GAS SURFACE INTERACTIONS:

*molecular dynamics approach*

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Outline

- Molecular surface processes: inelastic and reactive (atom recombination)
- Collisional data and lack of a data base
- Molecular dynamics approach: strategy
- Potential Energy Surface determination: semiempirical and ab initio approaches
- Collisional models
- Time-dependent semiclassical approach
- O, N recombination on silica surfaces at high temperatures:
  - dynamics
  - energetics
  - surface structure effect
  - surface temperature effect
CHEMICAL SURFACE PROCESSES: MD approaches

Gas-Wall interactions:

- dissociative chemisorption
- atom recombination

\[
\begin{align*}
\text{H}_2 & - \text{CO} - \text{O}_2 - \text{N}_2 - \text{NO} \ldots \\
\text{H} - \text{N} - \text{O} - \text{Xe} \ldots .
\end{align*}
\]

Aerothermodynamics

TPS system:

- O - O\(_2\) – N – N\(_2\) – CO – CO\(_2\) /on
- silica and silica based materials
- SiC -- UHTC ceramics (ZrB\(_2\) et al)

Interstellar media

H\(_2\) formation/
carbon covered ice grains
Inelastic processes

- __direct mechanism__
  \[
  AB(v, j) + w \rightarrow AB(v', j') + w
  \]

- __indirect mechanism__
  \[
  AB(v, j) + w \rightarrow [AB^*w] \rightarrow AB(v', j') + w
  \]

* molecular surface complex: thermalisation
  \[
  \tau_{ad}
  \]
1) **dissociation**

\[
AB\left( E_{\text{kin}}, E_{\text{int}} \right) + w \rightarrow [AB]_{ad} \rightarrow A + B + w
\]

2) **atom recombination**: different mechanisms

\[
A + B_{ad} + w \rightarrow \quad AB\left( v, j \right) + w
\]

\[
\left\{ \begin{array}{c}
AB_{ad} \\
AB_{ad} \rightarrow AB\left( v', j' \right)
\end{array} \right. + \Delta E_{\text{exo}}
\]

surface heating
Energy flow pathways

$O + O + w \longrightarrow O_2(v,j) + w + \Delta H_{exo}$

- Molecular Internal states
  - vibrations/ rotations/ electronic exc.
  - translation

- Flux to the surface
  - phonons and/or
  - electron-holes

$\Delta E_{int} = D(O_2) - E(O_{ad}) - E(O_{ad}) - \Delta E_{surf}$
Surface reactions

- Surface oxidation
- Sputtering
- Implantation
- Neutralization

\( \text{higher } E_{\text{kin}} / \text{KeV} \)
COLLISIONAL DATA of heterogeneous processes

- $\gamma (v,j \mid T_s)$ and $\gamma (T_s)$: state-to-state and global sticking coefficient
- $\beta (T_s)$: energy accommodation coefficient
- $N (v,j)$: rot-vibrational distribution in the final states
- $I(\theta, \varphi / T_s)$: angular distribution in intensity and energy
- $\tau_{ad}$: lifetime and probability for ads and ad/des
LACK of a DATA BASE for HETEROGENEOUS PROCESSES

- recombination coefficients
- energy accommodation $\beta$ \textit{very sparse}
- state-to-state rate constants \hfill (if not absent)

( sometimes taken from analogous gas-phase reactions )

\textit{basic plasma-surface processes remain largely unknown}

-- State-to-state collisional data --
Sticking coefficient is highly specific:

\[ S_o( v, j, E_{\text{kin}} | \text{Surface parameters}) \]

depending on the plasma environment

- coverage
- surface modifications: steps, terraces, holes
- Contaminations, etc

molecular and surface parameters should be taken under control: selecting molecules in well defined energy states

impinging a well characterised surface target

( generally not possible under plasma operating conditions )
Molecular Dynamics Approach: possible answers to (some) unsolved issues in surface catalysis

focused on: dissociative adsorption of H2, O2, N2, NO, and others diatomics on metal surfaces: Cu, Fe, W, Au etc

recent investigations: larger molecules and clusters: metal oxides, silicon, diamond
MD Model Calculations:

- Potential Energy Surface
- Collisional Model
Potential Energy Surface determination

prerequisite for any MD calculations

- most critical aspect of surface reactions

- ‘true’ interaction potential is unknown even for elementary systems:
  
  H2, CO, O2 and other diatomics / metals

large uncertainties exist:

- binding energies
- activation energies
- nature of the energetic barriers
$E_{act} \text{ H}_2 / \text{Cu}$

![Graph](image)

- **ab initio calculations**: $0.3 \div 1.5 \text{ eV}$
- **Molecular Beam experiments**: $\sim 0.5 \text{ eV}$

(Lettnek et al. 1993)
different electronic structure calculations using different approximations give different values of the activation energy

- SCF-CI cluster calc. 1.5 eV *Madhavan-Whitten JCP 1982*

- H$_2$/Cu$_2$ 1.0 eV *Harris + Andersson PRL 1985*

- jellium 0.9 eV *Johansson S.S. 1981*

- L-DFT 0.4 eV *White+Bird CPL 1994*

*early semiempirical LEPS calculations: 0.2-0.5 eV (Gelb+Cardillo 1976)*
N-silica interaction potential: ab initio cluster calculations

N-Si$_7$O$_{14}$H$_{14}$ B3LYP/6-311+G*

$E_b(N) = 2.70$ eV

$R(N-Si) = 1.65$ Å

$N_2$/silica: repulsive
Semiempirical methods:

- noble atom-surface interaction: *universal rules*

- spectroscopic data
  -- *absorption energies*
  -- *bonding energies*
  -- *inter and intramolecular frequencies of adsorbed molecules*
  -- *equilibrium geometries of ads. molecules*

-- Analytical fit to *ab initio* data *and* experimental data
Normal mode frequencies of CO bonded on the on Top and Bridge site of Pt(111)

On Top

\[ \nu_1 = 2084 \text{ cm}^{-1} \]
\[ \nu_2 = 469 \text{ cm}^{-1} \]
\[ \nu_3 = 387 \text{ cm}^{-1} \]
\[ \nu_4 = 48.5 \text{ cm}^{-1} \]

Bridge

\[ \nu_1 = 1850 \text{ cm}^{-1} \]
\[ \nu_2 = 425 \text{ cm}^{-1} \]
\[ \nu_3 = 360 \text{ cm}^{-1} \]
\[ \nu_4 = 350 \text{ cm}^{-1} \]

from He scattering exp.
(Toennies et al.)
\[ V_{\text{CO-Pt}(R)} = \sum_{i=1}^{N} \sum_{\alpha=1}^{2} \exp(-\beta_i R_{i\alpha}) (D_i \exp(-\beta_i R_{i\alpha}) - E_i + B_i R_{i\alpha} + C_i R_{i\alpha}^2) \]

\[ + (D_{\text{CO}} (1-\exp(-\beta(r-r_{eq})))^2 \]

\[ V_{\text{C,O-Pt}(R)}: \text{ similar Morse functions} \]

\[ \beta_i = b_i \cdot f_1 + b_{bi} \cdot (1-f_1) \quad B_i = h_i \cdot f_2 \quad b_i, d_i, e_i, h_i, k_i: \text{CO/Pt} \]

\[ D_i = d_i \cdot f_1 + d_{di} \cdot (1-f_1) \quad C_i = k_i \cdot f_2 \quad b_{di}, d_{di}, e_{ei}: \text{C,O/Pt} \]

\[ E_i = e_i \cdot f_1 + e_{ei} \cdot (1-f_1) \]

\[ f_1 = \exp(- (r_i - r_{eq})^2 \cdot a_1) \; ; \; f_2 = \exp( (r_i - r_{eq})^2 \cdot a_2): \text{switching functions} \]

Potential parameters for CO/Pt are fitted to reproduce the experimental vibrational frequencies of adsorbed CO.
--- Normal Mode Analysis ---

\[ |H - E \lambda| = 0 \]

**Force matrix:**

\[
H = \frac{1}{\sqrt{m_i m_j}} \frac{\partial^2 V}{\partial R_{j\beta} \partial R_{i\alpha}}
\]

The potential parameters are obtained by minimization of the function:

\[
SU = \left( V_{\text{Top}}(\mathbf{x}) - V_{\text{Top}}^{\text{ex}} \right)^2 + \left( V_{\text{Br}}(\mathbf{x}) - V_{\text{Br}}^{\text{ex}} \right)^2 + \left( \frac{\partial V}{\partial \mathbf{Z}} \bigg|_{\text{Top}} \right)^2 + \left( \frac{\partial V}{\partial \mathbf{Z}} \bigg|_{\text{Br}} \right)^2
\]

\[
+ \sum_{k, \text{Top}} \left( \omega_{k, \text{Top}}(\mathbf{x}) - \omega_{k, \text{Top}}^{\text{ex}} \right)^2 + \sum_{k, \text{Top}} \left( \omega_{k, \text{Br}}(\mathbf{x}) - \omega_{k, \text{Br}}^{\text{ex}} \right)^2
\]
<table>
<thead>
<tr>
<th>$\nu_1$</th>
<th>$\nu_2$</th>
<th>$\nu_3$</th>
<th>$\nu_4$</th>
<th>$\nu_5$</th>
<th>$\nu_6$</th>
<th>$V_0$(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>On Top</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2084.$^a$</td>
<td>469.$^c$</td>
<td>387.$^b$</td>
<td>48.5$^b$</td>
<td></td>
<td></td>
<td>−1.30$^e$</td>
</tr>
<tr>
<td>2036.</td>
<td>451.</td>
<td>307.</td>
<td>64.</td>
<td></td>
<td></td>
<td>−1.40</td>
</tr>
<tr>
<td><strong>Bridge</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1850.$^{a,b}$</td>
<td>425.$^b$</td>
<td>369.$^f$</td>
<td>350.$^d$</td>
<td>141.$^b$</td>
<td>60.$^b$</td>
<td>−1.14$^e$</td>
</tr>
<tr>
<td>2007.</td>
<td>319.</td>
<td>261.</td>
<td>178.</td>
<td>88.</td>
<td><strong>185i</strong></td>
<td>−0.97</td>
</tr>
</tbody>
</table>

- $^d$ Baró, Ibach J.C.P. 71,4812,(1979)

Cacciatore et al: JPC. 2004
Contour plot of the CO-Pt(111) interaction potential

Bridge perpendicular

$E_{\text{act}} = 0.94\text{eV}$

$r \ (\text{CO}) = 2.3 \ \text{Å}$

$Z \ (\text{CO-Pt}) = 1.76\text{Å}$

*Cacciatore, Rutigliano* J. Phys. Chem. 2004
Intramolecular potential: $\text{CO}_2/\text{Pt}(111)$
COLLISIONAL MODELS: Effects to account for

- number and complexity of the effects and phenomena is high
  - many basic questions are still far from being solved

approximate collisional methods

CLASSICAL

SEMICLASSICAL

QUANTUM
Classical Trajectory Method

\[ H_{cl} = \sum_i \left( \sum_{\xi=x,y,z} \frac{P_{i,\xi}^2}{2M_i} \right) + \sum_{\alpha} \left( \sum_{\xi=x,y,z} \frac{P_{\alpha,\xi}^2}{2M_\alpha} \right) + \sum_{i,j} V_g(R_{i,j}) + \sum_{\alpha,\beta} V_S(R_{\alpha,\beta}) + \sum_{i,\alpha} V_I(R_{i,\alpha}) \]

Potential of the surface

\[ V_S \Rightarrow V_{\alpha,\beta} = \frac{1}{2} K (R_{\alpha,\beta} - R_{eq}) \]

Adiabatic interaction potential

\[ \text{force constant} \]

Hamilton’s eq.s of motion

\[ \begin{align*}
\frac{\partial P_{i,\alpha}}{\partial t} &= -\frac{\partial H_{cl}}{\partial \xi_i} \\
\frac{\partial \xi_i}{\partial t} &= \frac{P_{i,\xi}}{M_i} \\
\frac{\partial P_{\alpha,\xi}}{\partial t} &= -\frac{\partial H_{cl}}{\partial \xi_\alpha} \\
\frac{\partial \xi_\alpha}{\partial t} &= \frac{P_{\alpha,\xi}}{M_\alpha}
\end{align*} \]
Initial variables

1) $$E_{\text{coll}}$$ collisional energy
2) $$(\theta, \phi)$$ direction of incident
3) $$v, j$$
4) $$(x^\circ, y^\circ)$$: aiming point
5) $$(\theta, \gamma)$$ orientation angles
6) Lattice atom coordinates

$$\xi_{\alpha} = \xi_{\alpha}^0 + \sqrt{\frac{2K_B T_S}{K}} \cos(\varphi_{\alpha}^0)$$ phase angle: $$\varphi_{\alpha}^0$$

$$P_{\alpha\xi} = -\sqrt{2M_k K_B T_S} \sin(\varphi_{\alpha\xi}^0)$$

$$r = r_e + \beta^{-1} \ln \left[ \lambda^{-2} \left(1 - \sqrt{1 - \lambda^2} \cos \varphi \right) \right]$$ phase angle $$(0, \pi)$$: $$\varphi$$

$$\lambda = \left[1 - (2v + 1)/a \right]$$

$$a = (\hbar \beta)^{-1} \sqrt{\mu D/2}$$
ADSORPTION PROBABILITY (Si abstraction): $F_2 / \text{Si}(100)-2\times1$

MD simulation: classical dynamics

$\text{Si} + F_2 \rightarrow \text{Si-F} + F$

Theory
- Ceyer et al.
- Behringer et al.
- Li et al.
- Engstrom et al.

$\begin{align*}
\text{Si} + F_2 & \rightarrow \text{Si-F} + \text{Si-F}\,\text{diss.} \\
\text{Si} + F_2 & \rightarrow \text{Si} + F_2\,\text{inel.}
\end{align*}$
Time-dependent collisional methods

Quantum 3D: $z, (r, \vartheta)$

- flat surfaces
- rigid surfaces

$V(t)$, $R(t)$, $\mathbf{V}(t)$, $\mathbf{R}(t)$

- $H_2$, $O_2$, and other diatomics on metals Cu, W, Ag, … graphite
Semiclassical approaches

\[ E_{\text{coll}} > E_{\text{act}} \]

Fully dimension

\[ \Rightarrow \text{phonon and e-h: quantization} \]
\[ \Rightarrow \text{molecular motions: } (X,Y,Z, r \ldots) : \text{classical} \]

\[ E_{\text{coll}} < E_{\text{act}} \]

Reduced dimension

\[ \bullet \text{phonons + e-h: quantum} \]
\[ \bullet \text{(Z, r): quantum} \]
\[ \bullet \text{(X,Y,\ldots) classical} \]

Formally complex

\begin{itemize}
  \item input/output
  \item computational time demand
\end{itemize}

Computationally affordable

\begin{itemize}
  \item \textit{parallel implementation}
Semiclassical Collisional Approach

- dynamics of the gas-phase atom/molecule
- phonon/electron dynamics

Classical

\[ H_{\text{eff}}(t, T_S) \]

Quantum

\[ H_{\text{eff}}^{ph} = \langle \Psi_{\text{ph}} | V_I | \Psi_{\text{ph}} \rangle \]

\[ H_{\text{eff}}^{e-h} = \langle \Psi_{\text{eh}} | V_c | \Psi_{\text{eh}} \rangle \]

\[ |\Psi(t)\rangle = U_I(t, t_0) |\Psi(t_0)\rangle \]

\[ V_I : \text{interaction potential} \]
Electron-hole pair excitation

\[ V_c = \frac{\Delta e}{R_{eq}} \]

The molecular motion is damped by the electronic transition

\[ H_{eff} = \langle \Psi_\alpha | H_e | \Psi_\alpha \rangle \]

\[ H_e = \sum_{i=1}^{N} H_i; \quad H_i = H_i + \frac{\Delta e^2}{|R(t) - r_i|} \]
Matrix elements: \[\langle \phi_i | V | \phi_j \rangle\]

1D Model:

\[U(x) = 2U_0 \cos \left( \frac{2\pi x}{a} \right)\]

Potential: Black pot.

\[\phi_k(x) = \sum_{G} \phi_{G}(k-G)x\]
Case studied focused on:

dissociative chemisorption and atom recombination

- $O + O / \beta$-cristobalite, $\beta$-quartz
- $H + H /$ graphite
- $H_2, H + H / Cu(100)$
- $N+N / \beta$-cristobalite
- $O+O / ZrB_2$
- $CO/ \text{SnO}_2; \text{MgO}$  \hspace{1cm} $Xe/\text{GaSe}(001)$
- $C+O / \text{Pt}(111)$  \hspace{1cm} $CO_2/ \text{Pt}(111)$  \hspace{1cm} $CH_4/\text{zeolite}$

_Cacciatore, Rutigliano, Sanna, Piermarini, Ciriaco, Bedra et al._
Main features:

- Influence of the vibrationally excited states
- *Reaction mechanism*
- *Energy disposal* in the product states
- *Phonon versus electron excitation*

Surface effects:

- Temperature
- *Absorption site, Surface coverage etc*
Phonons versus electron-holes excitation mechanism

H₂ + Cu(111) ----→ H + H + Cu(111)

**STICKING PROBABILITY** as a function of approach angle and the screening parameter $a$ ($K_c = a K_F$)

<table>
<thead>
<tr>
<th>$\Theta/a$</th>
<th>0.00</th>
<th>0.25</th>
<th>0.50</th>
<th>0.75</th>
<th>$\infty$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°</td>
<td>1.00</td>
<td>0.95</td>
<td>0.33</td>
<td>0.35</td>
<td>0.35</td>
</tr>
<tr>
<td>15°</td>
<td>1.00</td>
<td>0.85</td>
<td>0.30</td>
<td>0.20</td>
<td>0.35</td>
</tr>
<tr>
<td>30°</td>
<td>0.76</td>
<td>0.30</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>45°</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

*Cacciatore, Billing Susf.Sci. 1990*
1) \( \text{O} + \text{SiO}_2 \rightarrow \text{O}_{\text{ad}} \text{SiO}_2 \)

2) \( \text{O} + \text{O}_{\text{ad}} \rightarrow \text{O}_2(v,j) + \Delta E \)
Silica structure

Bulk structure:

Surface layer structure: bonding defects

2-membered rings

3-membered rings
E-R Reaction Probability: O on $\beta$-cristobalite $T_S = 1000K$
Experimental and Theoretical Recombination coefficient $\gamma(T)$

: E-R versus L-H dynamics  \[\text{O + O + silica} \rightarrow \text{O}_2(v) + \text{silica}\]

Rutigliano, Cacciatore, Balat; 2002-2004
Elementary Surface Processes

The energy flux to the surface is the result of a complex collisional mechanism involving various surface processes.

\[ \text{Products} = \begin{cases} O_2(v,j) & (\alpha) \text{ reaction} \\ O_{\text{gas}} + O_{\text{gas}} & (\beta) \text{ inelastic} \\ \frac{(O_{\text{ad}} + O_{\text{gas}})}{(O_{\text{gas}} + O_{\text{ad}})} & (\delta) \text{ adsorption/desorption} \\ \frac{(O_{\text{ad}} + O_{\text{ad}})}{[O_2]_{\text{ad}}} & (\gamma) \text{ adsorption} \end{cases} \]
Reaction probability for the different surface processes

\[ \text{Inelastic} \]

\[ \text{O}_{\text{gas}} + \text{O}_{\text{ads}} \cdot \text{silica} \rightarrow \text{O}_{\text{gas}} + \text{O}_{\text{gas}} + \text{silica} \]

\[ \text{Adsorption/Desorption} \]

\[ \text{O}_{\text{gas}} + \text{O}_{\text{ads}} \cdot \text{silica} \rightarrow \text{O}_{\text{gas}} + \text{O}_{\text{ads}} \cdot \text{silica} \]

\[ \text{Adsorption} \]

\[ \text{O}_{\text{gas}} + \text{O}_{\text{ads}} \cdot \text{silica} \rightarrow \text{O}_{\text{gas}} + \text{O}_{\text{ads}} \cdot \text{silica} \]

\[ \text{O}_{\text{gas}} + \text{O}_{\text{ads}} \cdot \text{silica} \rightarrow (\text{O}_2)_{\text{ads}} \cdot \text{silica} \]

\[ T = 1600K \]
REACTION ENERGETICS:

\[ \text{O} + \text{O}_{\text{ad}} + \text{silica} \rightarrow \text{O}_2 (v, j) + \text{silica} \]

\[ E_{\text{vib}} \]
\[ \Delta E_{\text{ph}} \]
\[ E_{\text{rot}} \]
\[ E_{\text{tr}} \]

\[ T_s = 1000 \text{K} \]
Vibrational population distribution: $O + O_{\text{ad}} + \text{silica} \rightarrow O_2(v,j) + \text{silica}$

$E_{\text{kin}} = 0.003 \text{eV}$

Non-thermal distr.s

$T_S = 1000 \text{K}$
**ADSORPTION PROCESSES**

- **highly exothermic**
- **chemical damage**

The reaction involves the interaction of oxygen with adsorbed oxygen:

\[ O + O_{ad} \rightarrow [O_2]_{ad} \rightarrow O + O_{ad} \]

Energy transferred to the surface in the reaction:

\[ \Delta E_{ph} / eV \]

![Graph showing the interaction time (\( \tau \)) and energy (\( \Delta E_{ph} \))](image)

- Interaction time (\( \tau \)) from 0 to 60
- Energy transferred (\( \Delta E_{ph} \)) from 0 to 2.0 eV
\( \Delta E_{ph} = 40\% \quad : \text{oxygen covered surface} \)

\( \Delta E_{ph} = 10\% \quad : \text{clean surface} \)
**SILICA SURFACE**

**β-quartz**
- Bonding angle O-Si-O: 108°
- Bonding length Si-O: 1.6Å
- Distance O-O: 2.6 Å

**β-cristobalite**
- Bonding angle O-Si-O: 109.48°
- Bonding length Si-O: 1.54Å
- Distance O-O: 2.54 Å

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Experimental Results (1)

Recombination Coefficient $\gamma$

- $\gamma_0$
- $0.1$
- $0.01$
- $0.001$

SiO$_2$ quartz

SiO$_2$ $\beta$-cristobalite

$1000/T$ (1/K)
Site Ontop

Recombination Probability vs Kinetic Energy (eV)

- $\beta$-cristobalite
- $\beta$-quartz

Cnr-IMIP Bari
**RECOMBINATION COEFFICIENT:**

Comparison between THEORY and EXPERIMENT

<table>
<thead>
<tr>
<th>Surface</th>
<th>$\gamma_{th}$</th>
<th>$\gamma_{exp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta$-quartz</td>
<td>0.008</td>
<td>0.0075</td>
</tr>
<tr>
<td>$\beta$-cristobalite</td>
<td>0.03</td>
<td>0.025</td>
</tr>
</tbody>
</table>

*MD calculations predict: $[\Delta E_{ph}]_{crist} < [\Delta E_{ph}]_{quartz}$*
CONCLUSIONS

- Good agreement has been found between the experimental and the theoretical $\gamma_0$.

- The comparison with the experimental data suggests a switching mechanism from the L-H to E-R reaction as the surface temperature increases.

- The energy accommodation coefficient $\beta \ll 1$.

- Surface damage due to the concurrence of different chemical-physics surface processes: the adsorption processes are the most effective.

  - $\Delta E_{ph}$ very large: for the adsorption processes.

  - Adsorption of atomic oxygen: chemical damage (formation of SiO$_x$ compounds).