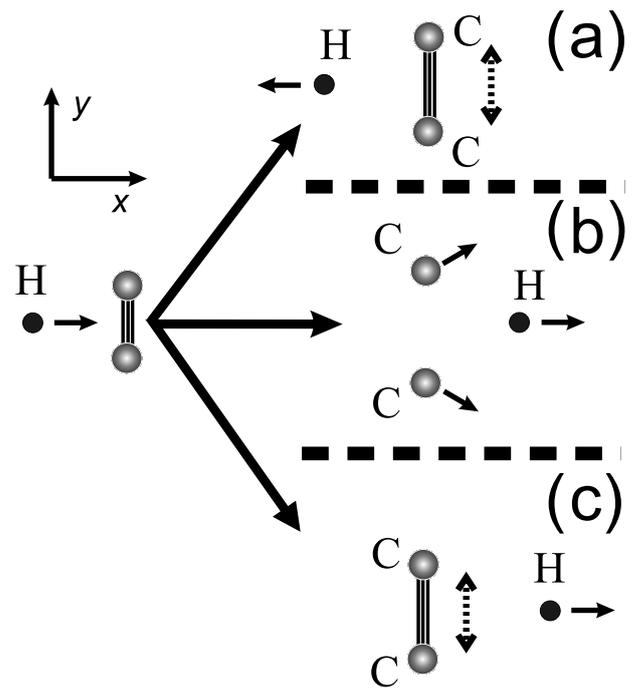


Figure 1. Schematic representation of the swift chemical bond breaking in a carbon dimer. From [35].

unit and in the excitation of the dimer vibrational degrees of freedom. If the atom is energetic enough, it will cause bond breaking in the dimer, case (b). The bond rupture is due to the repulsion between the carbon and hydrogen atoms, provided that they are close enough to each other. The kinetic energy of the H atom is spent for bringing the H atom close enough to the C atoms. The momentum the carbon atoms receive in the y -direction, p_y , is proportional to the effective force \bar{f}_y acting on the carbon atoms and the effective time $\bar{\tau}$ when the H atom is between the C atoms.

If the kinetic energy of the H ion, $E_{\text{kin}}[\text{H}]$, is low, then the H atom returns back without entering the region between the C atoms. Then \bar{f}_y and the y momentum are small and the bond is not broken. When the initial kinetic energy of the impinging particle is high enough for the H atom to stay for a long time in the region between the atoms (solid curve), the bond breaks. If we further increase the initial kinetic energy of the impinging particle, the bond breaking ceases, figure 1(c). The reason is that, although \bar{f}_y is large, the particle spends too little time in the region between the carbon atoms to cause any bond breaking ($\bar{\tau}$ is small). Thus there is an optimal energy for the bond breaking. The characteristic times of this process are very short, on the order of 10 fs.

To rule out dependence on the choice of potential, we have shown that the effect occurs as described above using three varieties of the Brenner potential, as well as in a tight-binding quantum mechanical framework which is completely independent of the classical simulations [35].

I emphasize that the swift chemical sputtering mechanism just described does not correspond exactly to any previously suggested sputtering mechanism. This is not the same as the definition of chemical sputtering given by Winters and

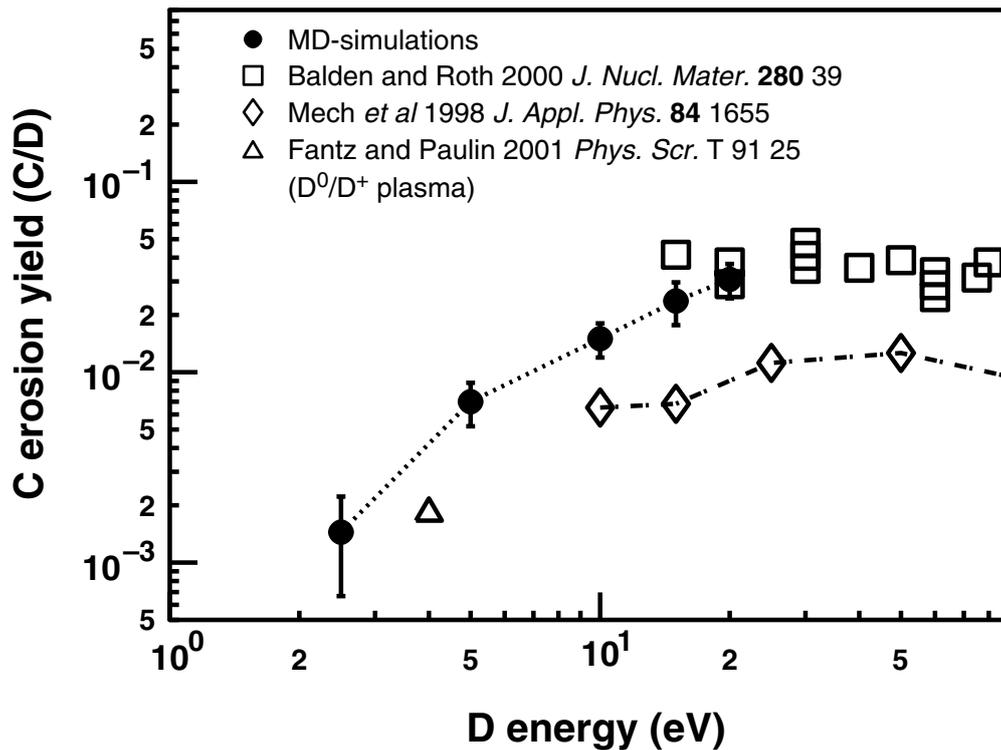


Figure 2. Sputtering yield of a-C:H compared to experiments. The large variation between the experiments is due to the fact that the sputtering is highly sensitive to the detailed surface structure. The data is from [41].

Coburn, since that states that a particle weakens a bond which then can desorb [38]. In our case, the bond breaks immediately. The mechanism is not physical sputtering either, since a simple numerical solution of the binary collision integral for the case just described, gives an energy transfer to C which is way too small to lead to breaking of the covalent bond. Finally, we have also observed that a He atom can produce sputtering with the same mechanism (although the yield is much lower than that for H). This proves that the mechanism does not require a covalent particle-C interaction, and thus that it cannot simply be considered a hyperthermal etching mechanism.

In addition to the study of the dimer model system, we have carried out extensive simulations of H, D and T bombardment of actual a-C:H material. The main results obtained can be summarized as follows. We have shown that the swift chemical sputtering mechanism leads to sputtering of small hydrocarbon molecules down to energies of about 2 eV, and that the sputtering yields obtained agree well with experiments [36], see figure 2. We have also observed that the sputtering yields are highly sensitive to the detailed surface structure [39], and that for high fluxes a H supersaturation can form on the surface, which can reduce the C sputtering by an order of magnitude [11]. These observations explain experimental results on the same systems. We have also examined the temperature dependence of the sputtering yield, offering a possible explanation to why the yield is observed to have a maximum at about 700–900 K [36] (although the Koppers mechanism is certainly also active at these high temperatures). Most recently, we have found that even if 10% of the bombarding particles are He, Ne or Ar, with the *same*

energy as the incoming H, the erosion yield does not change appreciably (more than ~10%) compared to the case of H bombardment only [40].

4. Modification of WC

The swift chemical sputtering mechanism cannot happen in appreciable amounts in metals, since it requires the presence of loosely bound atoms or molecules at the surface, that are only bound to the substrate by one or at most a few chemical bonds. Metallic systems energetically favour atomic configurations where each atom has numerous nearest neighbours, making swift chemical sputtering unlikely. But a natural question arises as to whether mixed systems with both metals and carbon can sputter chemically.

Using a recently developed potential model for the W-C-H system [42], we have examined the modification and erosion of WC by incoming D ions. Simulations of sputtering of pristine crystalline WC show only physical sputtering, with yields which agree well with experiments within the statistical uncertainties. Simulations of high-dose irradiation, where the change in the sample structure induced by each ion is taken into account, indicate that the WC amorphizes during low-temperature ion irradiation. This leads to formation of loosely bound carbon chains at the surface which can erode by chemical sputtering. On the other hand, during prolonged irradiation preferential sputtering (physical and chemical) will lead to a strong W enrichment at the surface [43], and then naturally the chemically enhanced sputtering of C will be much reduced or even completely cease. Thus the

possible chemical sputtering of WC is likely to be a transient effect important only in the beginning of the H irradiation or if the mixed material remains carbon-rich due to, e.g., co-deposition.

5. Hydrogen and helium migration in W

We have also recently examined the bubble formation and migration of H and He in W using a combination of DFT, classical MD and KMC [16, 44, 45]. We used the MD and DFT methods to examine the energetics of two H and He atoms near each other. These simulations showed that while it is energetically favourable for two He atoms to form a pair in W, with a binding energy of ~ 1 eV, two H atoms cannot form a bonded pair in W [16]. Moreover, once a He pair is formed, it can act as a seed for further bubble growth. This information, as well as experimental values for H and He migration in W, was then fed into a KMC model. The KMC model simulated H or He implanted in W for experimental initial penetration depths and ion fluxes. The results showed that He forms bubbles close to the surface, in agreement with experiments [46, 47]. Since hydrogen does not bind to other H atoms, the H bubble formation can only be initiated at lattice defects which allow for bubble growth. Hence the H is likely to migrate deep in the sample before bubble formation begins, in agreement with experiments [48–50]. Although some trap concentrations and binding energies have been identified in W, it is not clear which of these can act as seeds for bubble growth. Further study is clearly needed to resolve this issue.

6. Discussion and outlook

The results summarized above, as well as work on plasma-wall interactions carried out by other groups (see, e.g., [12–15]), has clearly shown that, also, atomistic simulation methods other than BCA can be valuable tools in the study of plasma-wall interactions. Nevertheless, it is important to select the problems to be studied with care and understand the limitations of the methods. MD simulations are not always reliable enough to give quantitatively reliable results even in the best-known systems [23], and in any case suffer from the timescale limitation. KMC simulations can handle long timescales, but rely on the appropriateness of the parameters fed into them, and can (at least in the conventional implementations) only handle slow processes which are not correlated with each other. For instance, it is not clear that a KMC method could describe long-term structural transformation, that may occur in loosely bound hydrocarbons at surfaces driven by van der Waals forces.

The basic mechanisms leading to hydrocarbon erosion from fusion reactor wall materials appear now to be fairly well understood, but the important question of whether the quantitative erosion yield can be reliably predicted theoretically remains unclear. The experimental yield values can differ by an order of magnitude (see, e.g., data in figure 2). The MD simulations show that this can be understood based on the detailed surface structure: surfaces with loosely bound hydrocarbon chains lead to high-carbon erosion rates. The

crucial question then is understanding when such chains form. This is a challenging question for MD simulations, since even if such chains form in the simulations, it is possible they would relax to more compact configurations during time scales beyond those treated by MD. Simulations including long-range van der Waals interactions [51] and possibly accelerated MD methods [52] might be able to shed light on this question.

Another open issue for the carbon erosion is the role of electronic excitations. Most of the incoming energetic particles are ions, which are neutralized on impact. This will lead to excited electronic states at the surface, which might affect the sputtering. This question is very demanding to study, but TDDFT methods might be suitable for examining the issue at least in simple model systems.

The ITER first wall will contain Be, C and W and mixtures of all of these elements. Hence it is important to understand not only pure element, but also mixed material formation and erosion. This is difficult both for MD and KMC methods, for the former because there are no interatomic potentials readily available for these materials, for the latter because the number of distinct migrating and recombination barriers increases superlinearly with the number of elements. Development of potentials for metal-carbon systems is complicated because most metal potentials are based on the effective medium theory [53, 54] while reactive carbon potentials are based on the Tersoff and Brenner approaches [55, 56]. However, these are similar in that both can be motivated from a second-order moment tight-binding approximation¹, and it is in fact possible to use the Tersoff functional form to develop metal potentials of comparable quality to the effective-medium theory ones [58]. Hence at least this approach can well be used to attempt to develop potentials for mixed materials in fusion reactors.

The retention of T in W is an important issue for pure W divertors. T could be retained in W in bubbles, or some fraction of it could migrate very deep into the divertor. Thus it is important to understand the trapping and detrapping reactions of T in W. Presently some experimental information on trapping energies is available [59, 60], but it is not clear what the microscopic structure of the traps is. This is something which could well be studied by DFT methods, possibly aided by classical MD simulations of H dynamics in the vicinity of traps to give insight of trapping pathways and capture radii.

In summary, in this paper, I have reviewed some recent atomistic simulation studies of plasma-wall interactions in fusion reactors, and discussed some significant additional open questions in the field which atomistic simulations might give insight into.

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¹ Brenner [57] shows that Tersoff and EAM formalisms are really the same in absence of angular terms.

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