

Modeling plasma surface interaction processes in plasma facing surfaces

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1 Introduction

Plasma surface interactions (PSI) are an inevitable part of laboratory plasmas created to study the various plasma phenomena. The high energy density in a plasma means that these interactions with surfaces usually change the surface characteristics. This property of the plasma to interact with surfaces is used by industry to modify surfaces to their needs (plasma nitriding, plasma assisted sputter deposition, etc). In fusion devices, plasmas have a very high energy density and PSI is a cause for concern. These plasmas erode or alter the plasma facing material (PFM) leading to a decreased lifetime or performance. The eroded impurity atoms can also get into the plasma and radiate energy thereby reducing the energy density of the plasma, making it unfavorable for satisfying the necessary criteria called the Lawson Criteria [1] for fusion to occur. Therefore it is important to understand the various PSI phenomena and the parameters they depend upon so as to optimize the experimental conditions for favorable results.

A plasma consists of electrons and ions kept apart by the high average energies they have. The electrons are highly mobile compared to the ions because of their smaller mass and they diffuse away faster than the ions. This results in a polarized electric field due to charge separation. When the electric potential due to charge separation becomes of the same order as the average energy of the electrons, the diffusing electrons are held back by the polarized electric field. The electron diffusion is therefore limited by the ion diffusion. This type of diffusion is called ambipolar diffusion [2]. Such a diffusion ensures that electrons are the first species to reach any surface that is exposed to the plasma. This results in the electric potential at the surface becoming lower than the plasma potential. Electrons are repelled from the surface and the positively charged ions are attracted to the surface. There is a finite region over which the potential drops from the plasma potential to the “floating potential” at the surface and this is called the sheath. Fig.1 shows a schematic of the sheath potential in front of a wall. This sheath depends on parameters like plasma density, plasma temperature, applied voltage to the plasma facing

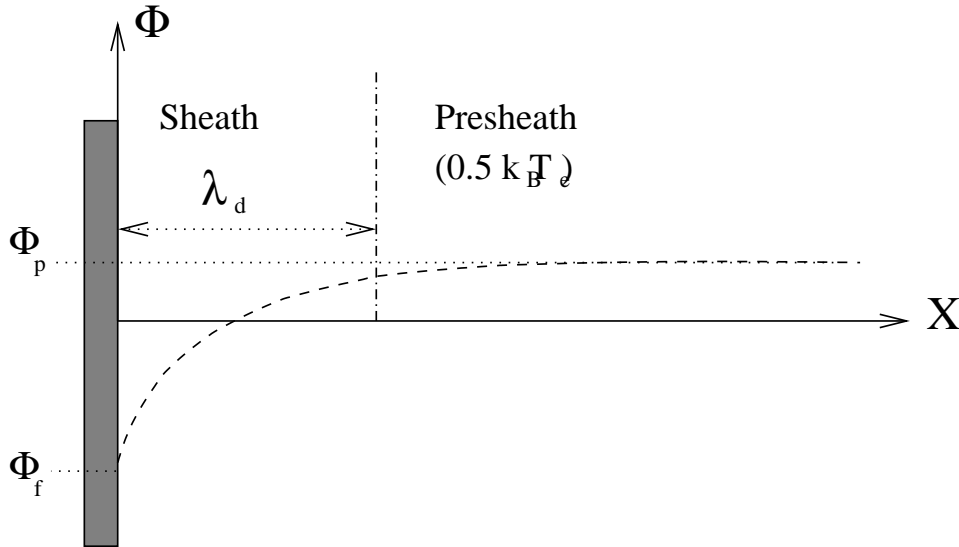


Fig. 1. Sheath potential in front of the plasma facing surface

surface, etc. In presence of a magnetic field near the plasma facing surface, the sheath structure is further complicated by the gyrating motion of electrons and ions. Details about sheath formation can be found in [3] and is beyond the scope of these notes. Here we concentrate only on the surface processes in PSI. In the next section a flavor of the underlying physical processes that occur in the plasma facing target is given. Most of the processes occur close to the surface (few Å to at most a few microns) and will be referred to as surface processes for convenience. In Section.3 the modeling paradigms and computational tools used to model these surface processes are discussed.

2 Surface processes in plasma surface interaction

In this section we discuss and classify the surface processes in PSI based on the underlying nature of the process. When a flux of ions which are accelerated in the sheath is incident on a surface, a wide variety of interactions can occur. These interactions can be classified based on the underlying physical mechanism (Fig. 2) into

- Momentum transfer processes,
- Diffusive processes, and
- Reactive-diffusive processes.

Classification of Plasma Surface Interactions

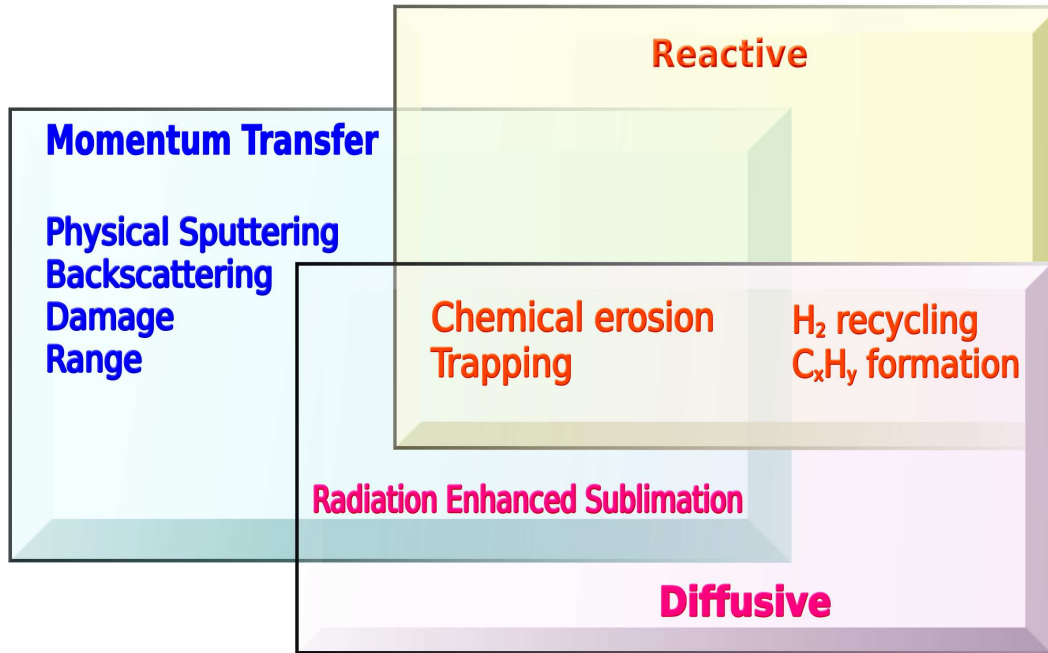


Fig. 2. Classification of plasma surface interactions based on the underlying physical mechanism

2.1 Momentum transfer processes

When an energetic ion is incident on a surface, it initially transfers its momentum to a target atom called the primary knock-on atom (PKA) [4] (Fig. 3). The incident atom can either lose momentum in subsequent collisions and finally come to rest in thermal equilibrium with the target (implantation) or get reflected from the target (backscattering). In fact the electrons in the target contribute to the slowing down by a mechanism known as electronic stopping power and the nuclei in the target contribute by a mechanism known as nuclear stopping. For a more detailed physics description of how an ion slows down in a target visit the URL <http://beam.helsinki.fi/~knordlun/mdh/rangetext.html> The PKA creates a collision cascade within the target and some of the cascading atoms can reach the surface of the target. If the atoms that reach the surface have more energy than the surface binding energy of the target material, they escape from the surface (physical sputtering). The cascading atoms also cause damage to the target and create interstitial target atoms.

The momentum transfer processes (physical sputtering and backscattering) depend on:

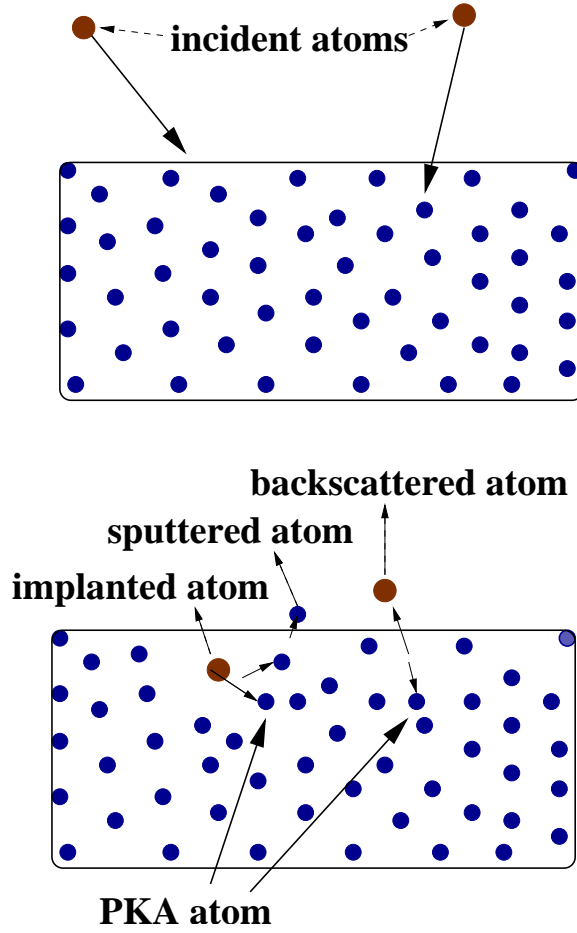


Fig. 3. Illustration of momentum transfer processes

- (1) Atomic masses of the projectile and target,
- (2) Energy of incidence of the projectile,
- (3) Angle of incidence of the projectile,
- (4) Surface roughness of the target.

2.2 Diffusive and reactive-diffusive processes

The momentum transfer processes discussed above create damage sites and interstitials within their range of penetration on the target. In the case of a graphite target, at high temperatures (> 1200 K) interstitial carbon atoms created by energetic incident ions/atoms diffuse along the damage sites or voids in the graphite, reach the graphite surface and get desorbed thermally (radiation enhanced sublimation – RES) [5] (Fig. 4). The incident atoms which have equilibrated with the surface diffuse within the target and can undergo chemical reactions with the target atoms to form new molecules. Some of these molecules diffuse to the target surface and can either be desorbed by incident atoms or be released thermally from the surface depending on the surface

temperature (chemical erosion) [6,7] Fig.4. In some cases an incoming energetic hydrogen atom or ion breaks a covalent C-C bond on the graphite surface by pushing apart the carbon atoms due to its short range repulsive potential. This can result in the ejection of either a carbon atom or a hydrocarbon and is called *swift chemical sputtering* [8] (Fig.5).

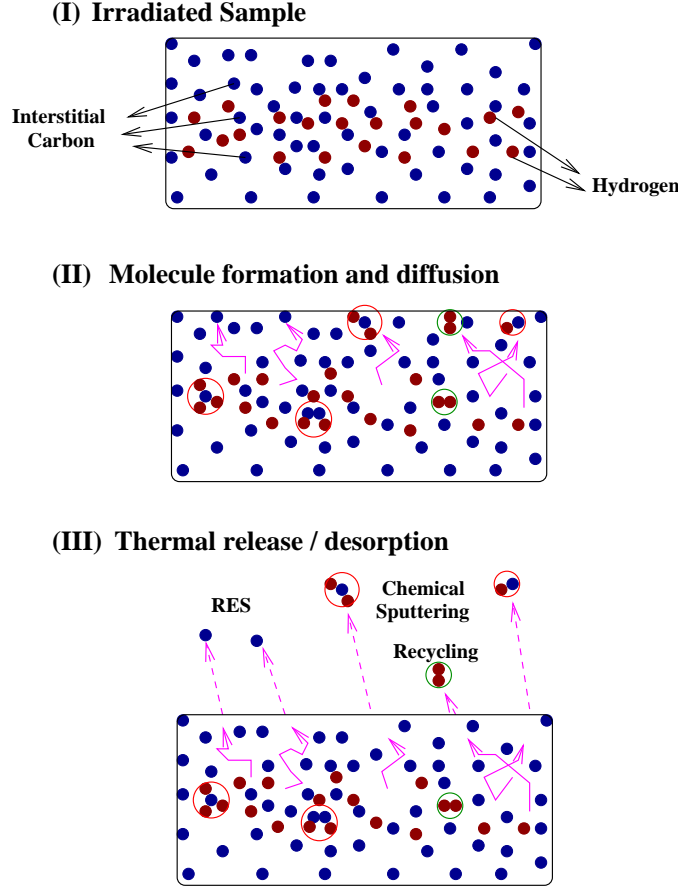


Fig. 4. Illustration of reactive-diffusive processes

The diffusive processes (RES) and the reactive diffusive process (chemical erosion) depend on:

- (1) The projectile mass,
- (2) The energy of the incident particle,
- (3) The target temperature,
- (4) Incident flux of particles.

All the above erosion processes (physical sputtering, chemical erosion and RES) are quantified in terms of the ratio of the flux of target atoms leaving the surface to the flux of incident atoms (yield). Backscattering is quantified by the number backscattering coefficient, R_N , defined as the ratio of reflected particle flux to incident particle flux, and the energy backscattering coefficient

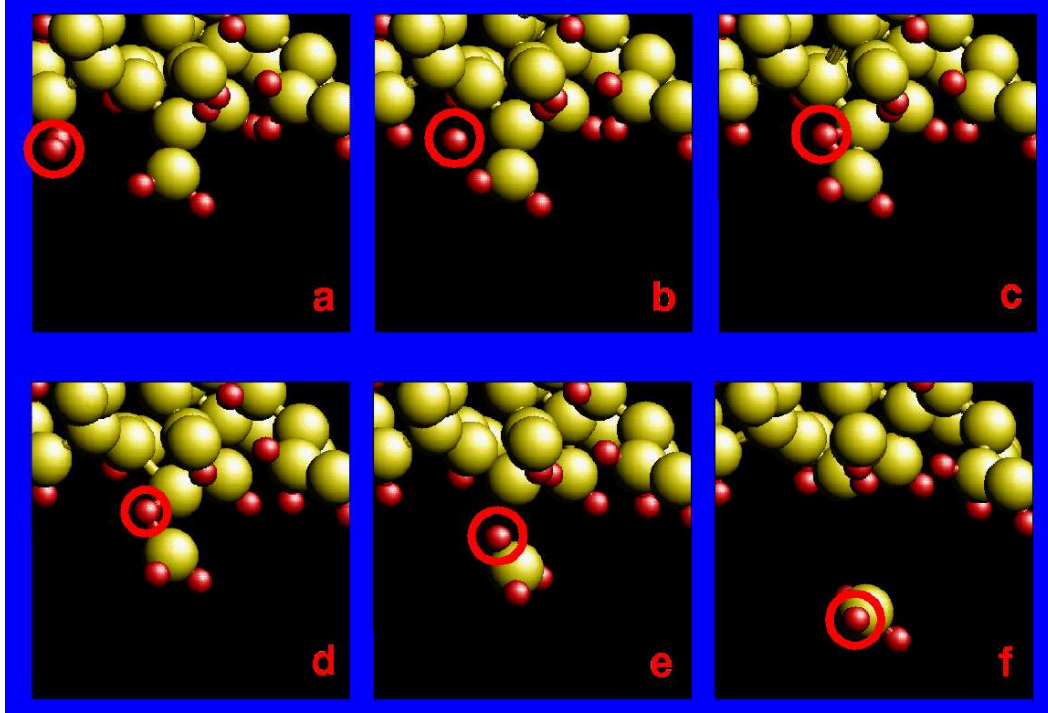


Fig. 5. Illustration of Swift-chemical-sputtering processes. Note how the energetic hydrogen atom (encircled) breaks the C-C bond by which a hydrocarbon molecule is bounded on the hydrogenated graphite surface (Thanks to Emppu Salonen, Institute of Physics, Helsinki, Finland, for this figure)

R_E , defined as the ratio of reflected energy flux to the incident energy flux. The energy deposited by the plasma on the surface determines the surface temperature which is an important parameter in determining the diffusion of various species and also molecular formation on the surface. If a high energy flux is incident on a surface, the surface temperature increases and this can cause thermal evaporation of the surface atoms.

2.3 Additional processes

In addition to the above surface processes there exists

- Arcing [9], wherein the electric field between the plasma and the surface becomes so high that field emission of the electrons occurs and an arc is ignited which creates a melt layer on the surface (in case of metals) or craters (on graphite which sublimates).
- Film or cluster growth on surfaces, where atoms and molecules get deposited on a target and agglomerate and grow [10].
- Blistering [11], wherein the implanted gas atoms in a target collect together at defects inside the material. When there is a continuous heat flux on the

material the gas can become hot and expand causing blisters on the material surface.

- Flaking [12], wherein the surface changes cause microscopic parts of the surface to break off (flake).
- Secondary electron emission [13], due to ion and electron impact.

These effects are not addressed by the above classification and are beyond the scope of these notes.

3 Modeling surface processes in plasma surface interactions

Now that we understand the underlying nature of the surface processes in PSI, modeling paradigms and computational physics methods to study these processes are introduced in this Section.

3.1 Modeling paradigms

There exist three types of approaches to study these processes (and this is probably true for most other processes; note that we are talking here only about modeling paradigms). They are:

- (1) Make simple analytical models of various processes that contribute to the processes or make semi-empirical or empirical fits to experimental data when simple analytical models are not available. An example of this approach is [14] wherein simple models for the sheath, heat diffusion in the target and semi-empirical formulae for the surface processes have all been coupled together. See <http://psic.sourceforge.net> to download the computer programs that implement the above coupled model.
- (2) The above approach is not suitable to understand the underlying surface process since it uses semi-empirical formulae. For example the semi-empirical formulae for chemical erosion of graphite has a flux dependent term in it. However it does not give an insight as to why a flux dependence is observed at all. For gaining such an insight, a specific computational tool like molecular dynamics (MD) [15,16] or Monte-Carlo (MC) (as used in [16,17]) must be used which simulates the nature of the problem. Examples where this has been done are: [8] to understand swift chemical sputtering; [17] to understand momentum transfer processes.
- (3) The reaction-diffusion problems usually occur over much larger lengths compared to the examples given above. Atomic interactions at the microscopic scales affect mesoscopic and macroscopic transport [18-20]. A

computation model at the atomistic scales for the whole macroscopic transport is computationally prohibitive. In such cases multi-scale models are used. In a multi-scale model a computational tool like MD will be used to parametrize the microscopic interactions. These parameters will be used as inputs to model transport at higher scales using MC methods [21–24].

See <http://www.ipp.mpg.de/~mow/PhDThesis> for a multi-scale model to study atomic diffusion of hydrogen in porous graphite.

3.2 Computational tools for modeling PSI

3.2.1 Monte-Carlo simulations

Monte-Carlo simulations use pseudo random numbers to carry out a large number (say N) of possible events. After the events are carried out the data can be analyzed to make definite statements about the statistical behavior of the system. For a detailed introduction to Monte-Carlo Simulations and then some ... check out: <http://www.acclab.helsinki.fi/~knordlun/mc/> Lecture 4 from the above link details various methods to generate pseudo random numbers which are essential for any Monte Carlo Simulation. The GNU Scientific Library [<http://www.gnu.org/software/gsl/>] has a host of pseudo random number generators and pseudo-random distributions.

An example to illustrate a Monte-Carlo method:

Example: Determining area of an irregular pond

In order to determine the area of an irregular pond you can stand somewhere near the pond (within throwing distance) and throw a large number (say N) of stones with equal probability of falling in a rectangle of known length (say L) and breadth (say B) encompassing the pond. Count the number of splashes (say N_s). Then the area of the irregular pool will be given by $\frac{N_s \times L \times B}{N}$.

MC methods for momentum-transfer processes

MC methods can be used also in simulating the momentum transfer processes (see Chapter.7 of [17] for a detailed description of this). It describes the MC modeling of a incident projectile as a series of binary collisions, called the binary collision approximation (BCA). In the BCA it is assumed that the other nearby target atoms do not contribute to the particle trajectory (which may be true if the target is a gas, but is only partially valid for solid and liquid targets). The physics involved in BCA is elementary two body collision theory (see Chapter.2 of [17] for this) implementing conservation of energy and momentum. The codes **TRIM-TRIDYN** based on the BCA approximation

has been very successful in describing momentum transfer processes in PSI down to incident energies of a few tens of eV. The main random processes simulated using MC in the BCA codes are:

- distance between successive collisions,
- the impact parameter, and
- the azimuthal scattering angle.

MC methods for reactive–diffusive processes

Kinetic Monte–Carlo (KMC)

KMC can be used to simulate diffusion of thermalised atoms in a target. A thermalised atom in a target can be bound to internal surfaces (grain boundaries) in the target either by physical adsorption or by chemical bond. All the thermalised atoms can be therefore considered to be trapped in potential wells of depth E_m within the target. These atoms oscillate in the potential wells with a frequency (say ω_o) roughly equal to the target phonon frequency. The probability of the trapped atoms escaping the potential well is given by $e^{\frac{-E_m}{k_B T}}$. A description of the jump process is given in Fig.6. Once they escape

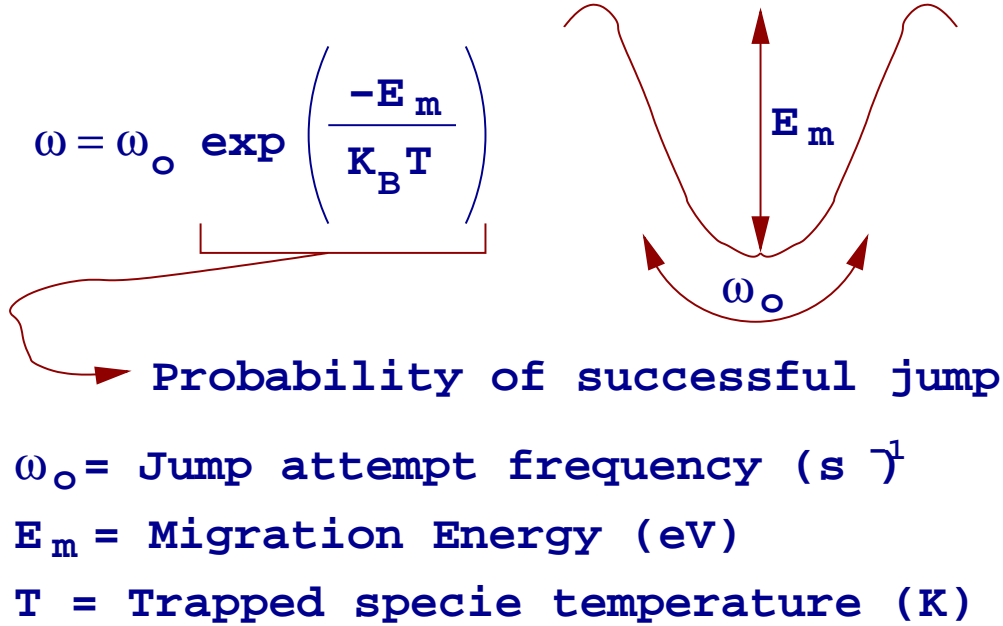


Fig. 6. Illustration of the jump process in a KMC simulation

from the trap they move in the solid till the get trapped again. Thus they diffuse in the solid by several such trapping–detrapping events.

Fichthorn and Weinberg [25] established that Monte–Carlo simulations can be used to simulate the dynamics of such a diffusive process with the time between

two successive jumps given by $\Delta t = -\frac{\ln(U)}{\sum_i n_i r_i}$ where, n_i is the number of atoms capable of undergoing a transition (in our case either physical desorption or breaking of a chemical bond) labeled i , U is a uniform random number between zero and one, and r_i the transition rate given by $\omega_{i_o} e^{\frac{E_m}{k_B T}}$. Therefore thermal atomic/molecular transport can be simulated using an algorithm called the Boris-Kalos-Lebowitz (BKL) algorithm:

- (1) *Initialize the system at time $t = 0$. i.e set up distributions of the trapped atoms at $t = 0$.*
- (2) *Loop depending on time to be simulated or number of KMC steps to be simulated.*
- (3) *Form a list of all rates r_j in the system. i.e calculate r_{desorb} and $r_{\text{bondbreak}}$.*
- (4) *Calculate the cumulative function $CR = \sum_i R_i = \sum_i n_i r_i$ i is the total number of possible transitions of the system*
- (5) *Get a uniform random number $U \in [0, 1]$.*
- (6) *Find the event to carry out, i by finding the i for which*

$$R_{i-1} < U \times CR < R_i$$

- (7) *Carry out event i .*
- (8) *Check proximity of other atoms and carry out recombination reaction.*
- (9) *Get a new uniform random number $U \in [0, 1]$*
- (10) *Update the time with*

$$t = t + \Delta t$$

where

$$\Delta t = -\frac{\ln(U)}{R}$$

and update the KMC step count.

- (11) *Go to step (2) if end criterion of loop is not reached.*
- (12) *Postprocess for quantities of interest.*

Then the average mean square deviation of the particles gives us the diffusion coefficient of the thermalised atoms in the target. Reactions are implemented in such an ansatz by letting particles coming closer than a certain distance to each other to recombine to form molecules and then diffusing the molecules also as described above.

Implementing the above algorithm helps us to obtain diffusion coefficients and reaction rates of the diffusing and recombining particles [21,23]. *Finding the diffusion co-efficient using KMC and scaling up to use the values in a Monte Carlo Diffusion (MCD) method will be part of the tutorial session.*

Monte Carlo Diffusion The N body, diffusion equation is given by

$$\frac{\partial n}{\partial t} = \nabla(D\nabla n) + S \quad (1)$$

where n is the density, D is the diffusion coefficient of the particles, t is the time variable, S is the sources or sinks in the system during the diffusion, and ∇ stands for the gradient in 3 dimensions. n is determined by the distribution of the N atoms in the simulation volume. The diffusion can be represented as a random walk of the N particles with the jump size given by

$$\Delta r = \sqrt{2 d D \Delta t} \zeta \quad (2)$$

where Δt is the time step, d is the dimensionality of the system and ζ is sampled from a random number distribution satisfying $\langle \zeta \rangle = 0$ and $\langle \zeta^2 \rangle = 1$. This representation is valid for $\frac{D}{\Delta t} \gg \sqrt{2 D \Delta t}$. Interactions can be easily included in the simulation by increasing or decreasing (depending on whether the interactions are sources or sinks) the number of particles diffusing at each time step by $e^{-\frac{\Delta t}{\tau}}$ where τ is the characteristic time for the interaction to occur.

Note that Eqn.2 at first glance looks like a rewritten form of Eqn.3.

$$D = \lim_{t \rightarrow \infty} \frac{1}{2dt} [r(t) - r(o)]^2 \quad (3)$$

where $r(t)$ is the position of the atom at time t . This is proportional to the slope of the mean square displacement of a single particle undergoing Brownian motion at the long time limit and is also known as the "tracer diffusion coefficient" [26]. In fact it is derived using the differential calculus of stochastic processes called *Itô calculus* [27]. Such a treatment is necessary because the position variable $r(t)$ in Eqn.3 is obtained by a stochastic process (random walk).

The MCD algorithm to simulate diffusion:

- (1) *Initialize the system at time $t = 0$. i.e set up X , Y and Z positions (rx, ry, rz) of the trapped atoms at $t = 0$, Δt , etc.*
- (2) *Loop depending on time to be simulated or number of MCD steps to be simulated.*
- (3) *Loop over various species 'k' (if you have multiple species).*
- (4) *Loop over particles 'i'.*
- (5) *Get a uniform random number ζ from a gaussian distribution U_{Gauss} with a mean value = 0 and a variance = 1.*
- (6) *$rx(i) = rx(i) + \zeta$.*

- (7) Get a uniform random number ζ from a gaussian distribution U_{Gauss} with a mean value = 0 and a variance = 1.
- (8) $ry(i) = ry(i) + \zeta$.
- (9) Get a uniform random number ζ from a gaussian distribution U_{Gauss} with a mean value = 0 and a variance = 1.
- (10) $rz(i) = rz(i) + \zeta$.
- (11) Update the time with

$$t = t + \Delta t$$

- (12) Check for end of particle, species and time loop and either go to step (4), step(3) or step(2) respectively.
- (13) Postprocess for parameters of interest.

Exercise: How do you simulate reactions in the above algorithm?

3.2.2 Molecular Dynamics Simulations

These brief notes try to give an idea of molecular dynamics (MD) simulations. Links to tutorials and books are presented throughout the text as references for further in-depth reading.

Why molecular dynamics?

From a computational physics point of view, the name “Molecular” in MD is a misnomer, because the techniques used are general and applicable to any N body interaction problem. However the name is appropriate from a point of view of a person who is interested to study the modification of surfaces due to plasma-surface-interactions (PSI). Using MD simulations one can study the changes in surface composition (including chemical reactions given the right interaction potentials), structure, erosion, film growth and various physical properties of the modified surface. MD can also be used to obtain various macroscopic properties and transport properties like thermal conductivity, viscosity, diffusion coefficient, etc. For an illustrative example of using MD to study PSI, see Fig.5.

Brief introduction to molecular dynamics simulations

The most intuitive method to study microscopically the motion of atoms and

their interactions amongst themselves is to solve the N body force equation,

$$m_i \ddot{\vec{r}}_i = \sum_{i \neq j, j=1}^N -\nabla \Phi_{ij} \quad (4)$$

where \vec{r} is the position vector of a particle denoted by i , m_i is the mass of the i^{th} atom and Φ_{ij} is the interatomic potential between the i^{th} atom and the j^{th} atom. Molecular dynamics (MD) does exactly this using a computer, since even for very small N, or for complicated forms of Φ_{ij} , the above equation is not analytically solvable.

Solving the above equations on a computer has the following limitations:

- The inherent limitation of the time step being around a femtosecond to simulate materials, so as to cater to numerical stability.
- The number of atoms simulated is limited to between 100 and $\sim 10^9$, depending on the type of potential used and the speed of computers.

Limitation in the time step

The limitation of the time step to a femtosecond can be understood as follows: Numerical schemes to solve Eqn.4 use a Taylor expansion

$$r(t + \Delta t) = r(t) + \dot{r}\Delta t + \frac{\ddot{r}}{2}(\Delta t)^2 + \dots \quad (5)$$

Different schemes truncate at different orders of the time step Δt which determines the accuracy of the position calculation and also the time step to be used. In brief, for numerical stability it is required that the change in potential with a change in position of the coordinate of a particle in time Δt must not be large (note that the second term of the Taylor expansion in Eqn.5 is equal to $-\nabla\Phi$). A simple rule of thumb frequently used is that the particle can move at most $(1/20)^{th}$ the distance between two neighboring atoms ([28] lecture 2). Typical interatomic distances in a graphene plane is $\sim 1.4 \text{ \AA}$ and the typical velocity of an interstitial hydrogen atom which has equilibrated with the graphene plane at say 900 K is $\sim 0.047 \text{ \AA/femtosecond}$. Therefore the time step has to be 1.5 femtoseconds in this case and one would have to loop over $\sim 10^{15}$ iterations to simulate one second!!

Limitation in the number of atoms simulated

The second limitation depends on the choice of the interatomic potential, Φ . Quantum mechanical approximations like Hartree–Fock (HF) methods, density functional theory (DFT) [29,30], tight binding (TB) [31]) can be used to calculate Φ at each step. However this limits the number of atoms that can be simulated. On the other hand, analytical potentials can handle much larger

numbers of atoms. There exist many two body potentials which can be used to simulate noble gases and other spherically symmetric structures [32,33]. For structures which are not spherically symmetric, special care has to be taken to incorporate the symmetry of the solid being modeled (eg. the three body Stillinger-Weber potential [34]). There also exist standard potentials for special classes of systems like the embedded atom method (EAM) for metals [35]. Recently, analytical reactive bond order potentials (REBO) have become very attractive for simulating covalently bonded [36]. For a discussion on interatomic potentials from quantum to empirical to REBO see ([28] lectures 7 to 11), and for a discussion on the development of REBO see [36]. Table.1 (reproduced with permission of K. Nordlund), shows a rough estimate of the maximum number of atoms, N_{max} , that can be simulated in a week or so, on a single processor machine (in 2002 I guess).

Table 1

Rough estimate of the number of atoms that can be simulated in MD for different methods of evaluation of interatomic forces

Potential Model	Type	Scaling	N_{max}
HF	Quantum mechanical	$O(N^{4-8})/O(N)$	50
DFT	Quantum mechanical	$O(N^3)/O(N)$	200
TB	Quantum mechanical	$O(N^3)/O(N)$	1000
	(often semi-empirical)		10000
Many body and pair	classical, semi-empirical	$O(N)$	10^7

The MD algorithm

Now that we know why we want to do MD (insight into PSI and material properties) and what equations we are solving (N body force equation) and the limitations of the MD simulation technique, we get on to the algorithm used. The pseudocode for a typical MD main program looks as follows:

```

01 ReadInputs ();
02 PrintInputs ();
03 InitParams ();
04 while (TimeNow <= MaxT)
05 {
06     TimeNow = TimeNow + DeltaT;
07     ComputeForces ();
08     TakeTimeStep ();

```

```

09      ApplyBC ();
10      EvalProps ();
11  }
12  PostProcess ();

```

The line numbers are printed on the first two columns to aid explanation. Line number 01 contains the function which reads in inputs like number of atoms, maximum time of simulation ($MaxT$), temperature of the system of atoms, etc. Line 02 just prints out the input read in for checking/logging the run. Line 03 initializes various parameters like positions of the atoms, their velocities, initializations for statistical post-processing of macroscopic parameters, etc. Line 04 – 11 loops over in time steps of $DeltaT$ till the maximum time to be simulated $MaxT$ is reached. Line 07 computes the forces on each of the atoms due to all other atoms. Line 08 computes the new positions and velocities from the computed forces using numerical methods ([16] pages 69-84). Line 09 applies the boundary conditions (periodic, slab, etc depending on the problem as described below in the next sub-section). Line 10 evaluates various properties of the system like temperature, pressure, kinetic energy, potential energy, etc so as to check energy conservation, etc (this is again described briefly in the next subsection). Finally at the end of the simulation, line 12 deals with post-processing of the results (described briefly again in the next subsection).

Other important aspects of a MD simulation

Other aspects of a MD simulation involve:

- Speeding up techniques,
- Boundary conditions depending on the problem,
- Fixing the macroscopic parameters of the system of particles like temperature, pressure and volume,
- Post-processing to check the consistency of the simulation and to analyze the results.

These are basic to MD simulations and good introductions to all these aspects can be found in [15,16,28,37].

Speeding up techniques and boundary conditions

Since the computation time of a MD simulation scales with the number of atoms in the simulation, one would want to use the minimum number of atoms as is possible without compromising on the accuracy of the results. To this end truncation of potentials, creating neighbor lists and judicious use of boundary conditions is important. When the interatomic potential falls off rapidly with distance, short range interactions dominate the simulation. The contribution

of atoms beyond a critical distance r_c becomes small and this error can be evaluated and corrected. This kind of simple truncation of the potential where the potential beyond r_c is neglected can lead to infinite gradients in Φ at $r = r_c$ which leads to a numerically unstable situation as discussed above. Therefore the potential is truncated and shifted such that it becomes zero at $r = r_c$. In this case the potential energy and pressure on a system with a truncated and shifted Φ changes and corrections must be evaluated and applied. To further save computation time a list of atoms, called the neighbor list, within r_c is maintained. This list is updated with a frequency depending on the rate at which atoms may move into or out of the neighborhood.

In order to simulate homogeneous bulk systems, periodic boundary conditions (PBCs) are used. This is illustrated in Fig.7 for a two dimensional system. Box **A** having size L_x and L_y in the X and Y directions is replicated at its 4

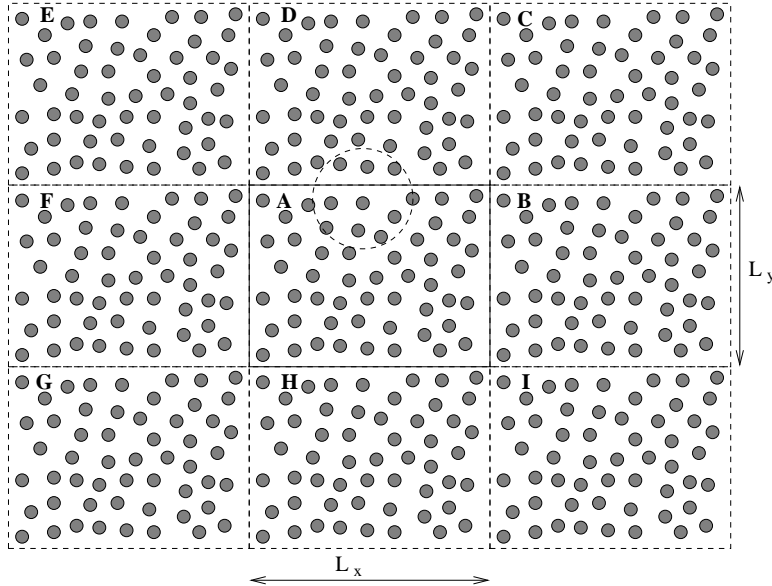


Fig. 7. Illustration of periodic boundary conditions (PBCs) in a MD simulation

edges and 4 corners to form boxes labeled **B, C, D, E, F, G, H, I**. The force calculation for atoms within a distance r_c of these corners or edges (note the dashed circle on the top edge of **A**) involves those atoms that lie at the bottom edge of box **A** which due to PBCs also lie in box **D**. Note that such an ansatz is valid only when evaluating physical quantities with local correlations. Only fluctuations that have a wavelength not greater than the single box size can be simulated. Care must also be taken to avoid spurious correlations that can creep in due to assumed periodicity of the system and care must be taken that $r_c < L_{x,y}/2$.

Other boundary conditions that can be used are "free" or "open" boundary

conditions which can be used when simulating a small collection of atoms or a long molecule which is unbounded. In this kind of boundary condition, the force calculation is carried out over existing atoms within r_c without any replication of boxes. Such boundary conditions can also be used to simulate surfaces where no replication is carried out along the direction normal to the surface, (say Z , with the surface lying at $Z = 0$). PBCs are implemented along the plane (say $X - Y$) in which the surface extends. At $-L_z$, where L_z is the dimension of the system along Z , the bottommost atoms can be held fixed with atoms lying within r_c of these atoms assigned a temperature equal to the bulk temperature (assigning a temperature is discussed under the topic **fixing macroscopic parameters** below). Note that some potentials fitted for modeling bulk phenomena may not be suitable for modeling surfaces correctly. Furthermore in the special case of simulating interactions of fast particles with a surface, special considerations have to be made for the time step, and boundary conditions called "slab-boundary-conditions" are applied. In this case, the atoms lying at the faces bounding the system in the X and Y directions are held fixed and atoms lying within a distance r_c from these faces are assigned a temperature equal to the bulk temperature. The system size and impact position of the fast particle must be chosen such that the collision cascade does not extend to the temperature controlled regions.

Fixing macroscopic parameters

Statistical mechanics provides a link between the macroscopic properties of matter (like temperature, pressure, etc.) and the microscopic properties (like positions, velocities, individual kinetic and potential energies) of atoms and molecules that constitute it. These macroscopic properties reflect the time average behavior of the atoms at equilibrium (i.e in one of the many possible degenerate minimum energy states accessible to the system).

Before doing the MD simulation one is faced with the task of initializing the atomic positions and velocities. In the case of crystalline solids the starting positions will be defined by the crystal symmetry and positions of atoms within the unit cell of the crystal. The unit cell is then repeated to fill up the desired dimensions of the system. Realistic atomic displacements from crystal lattice sites can also be derived using the Debye model [28] (Lecture 2, page 12). For amorphous solids the particles can be randomly distributed within the desired dimensions making sure that there exists a minimum distance between the atoms so that strong local forces do not exist in the system.

The initial velocities are set by assuming a Maxwell-Boltzmann distribution for velocities along the three dimensions. This is done by using Gaussian distributed random numbers multiplied by a mean square velocity given by

$\sqrt{2k_B T/m}$ in each of the three directions and making sure that the system has total momentum equal to zero. Generally speaking, if sensible (tailored to avoid large impulsive forces) position and velocity distributions are chosen, particle positions at equilibrium relax to oscillating around the minimum energy locations of the potential Φ . A Maxwellian distribution of velocities is naturally obtained in the simulation.

Therefore the initial temperature and total energy of the system has been fixed. The temperature is fixed by the velocity distribution. The total energy of the system is given by the sum of the total kinetic energy KE_{tot} in the system given by

$$KE_{tot} = \sum_{i=1}^N \frac{1}{2} m (v_{x,i}^2 + v_{y,i}^2 + v_{z,i}^2) \quad (6)$$

and PE_{tot} the total potential energy of the system given by

$$PE_{tot} = \sum_{i=1}^N \Phi_i(r_i) \quad (7)$$

with $v_{x,y,z}$ being the velocities, r being the positions of atoms, and i being the index that sums over all the atoms N in the system. $\Phi_i(r_i)$ is the potential energy of the i^{th} atom due all other atoms in the system. In a optimized MD simulation, with truncated-shifted potentials, $\Phi_i(r_i)$ is calculated by summing over the potential energy at r_i due to the atoms in the neighbor list and adding truncation and shifting corrections.

The recipe used to fix the temperature above should not be used at every time step since this fixes the temperature rigidly. This also destroys the purpose of solving Eqn.4. Normal temperature fluctuations are also suppressed. There are many methods to control temperature and pressure [38–40]. In the Berendsen temperature control scheme, all velocities are scaled at each time step by a factor λ given by

$$\lambda = \sqrt{1 + \frac{\Delta t}{\tau_T} \left(\frac{T_o}{T} - 1 \right)} \quad (8)$$

where, Δt is the time step of the simulation, τ_T is the time constant for temperature control and has to be greater than $100\Delta t$, T_o is the desired temperature and T is the current temperature. The Berendsen pressure control is implemented by changing all atom positions, and the system size is scaled at each

time step by a factor μ given by:

$$\mu = \left[1 - \frac{\beta \Delta t}{\tau_P} (P_o - P) \right]^{\frac{1}{3}} \quad (9)$$

where τ_P is the time constant for pressure control which should be typically greater than $100\Delta t$, P_o is the desired pressure and P is the current pressure. β is the isothermal compressibility of the system. This type of temperature and pressure scaling gives realistic fluctuations in temperature and pressure when large values of τ_T and τ_P are chosen.

Post processing of results

Solving Eqn.4 gives the particle positions and velocities at each time step. The total kinetic energy, potential energy and total energy can also be output using Eqns.6 and 7, averaged over a certain number of fixed time steps. Depending on the type of ensemble simulated, various macroscopic parameters of the simulation like temperature, pressure, specific heat at constant pressure or at constant volume, etc can be output. Various transport coefficients are related to time correlation functions of various measurable quantities in a MD simulation as given by the Green-Kurbo relations. See [16] (Section 4.4.1 and Appendix C) for details.

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