Excited-State Quantum-Classical Molecular Dynamics

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or

Our views at opportunities and challenges in Computer Simulation of PSIF

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[1]Physics *[2]Computer Science and Mathematics*
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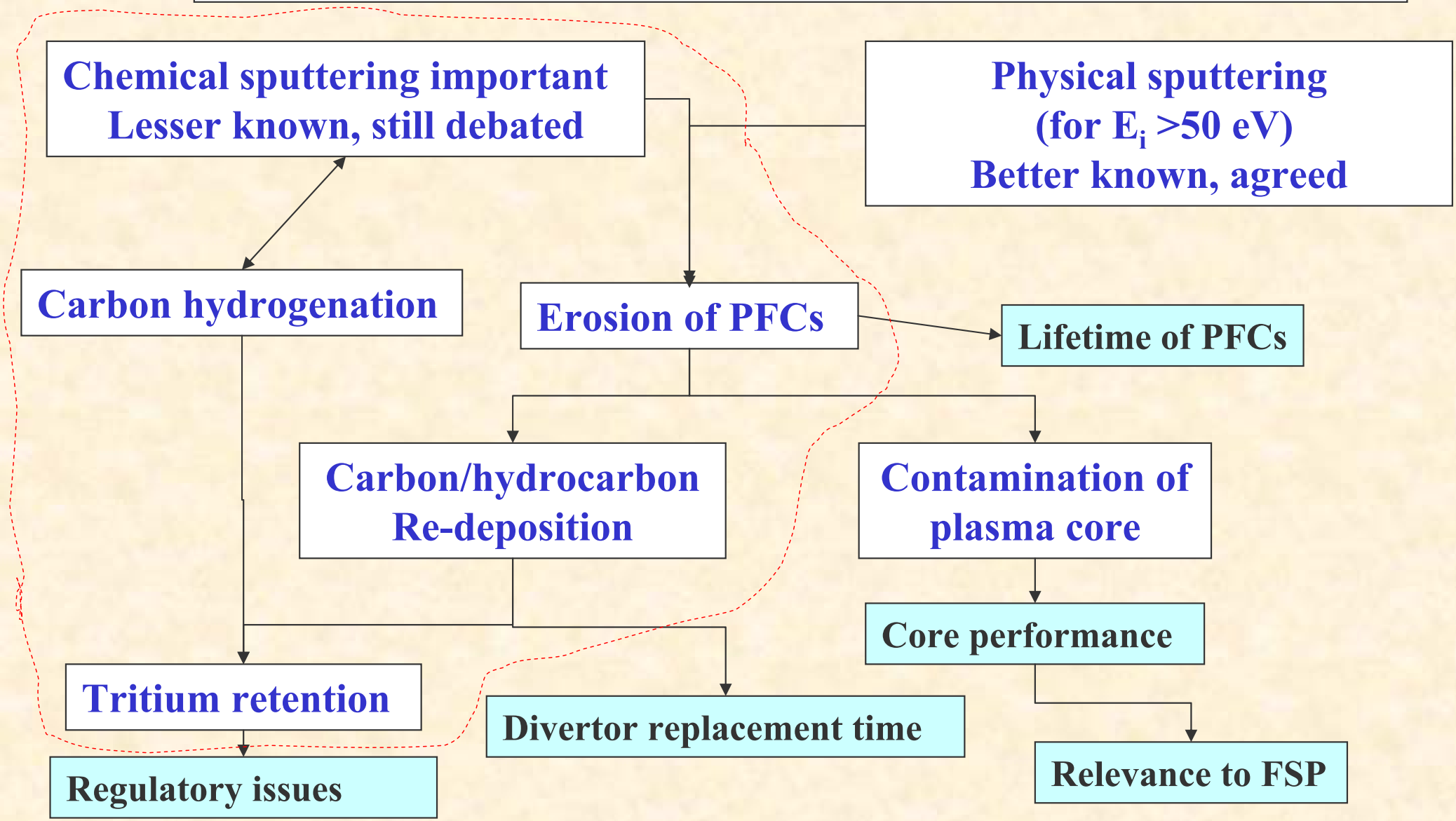
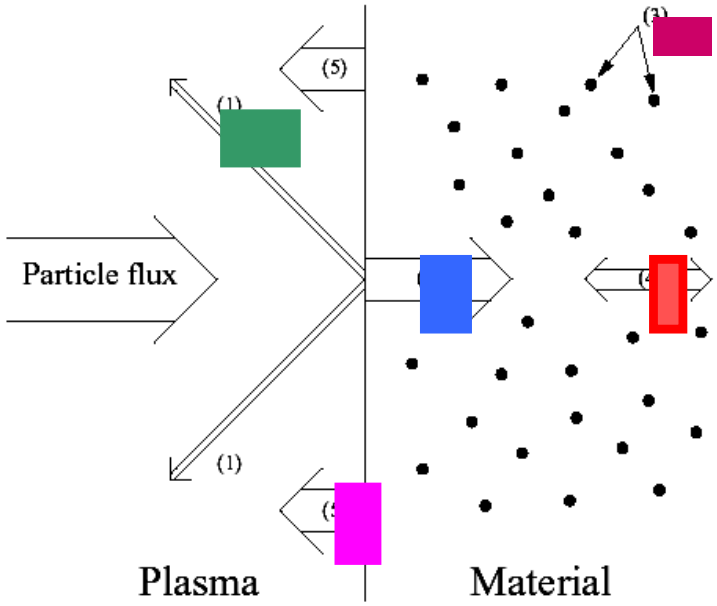
Plasma-facing components (PFCs) : key issue for ITER decisions



Carbon is the best studied example; W, Be, Ta, Mo, Si and B doped C??



Multitude of processes!

(1) elastic reflection;
(2) implantation;
(3) trapping/detrapping;
(4) diffusion;
(5) re-emission.

Most complex: Chemical sputtering

Inelastic processes!

All these at the "same footing", in competition!

FUNDAMENTALY MULTISCALE PROBLEM

Chemical sputtering

***Bombardment** by ions, atoms, molecules*

***Chemical reactions** inside the surface (Breaking C-C bond, H passivation)*

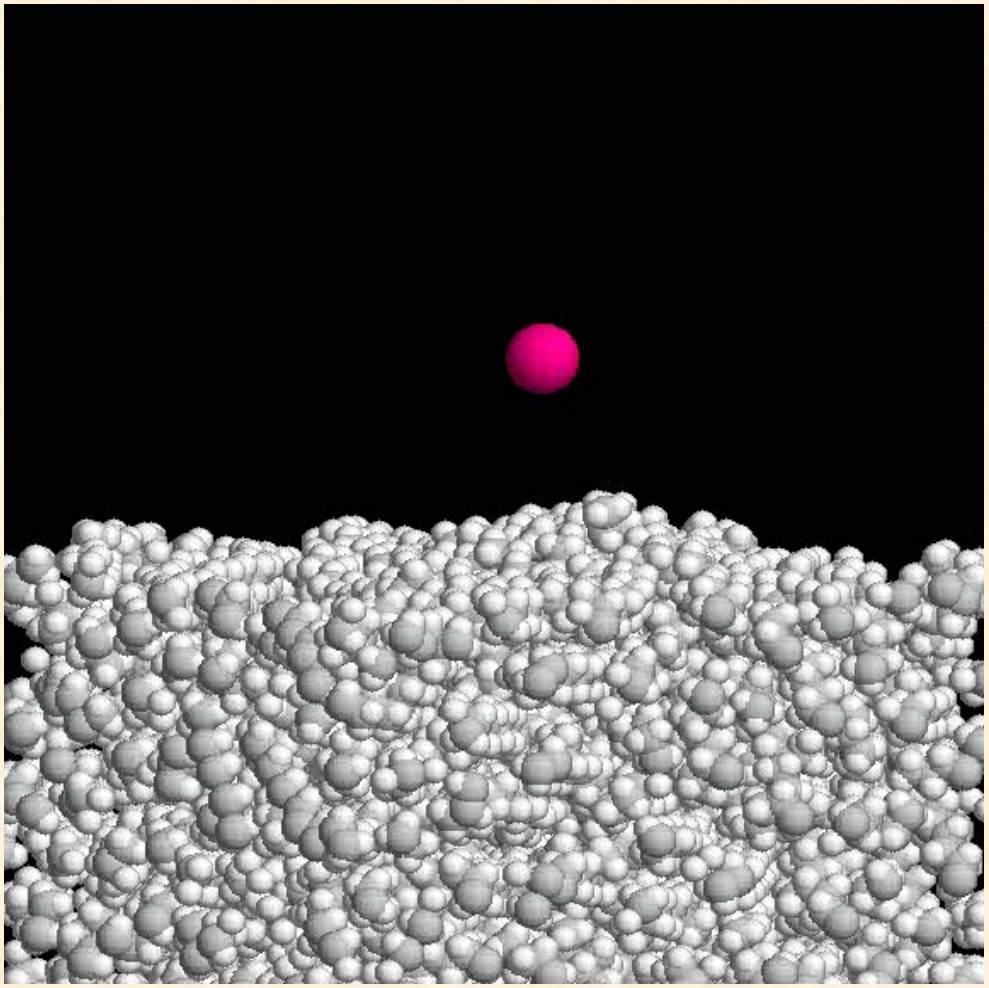
*Produced volatile particles **diffuse***

***Desorbed** into the gas phase*

*Some promptly **re-deposited**, **Most released into the plasma***

Erosion** of PFC, plasma **contamination

*Released particles transported with plasma, changed, **deposited** to some other PFC*



Ar ion on supersaturated a:C (100 eV)

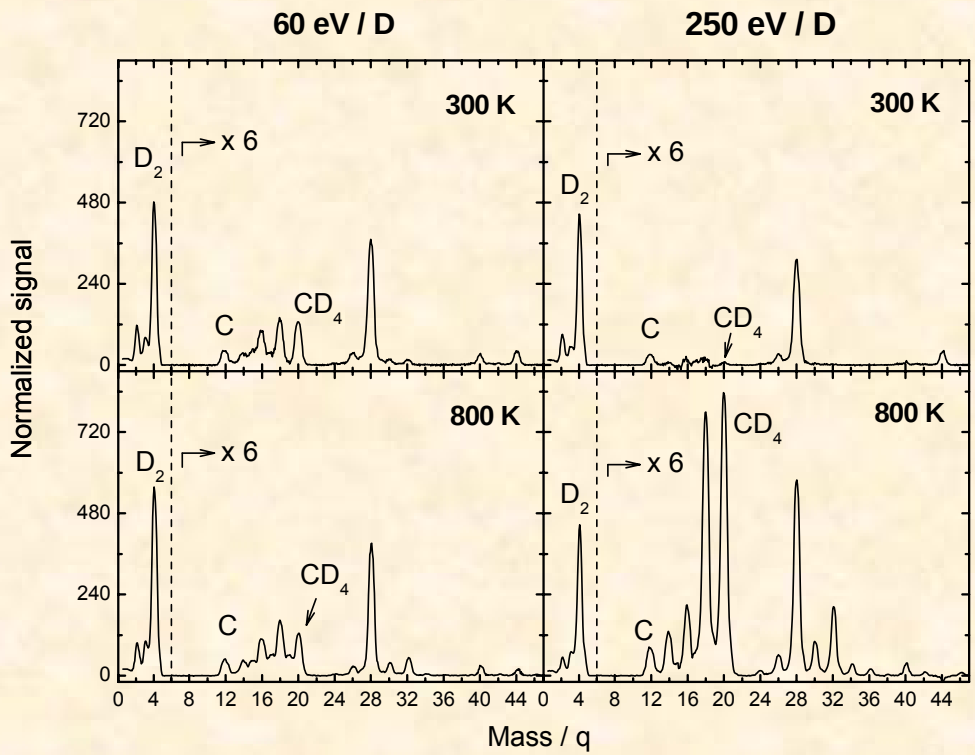
Courtesy of S. Stuart

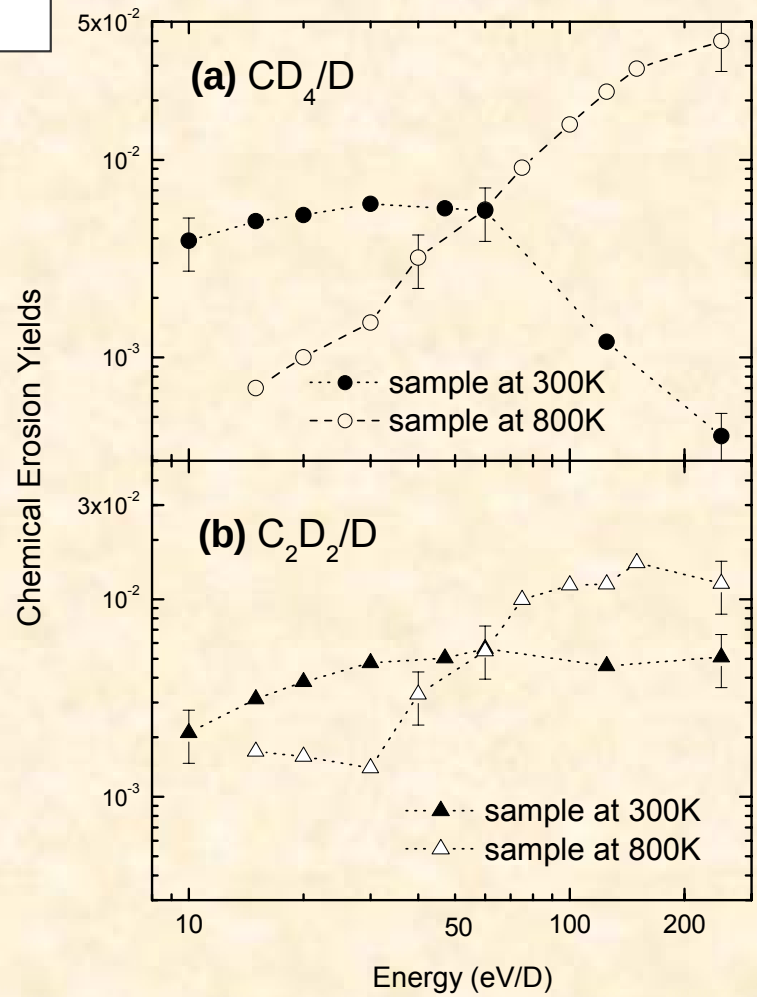
The yield is function of ?

- Projectile species (H, H_2, Ar, N, He,C,…)
- Surface microstructure (crystalline, amorphous a-C, polycrystalline)
- Impinging projectile energy (1-100 eV), angle
- Hydrogenation level (sp^2/sp^3 ratio)
- Surface temperature (300-1500K)
- Flux density (10^{21}-10^{25} $m^{-2}s^{-1}$)
- Isotopic effect (D, T)
- Doping (Si, B)

- Carbon used as the test, best-studied example.

"In-house" (ORNL) Fred Meyer initial experiments on chemical sputtering

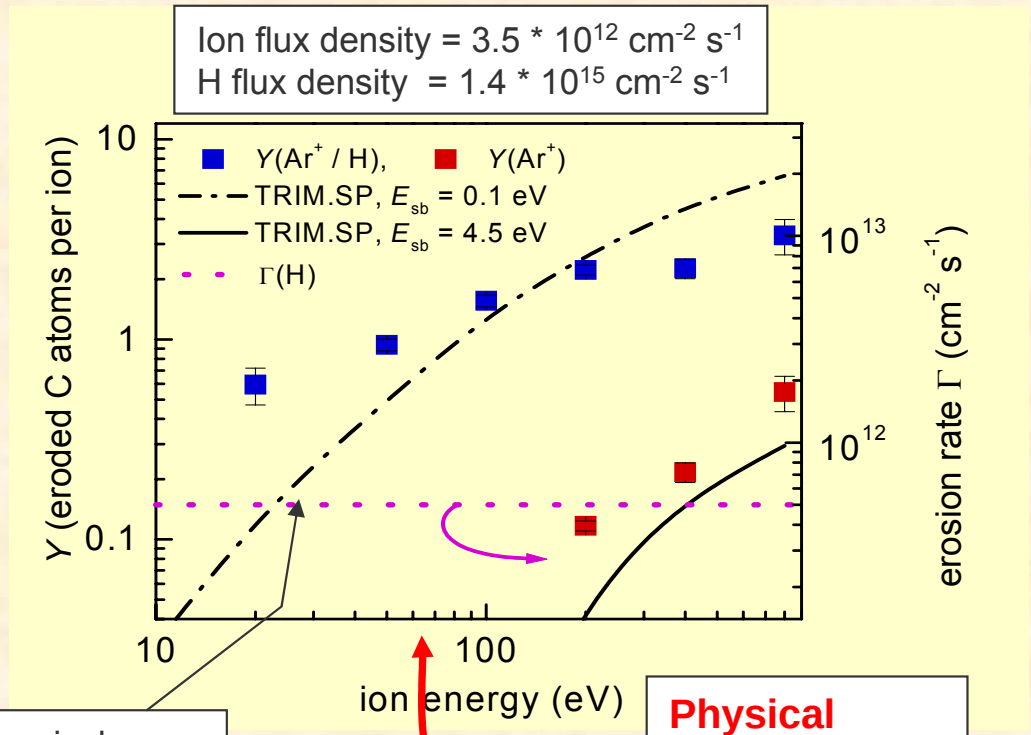




Possibility of direct interaction of experiment and theory!

Courtesy of L. Vergara

A Beautiful Experiment

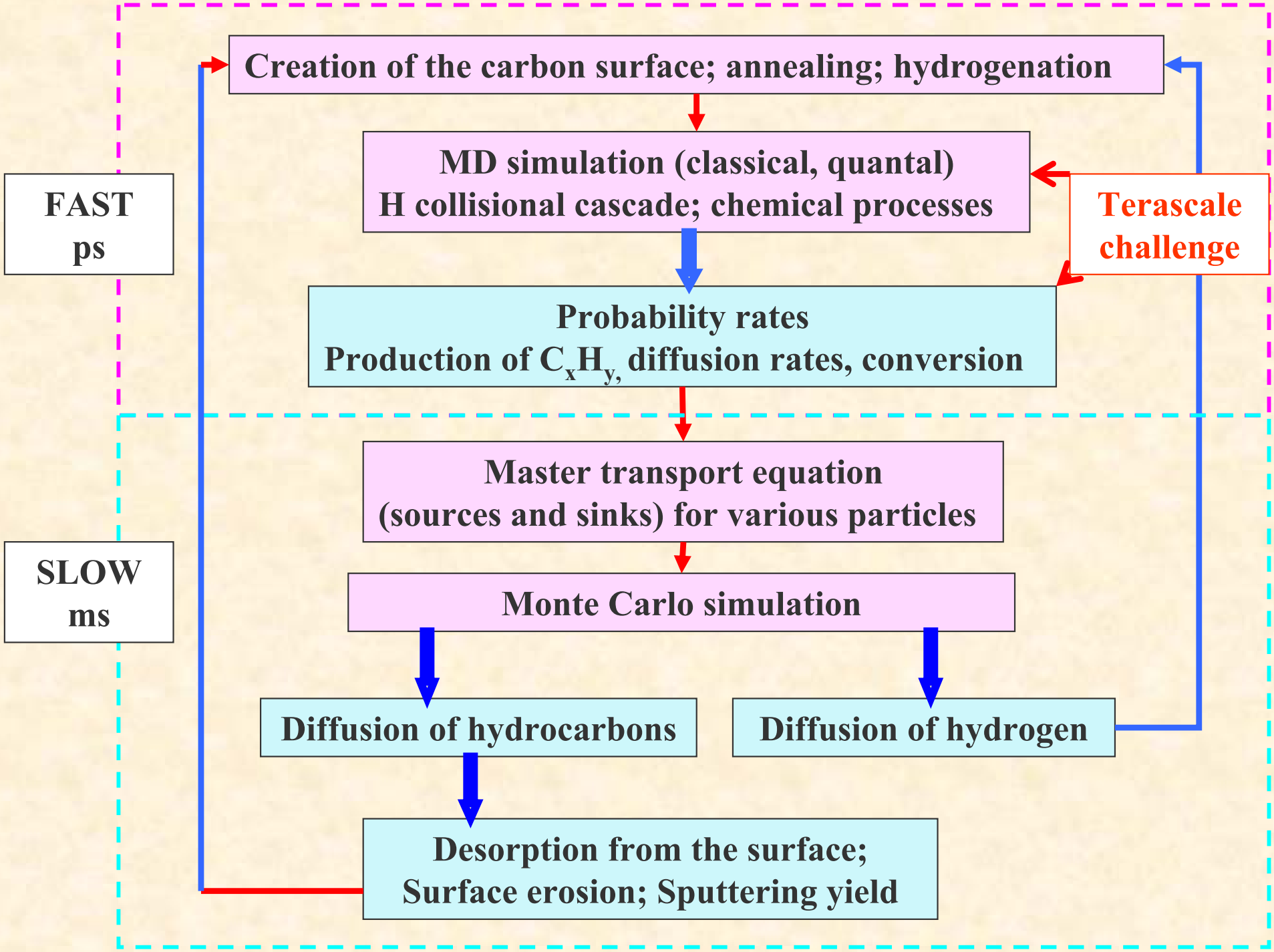


Chemical erosion due to atomic H alone (320K)

Physical sputtering threshold: ~ 60 eV

separation of chemical and kinematical effects due to use of Ar+ and H

Ch. Hopf, A. von Keudell, and W. Jacob, "Chemical Sputtering of Hydrocarbon Films", J. Appl. Phys. ***94****, 2373 (2003).*


Creation of the carbon surface; annealing; hydrogenation
MD simulation (classical, quantal)
H collisional cascade; chemical processes
Terascale challenge
FAST
ps
Probability rates
Production of C_xH_y, diffusion rates, conversion
Master transport equation
(sources and sinks) for various particles
SLOW
ms
Monte Carlo simulation
Diffusion of hydrocarbons
Diffusion of hydrogen
Desorption from the surface;
Surface erosion; Sputtering yield

Computational Issues and Objectives
Solving for dynamics of an atom+surface system

1. Preparing the system for the simulation

Projectile:

De Broglie λ_H~ 1 a.u. for E_H~ 1 eV →QM motion of projectile?

v_H~0.06 a.u. for E_H~100 eV →quasi-adiabatic evolution, classical motion of heavy particles

Various impinging projectiles, angles, Maxwellian energies (1-100 eV)

Surface:

- Random C or C:H network (a-C)
- Simulated annealing at desired T
- Numerical cell: Scattering-free boundaries (100 eV ~2nm)
  → A few thousands of atoms
- 2D periodic boundary
- Hydrogenation [annealing and/or cumulative exposure to H (D,T)]

What is molecular dynamics?

- Evolution of a system of particles over time: Duration ~1 ps
- Equations of motion are solved for each particle at a series of small time steps (energy conservation) 0.1-1 fs

$$\mathbf{F} = m\mathbf{a}$$

What is quantum-classical molecular dynamics?

- Key physics input in MD is the inter-atomic potential function

$$\mathbf{F} = -\nabla U$$

- Wide range of techniques for: Potential energy: Modeled, predefined function → Classical MD
- Potential energy is calculated at each time step by solving Schrödinger equation for electrons with adiabatic instantaneous Hamiltonian → Quantum-Classical MD

Classical Molecular Dynamics

- System sizes reported 10-10^9 atoms, simulation times up to 100 ns
- Brenner (1990, 2002) (REBO) analytical potential for C, H parameterized using large number of experimental data

$$E = \sum_{i,j} V_{rep}(r_{ij}) - b_{ij}(r_{ij}) V_{attr}(r_{ij})$$

Reactive, heterogeneous bonding, leaves out non-bonded repulsion, torsion

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- Adaptive Intermolecular Reactive Bond Order (AIREBO) potential

: torsion, dispersion, Van der Waals,
qAIREBO + electrostatic interactions (new) } ***Stuart (2000,2004)***

  - Slower (~N^2) than Rebo (~N)

Variable-time-step AIREBO code (Stuart), parallel version:

Quantum-Classical Molecular Dynamics

Multiscale

Tight-Binding method

"Minimal" QM model, semi-empirical

Many-body H → empirical TB Hamiltonian

$$H_{TB} = \sum_{i=1}^{N} \varepsilon_i + \frac{1}{2} \sum_i \sum_j U(r_{ij})$$

- U_{ij} = pair-repulsive potential,
- ε_i from self-consistent solution $H\Phi_i = \varepsilon_i \Phi_i$ (valence electrons)
- Diagonalization problem: Scaling N^3 (TB simplifications → N^2, N)
- Parameterization by "ab initio" methods.
- Parameterized well for C, Si, hydrocarbons

Accessible at ORNL:

- ***Density matrix TB code,***
- ***Slater-Koster type code***
- ***TBMD developed at NRL (DoD)***

Hope for the "production" phase: TB, parameterized by CP-MD calculations.

Parameter-Free Quantum Molecular Dynamics
Car-Parinello Molecular Dynamics (CP-MD)

- Classical motion of the nuclei
- Electronic "forces" calculated quantum mechanically at each time step
- CP: Electronic and atomic motion updated simultaneously
- No adjustable parameters

"Heart" of the method is Plane-Wave DFT :
Valence electrons: Expansion in plane waves
periodicity of the simulation cell

$$\Psi = \sum_{\ell}^{N_\ell} f_\ell(K_\ell) e^{-iK_\ell \cdot r}$$

Core electrons: Pseudopotentials (?)

Successful application of the CP-MD approach to the sputtering problem requires a simulation cell of a few thousands atoms.
Available in ORNL: CP-PWDFT code of NWChem
(2D boundary conditions, a variable-time-step propagation (E. Bylaska))

Computational efficiency of multi-body methods

Model	Type	Scaling	N_{max}[1]
Full solution of Schrödinger equation	quantum mechanical, ab initio	$O(e^N)$	1
HF (Hartee-Fock)	quantum mechanical, ab initio	$O(N^{4-8})$/ $O(N)$	50
DFT (density functional theory	quantum mechanical	$O(N^3)$/ $O(N)$	200
TB (Tight-binding)	quantum mechanical (often semiempirical)	$O(N^3)$/ $O(N)$	1000 10000
Many-body potential	classical, semiempirical	$O(N)$	10^7
Pair potential	classical, semiempirical	$O(N)$	10^7

Actual efficiency A $O(N^x)$

A~100

A~100

CPMD code has recently achieved teraflop performance on clustered SMP servers as the IBM pSeries 690 cluster (about 1000 processors)

The first demonstration of teraflop performance for a parameter free molecular dynamics on a system consisting of ~ 1000 atoms.

Macroscopic master equation for the long-time evolution

Dynamic variable: ρ, phase space probability density of all active particles

$$\rho = \rho\left(\{\vec{r}_k, \vec{p}_k\}, t\right) \qquad k: \text{species}: H, CH, CH_3, CH_4 \ldots$$

Boltzmann-like collisional relaxation operator

$$\frac{\partial \rho}{\partial t} + \sum_k \vec{p}_k \nabla_{\vec{r}_k} \rho = R\,\rho$$

Hydrocarbon formation rates
Diffusion rates
Desorption rates
Particle transfer rates

MD simulations

Monte Carlo solution of the master equation

(C. Reinhold)

Test particle discretization

Idea borrowed from standard transport methods

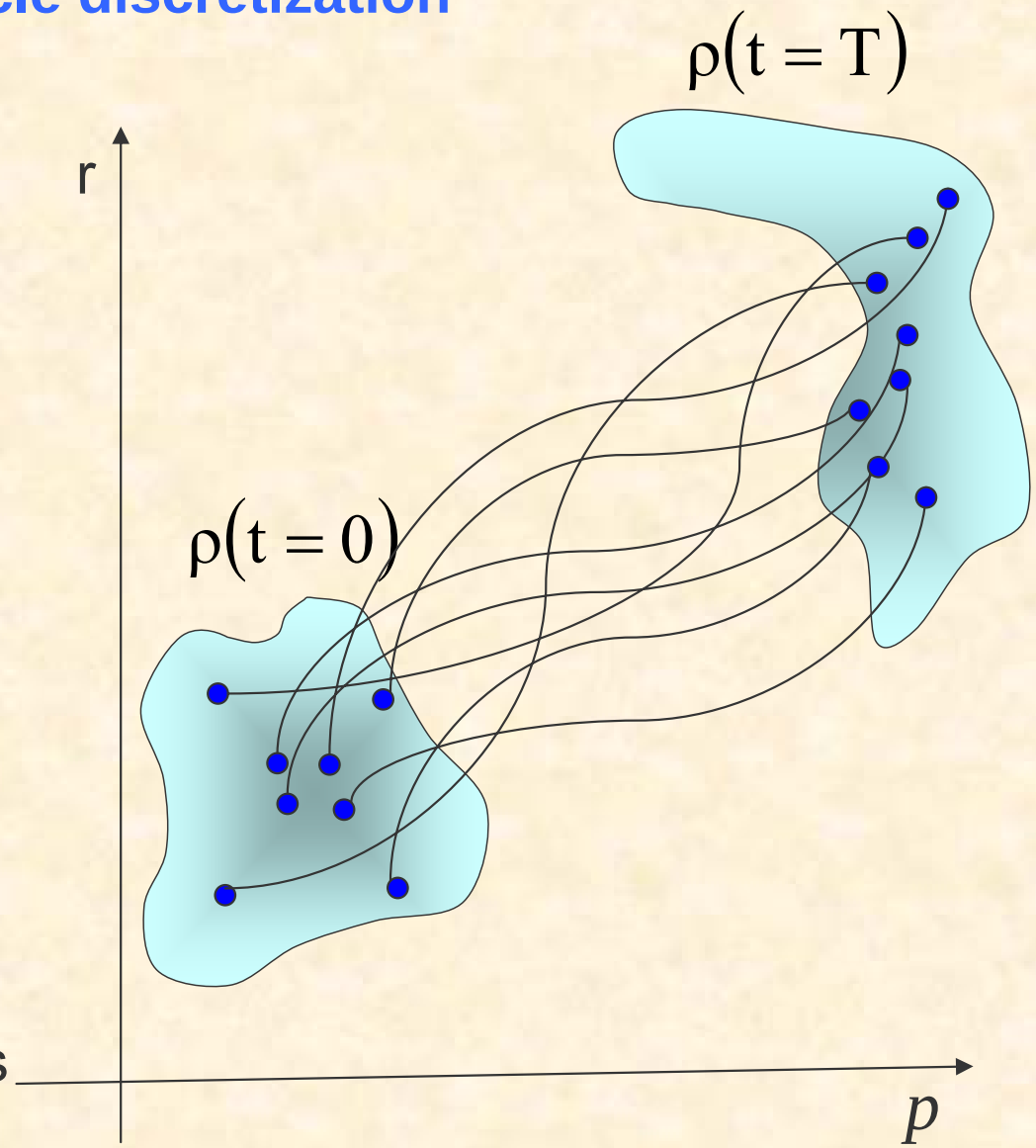
Boltzmann equation can be solved through Langevin equation for Brownian particles

$$\frac{d\vec{p}}{dt} = \vec{F}(t)$$

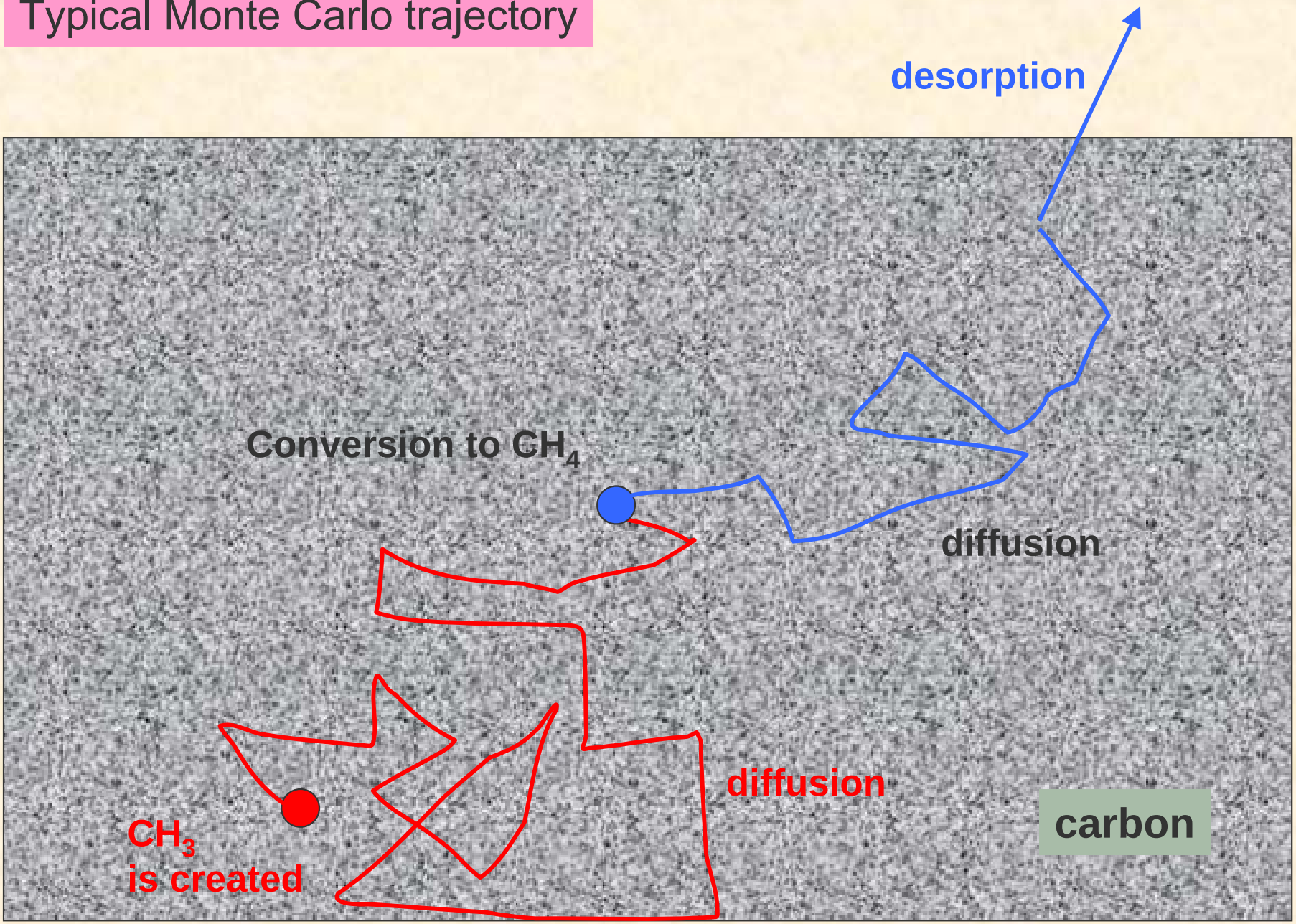
$$\vec{F}(t) = \sum_n \Delta\vec{p}_n \, \delta(t - t_n)$$

Stochastic force

Drawn at random from collisional rates

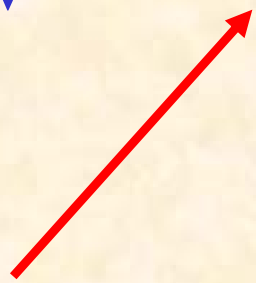


Typical Monte Carlo trajectory



What do we want to achieve?

Tens and hundreds eV impinging energy



Processes:
Charge transfer, electronic excitation, break-up reactions, associative reactions

- Not likely and/or not possible to evolve just on the ground electronic surface
- If excited states (to n) involved cross sections incerase as n^4

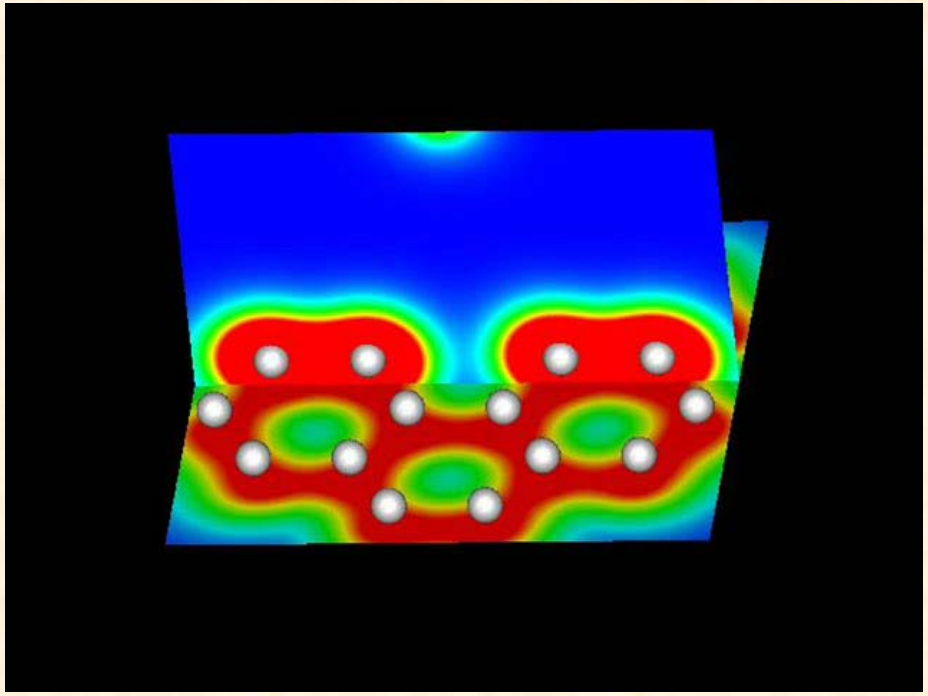
Not "overheating":
These come "at the same footing" with multitude of BO processes

We propose to generalize QC-MD by including transition dynamics between excited electronic states

Developing the method and code is of general importance in contemporary multibody science

Why excited states?

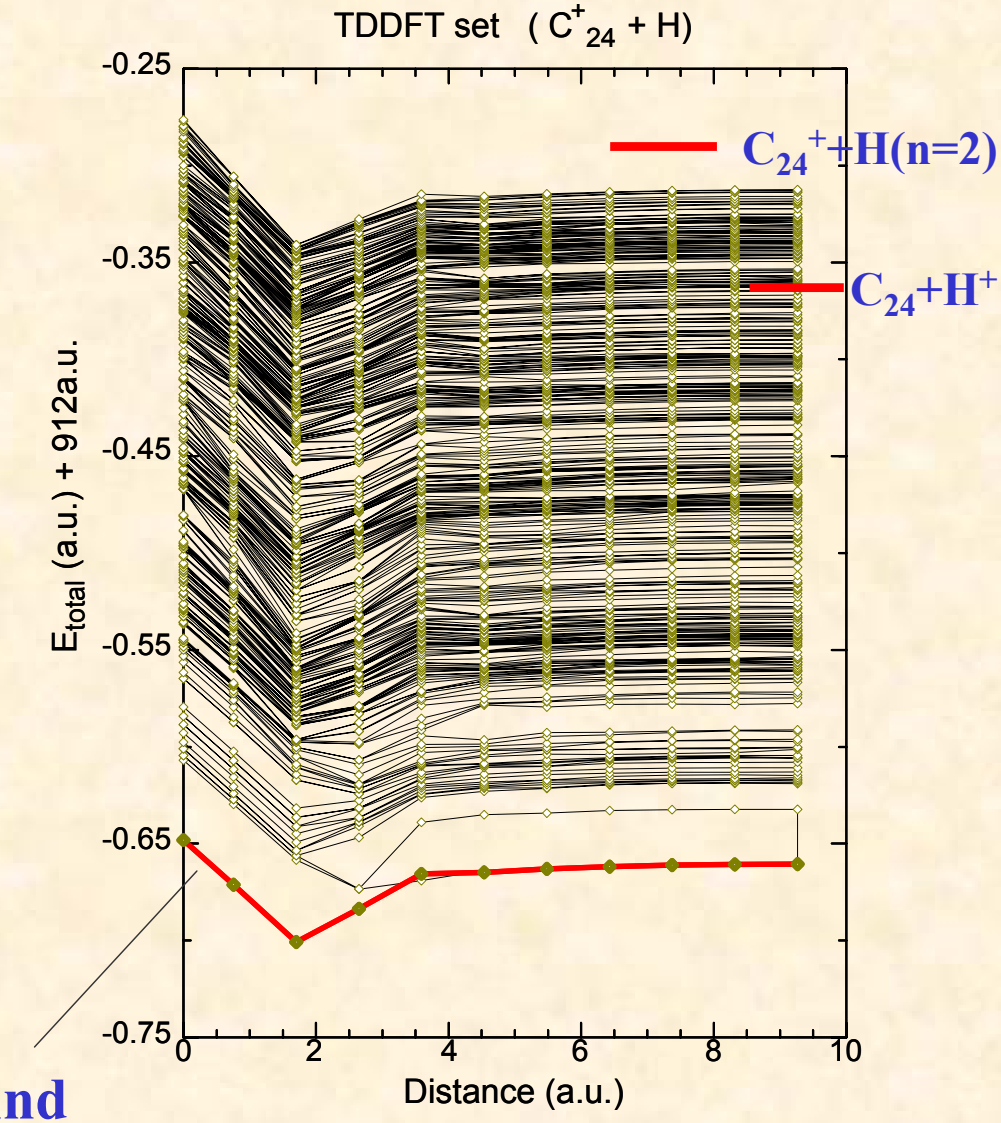
Illustration:



Example:

H impinging at C^{+}_{24} cluster

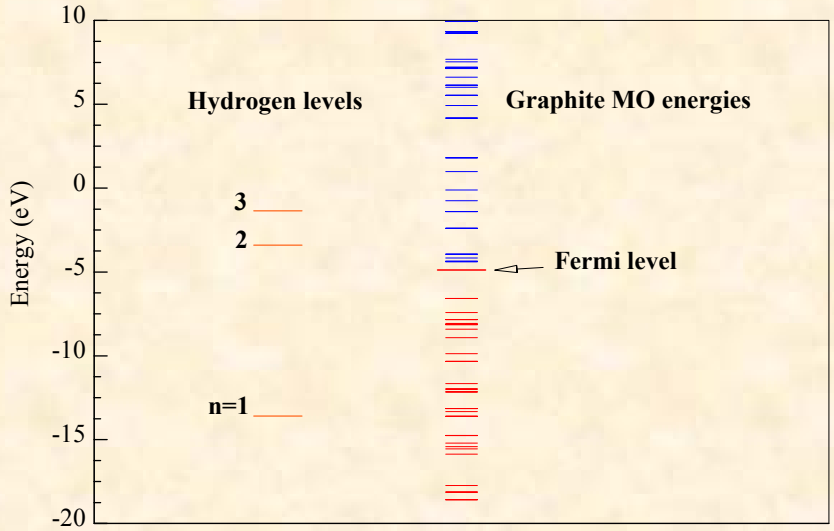
(Krstic, Reinhold 2003)

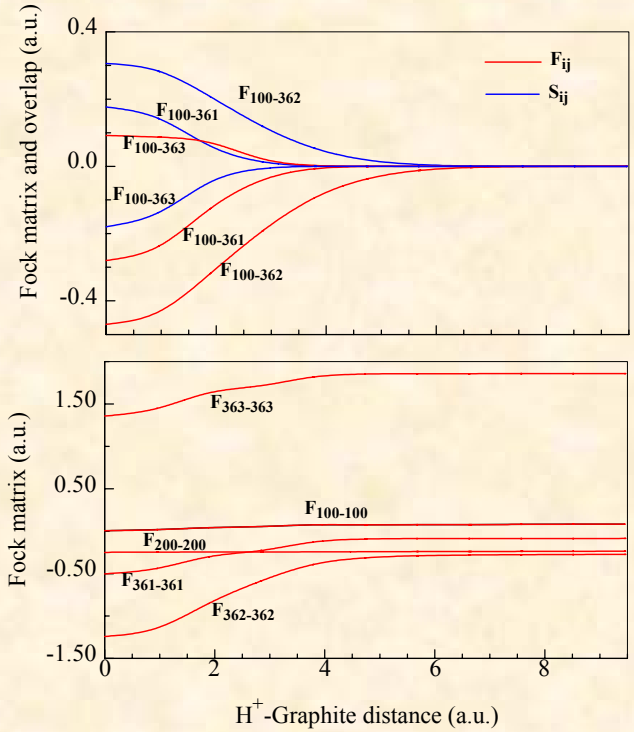


Ground electronic state (Born-Oppenheimer)

Graphite surface: single layer, 24 C-atoms, HOPG
H^+ from about 10 a.u. to 0, along perpendicular-to-graphite classical trajectory
DFT:XC=PBE0; 144 “active” electrons, 365 basis functions (15 on each C, 5 on H)

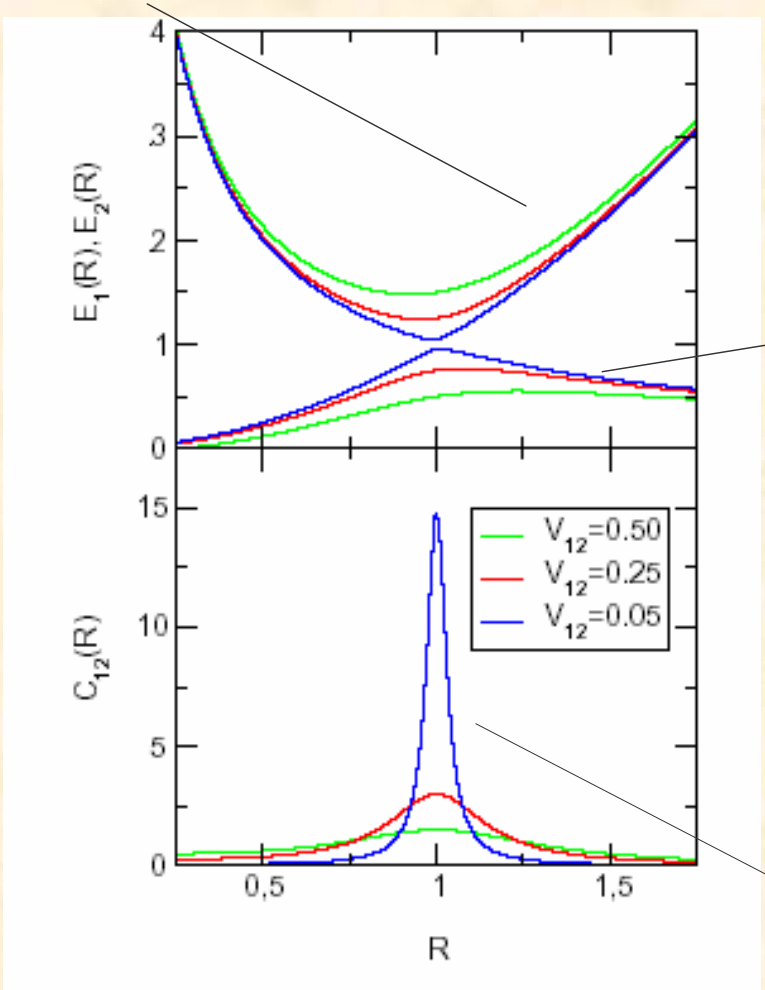
Diabatic basis





Dominant excited state processes?

excited state



Coupling with excited states common whenever energetically allowed

BO ground surface
(battle-field for most of the current MD simulations)

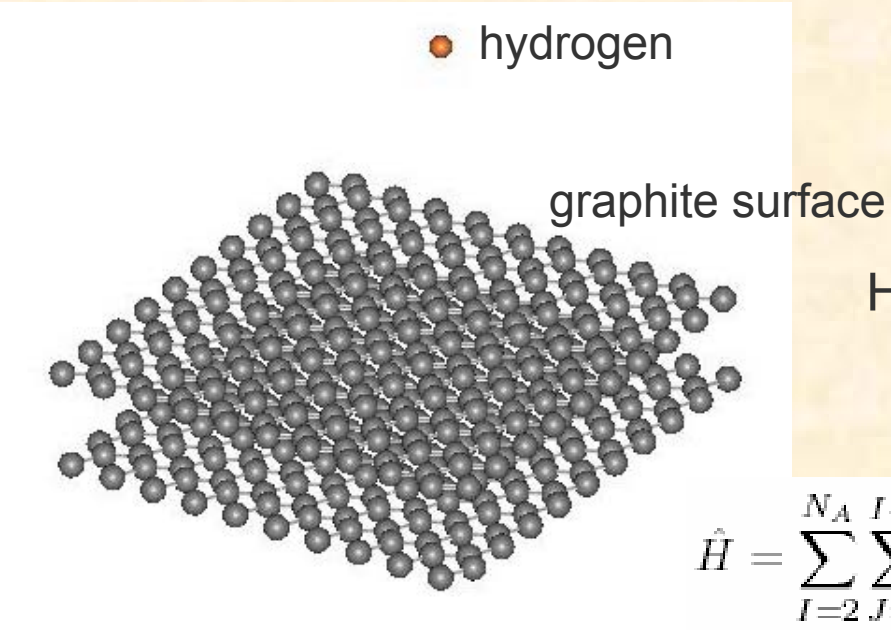
Nonadiabatic coupling

Typical situations (with 2 heavy particles)

Avoided crossings

Characteristic of the problem:

Multi-body, large number of electrons and atoms takes part in a process



Stationary behavior by Schrodinger equation

$$H\Psi = E\Psi$$

H in space of N-electron functions (N_A atoms)

$$\Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$$

$$\hat{H} = \sum_{I=2}^{N_A}\sum_{J=1}^{I-1}\frac{Z_I Z_J}{|r_I - r_J|} - \sum_{I=1}^{N_A}\sum_{j=1}^{N}\frac{Z_I}{|r_I - r_j|} - \sum_{i=1}^{N}\frac{1}{2}\nabla_i^2 + \sum_{i=1}^{N}\sum_{j=1}^{i-1}\frac{Z_e^2}{|r_i - r_j|}$$

Ab initio: Currently impossible task!

Possible simplification: Mean-filed theories (HF and DFT)

$$V_{mean-filed}(\vec{r}) = \int \rho_{N-1}(\vec{r}\,')\frac{1}{|\vec{r} - \vec{r}\,'|}d\vec{r}\,'$$

P probability density for finding other electrons at $\vec{r}\,'$

DFT, K theorem: Knowing exact all single electron densities is ≡ knowing $\Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$

Runge and Gross generalization to time-dependent problems

Technical details of the research

Motion of atoms, ions, molecules defined by classical equations of motion using electron-averaged Hamiltonian

$$\bar{H} = \sum_{\alpha} E_{k,\alpha}(t) + \langle \Psi(r,t) | H_{el}(r, Q(t) | \Psi(r,t) \rangle$$

(Ehrenfest trajectories, weak coupling)

Conservation of total energy

$$d\bar{H}/dt = 0$$

yields

$$i\frac{\partial \Psi}{\partial t} = H_{el}\left(\mathbf{r}, \mathbf{Q}(t)\right)\Psi$$

Schrodinger equation for electronic motion

Solving all-state time-dependent Schrodinger equation for electronic motion is the main challenge

Method & code development

First step: TD Hartree-Fock (and DFT)

$$\Psi(\mathbf{r},t) = A\prod_{i=1}^{N}\varphi_i(\mathbf{r}_i,t) \qquad i\frac{\partial\varphi_i}{\partial t} = F\varphi_i$$

Initial value problem in a coupled, time-dependent, nonlinear set of equations

Next step: Multiconfiguration TDHF – here to the level of CIS

$$\Psi = \sum_J a_J \Phi_J(r,t)$$

$$J = (j_1, j_2, \ldots, j_N), \# a_J = \begin{pmatrix} F \\ N \end{pmatrix}$$

$$j_i \le F,$$

$$F = N \rightarrow TDHF$$ **uncorrelated**

$$F \rightarrow \infty$$ **EXACT** Ψ

$$i\frac{da}{dt} = A_H(\varphi)a$$

Nonlinear equations

$$i\frac{\partial\varphi}{\partial t} = B_H(a,\varphi)\varphi$$

In CIS F=N+1

Numerical scaling:

To store $\Psi(q_1, q_2, \ldots, q_N; t)$ on a grid of P points

TDSE requires P^{3N} complex numbers

(example: O with 8 electrons and P=10, requires 10^{24} complex numbers
IMPOSSIBLE!!!

MCTDHF: requires $FP^3 + \binom{F}{N}$ complex numbers

The same oxygen example: F=12 ~12,000 complex numbers

Technical peculiarity of our approach:
Use of MADNESS (Harrison, Fann)

(Multiresolution Adaptive Numerical Scientific Simulation) =
framework for scientific simulation in many dimensions using adaptive multiresolution methods in multiwavelet bases.

Robust approach to:

- **basis completeness,**
- **computational speed,**
- **discretization of differential operators**
- **variable step**
- **ETF's problem suppressed**
- **Continuum at the "same footing"**
- **Nonlinear integrators**

Specific tasks underway:

MD-TDHF 1)

$$C^{+} + C_{n} \rightarrow C + C_{n}^{+}$$

2)

$$C^{+} + C_{x}H_{Y} \rightarrow C + (C_{x}H_{y})^{+}$$

MD-CIS

$$C^{+} + C_{x}H_{y} \rightarrow C_{x+1}H_{y-1} + H^{+}$$

Understanding these processes (cross sections, rate coefficients, probability rates) → self- sputtering of carbon ions on carbon

Proof of principle:
Verification of the code and theory by

1) Well characterized single-electron processes (HF)

$$H^+ + H(1s) \rightarrow H^+ + H(2s)$$

$$H^- + F \rightarrow H + F^-$$

2) Charge exchange and particle rearrangement (CIS)

$$D^+ + CH_4 \rightarrow D + (CH_4)^+$$ **(0.76 eV endothermic)**

$$\rightarrow H + (CH_3D)^+$$

All processes well known experimentally!

Resume & Conclusions

Set the groundwork for computer simulations of plasma-material interactions

Computer simulation studies of reactive processes in plasma-facing materials

1 Classical Molecular Dynamics Studies

2 Quantum Molecular Dynamics simulations

3 Inelastic ("excited") processes at the Plasma-Wall Interface

Slow phenomena at the Plasma-Wall Interface

1 Diffusion of reaction products, chemical sputtering yields

2 Diffusion, trapping, emission and hydrogen retention

-Targets: C crystalline, polycrystalline structures; CFC, doped C, Tungsten, Beryllium

-Plasma particles: H_2 , N (N_2), C, W, Be, inert gases, …

-New methods: Excited state MD

Our final goal is the self-consistent theoretical description and computer simulation of the manifold of the relevant multi-body processes

Tera-penta-flops ORNL computing resources crucial

Required accuracy: Defines time-scale for obtaining output!!!!

Quest for excited electronic states transition dynamics
Quantum-Classical Liouville Equation

Quantum Liouville equation governs dynamics of density operators

$$\partial_t \hat{\rho}(t) = -\frac{i}{\varepsilon}[\hat{H}(t), \hat{\rho}(t)] \qquad \varepsilon = \sqrt{\frac{m}{M}} \ll 1$$

- ***Partial Wigner transformation of H and density matrix (WT to heavy components- classical limit, light components retain quantum nature)+***
- ***1st order expansion in ε to full quantum dynamics + basis (adiabatic) representation for light particle***

→quantum-classical Liouville equation in Wigner-transformed density matrix X_a

$$\partial_t X_a = -\frac{i}{\varepsilon}[E, X_a] - [C \cdot P, X_a] + \frac{1}{2}[E, [C, \nabla_P X_a]]$$

$$-P \cdot \nabla_R X_a + \frac{1}{2}[\nabla_R E, \nabla_P X_a] + O(\varepsilon); X_a = X(R, P, t)$$

Quantum: ***Phase oscillations of coherences*** $X_{ij}(t) \propto \exp[\frac{i}{\varepsilon}(E_i - E_j)t]$

Quantum-classical: ***Nonadiabatic exchange of densities and coherences***

- ***Motion of heavy components*** $\propto C \cdot P \quad , \quad C_{ij} \propto < i | \nabla_R | j >$
- ***Non-local operator: R-dependence of heavy component density***

Classical: ***Transport X_{ij} along adiabatic potentials $E_{ij}(R)==(E_i+E_j)/2$***

How to do better?

1. Full CI is size consistent and extensive, but all forms of truncated CI are not.
2. Coupled Cluster approach convenient for large systems $\Psi_{CC} = \exp(T)\Phi_0$

CC operator T only single, double excitations => correlation corrections to infinite order

CCSD is future: Not more than 100 electrons currently!!!

Of critical importance further development of the ORNL computational resources:
Currently:
Cray X1, with 32 multi-streaming vector processors, 512 GB of GA memory,
27-node "power 4" IBM p690 system (x32 1.3 GHz Power4 processors),
184-node "power 3" IBM RS/6000
256-processor SGI-Altix (huge shared memory, 8 Gb per processor)

Questions:

1. What divertor material? Walls?
2. Does ITER needs PSIF modeling?
3. Coating, doping,…?
4. Is CMD satisfactory?
5. What are drawback if CMD?
6. What level of QMD is needed?
7. Are excited states needed?
8. Are “at the same footing” processes needed?
9. What are the most important parameters?