Development of a Detailed Surface Chemistry Framework in SPARTA

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Acknowledgments

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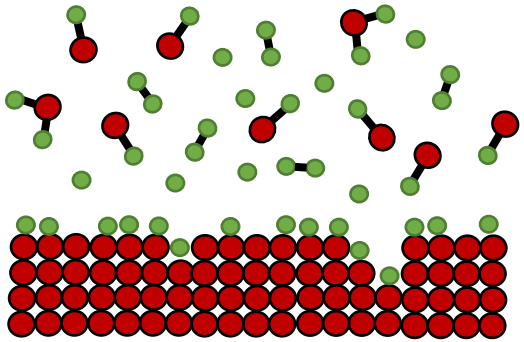
Outline

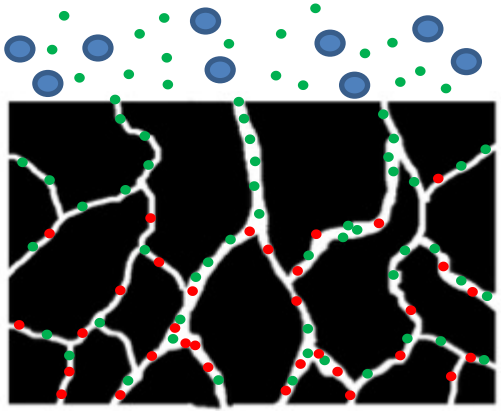
- Motivation
- Overview of Surface Chemistry Framework
- Gas-Surface (GS) Reactions
- Pure-Surface (PS) Reactions
- Applications
- Parallelization strategies
- Summary and Future Work

Motivation

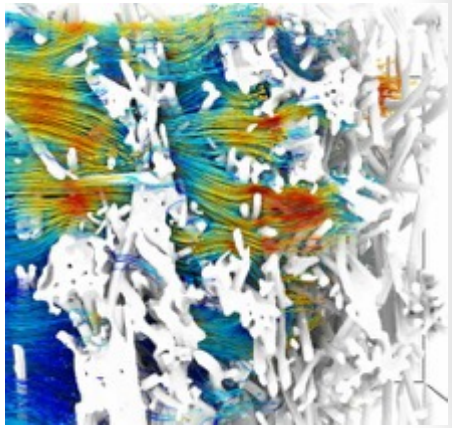


Adsorption and reactive surface chemistry

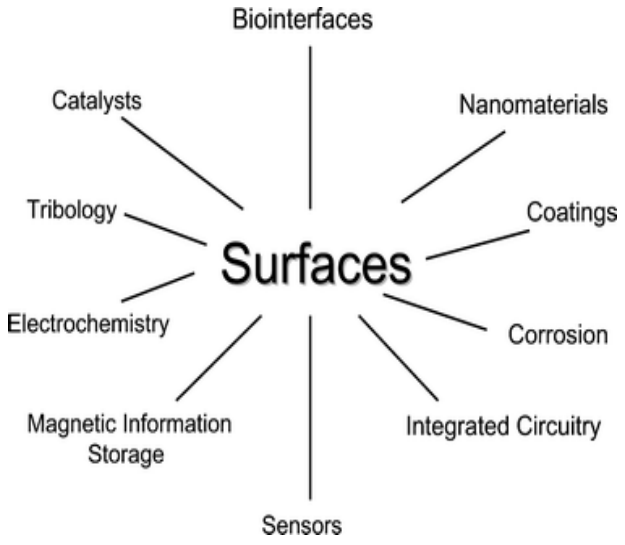
Ablative TPS
Image credit: NASA



Surface chemistry at microporous catalysts.



Flow through porous preform carbon TPS using SPARTA. Image credit: Sandstorm



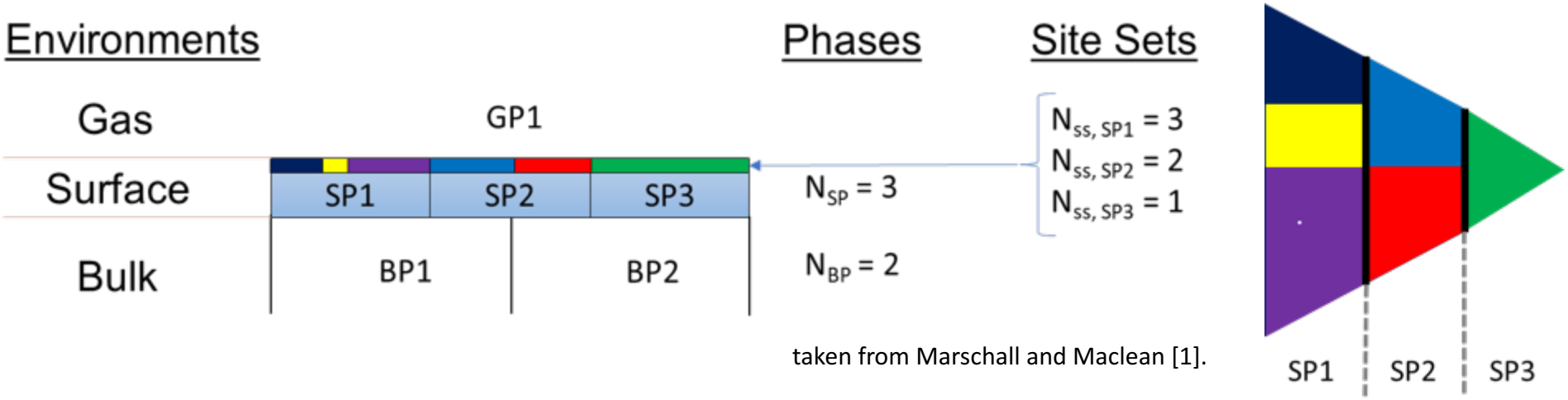
Somorjai and Li [1]

Objective:
To construct a general, detailed physics-based surface chemistry framework in DSMC.

[1] Somorjai, G. A., & Li, Y. (2010). Introduction to surface chemistry and catalysis. John Wiley & Sons.

Computational framework

- Finite-rate surface chemistry module with adsorption.
- Includes gas-surface (GS) and pure-surface (PS) reactions.
- Both catalytic and surface altering (oxidation/nitridation) reactions.
- Computational framework similar to Marschall, Maclean and Driver [2,3] for CFD.
- Langmuir model for surface sites.
- Diverse VDF and angular distributions of scattered products.

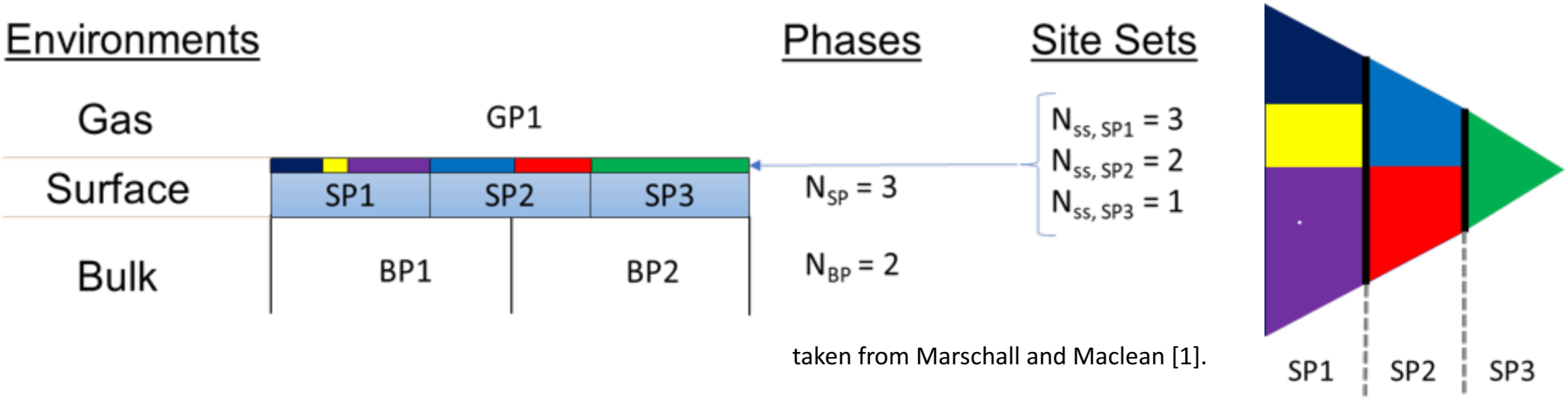


taken from Marschall and Maclean [1].

[3] Marschall, J., & MacLean, M. (2011). Finite-rate surface chemistry model, I: Formulation and reaction system examples. AIAA Paper, 3783, 2011.
[3] MacLean, M., Marschall, J., & Driver, D. M. (2011). Finite-rate surface chemistry model, II: coupling to viscous Navier–Stokes code. AIAA Paper, 3784, 2011.

Computational framework

- Particles adsorbed (deleted) and desorbed (created), surface element stores adsorbed particle concentration.
- Surface reactions based on concentration within surface element.
- Multiple triangulated elements (like cells) on surfaces
- Surface treated as infinite sink and source.



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[3] Marschall, J., & MacLean, M. (2011). Finite-rate surface chemistry model, I: Formulation and reaction system examples. AIAA Paper, 3783, 2011.
[3] MacLean, M., Marschall, J., & Driver, D. M. (2011). Finite-rate surface chemistry model, II: coupling to viscous Navier–Stokes code. AIAA Paper, 3784, 2011.

List of gas-surface (GS) reactions

- Reactants include both gas-phase and surface species.
- Comprehensive set of reactions – Includes reaction types from thermal regime and hyperthermal energy regime.

Symbol	Reaction type	Examples
1: AA	Associative Adsorption	$O(g) + (s) \longrightarrow O(s)$ $O_2(g) + (s) \longrightarrow O_2(s)$
2: DA	Dissociative Adsorption	$O_2(g) + (s) \longrightarrow O(s) + O(g)$ $O_2(g) + 2(s) \longrightarrow 2O(s)$
3: DIS	Dissociation	$O_2(g) + (s) \longrightarrow 2O(g) + (s)$ $CO_2(g) + (s) \longrightarrow 2O(g) + (s) + C(b)$
4: LH1	Langmuir-Hinshelwood type 1	$O(g) + (s) + O(s) \longrightarrow O_2(g) + 2(s)$ $O(g) + (s) + C(b) \longrightarrow CO(g) + (s)$
5: LH3	Langmuir-Hinshelwood type 3	$O(g) + (s) + O(s) \longrightarrow O_2(s) + 2(s)$ $O(g) + (s) + C(b) \longrightarrow CO(s) + (s)$
6: CD	Condensation	$C_3(g) + 3(s) \longrightarrow 3C(b) + 3(s)$
7: ER	Eley-Rideal	$CO(g) + O(s) \longrightarrow CO_2(g) + (s)$
8: CI	Collision Induced	$O(g) + CO(s) \longrightarrow CO(g) + O(s)$ $Ar(g) + O(s) \longrightarrow Ar(g) + O(g) + (s)$

Modeling of gas-surface (GS) reactions

- GS reaction probability computed when gas-phase species hits surface.
- Reaction probability function of:
  - rate constant
  - gas-phase particle properties (energy, angle, etc.)
  - surface conditions (temperature, surface coverage, etc.)

Reaction type	Sample	Probability
Adsorption	$A(g) + (s) \longrightarrow A(s)$ $A_2(g) + (s) \longrightarrow 2A(s)$	$\mathrm{P} = S^{\alpha}(\theta) = f(S_0, \theta, \alpha)$
Adsorption mediated reactions: Dissociation, LH1, LH3, Condensation	$A_2(g) + (s) \longrightarrow 2A(g) + (s)$ $A(g) + (s) + B(s) \longrightarrow AB(g) + 2(s)$	$\mathrm{P} = P_{ad} * k_{reac}$ $\mathrm{P} = P_{ad} * k_{reac} * \frac{N_{B(s)} F_N}{S_p}$
Eley-Rideal	$A(g) + B(s) \longrightarrow AB(g) + (s)$	$\mathrm{P} = 2k_{reac} \frac{N_{B(s)} F_N}{S_p} \frac{1}{v_n}$
Collision Induced	$A(g) + B(s) \longrightarrow A(g) + B(g) + (s)$	$\mathrm{P} = k_{reac} \frac{N_{B(s)} F_N}{S_p} (E_{in})^m \cos^n(\theta)$

List of pure-surface (PS) reactions

- Pure-surface (PS) reactants include only surface species (adsorbed and bulk).
- Comprehensive set of reactions

Symbol	Reaction type	Examples
1: DS	Desorption	$O(s) \longrightarrow O(g) + (s)$ $O_2(s) \longrightarrow O_2(g) + (s)$
2: LH2	Langmuir-Hinshelwood type 2	$N(s) + O(s) \longrightarrow NO(g) + 2(s)$ $O(s) + C(b) \longrightarrow CO(g) + (s)$
3: LH4	Langmuir-Hinshelwood type 4	$N(s) + O(s) \longrightarrow NO(s) + (s)$ $O(s) + C(b) \longrightarrow CO(s) + (s)$
4: SB	Sublimation	$3C(b) + 3(s) \longrightarrow C_3(g) + 3(s)$

Modeling of pure-surface (PS) reactions

- Characteristic time computed between two reactions: Time counter method [5].
- Characteristic time function of
  - reaction rate constant
  - surface conditions (temperature, surface coverage, etc.).

$$\tau_{reac} = \frac{-log(Rn)}{\nu_{reac}}$$

- Time counter algorithms developed to be independent of dt.

Reaction type	Sample	Frequency
Desorption Sublimation	$A(s) \longrightarrow A(g) + (s)$	$\frac{dn_{A(s)}}{dt} = -k_{reac} n_{A(s)}$ $\nu_{reac} = k_{reac} N_{A(s)}$
LH-2, LH-4	$A(s) + B(s) \longrightarrow AB(g) + 2(s)$	$\frac{dn_{A(s)}}{dt} = \frac{dn_{B(s)}}{dt} = -k_{reac} n_{A(s)} n_{B(s)}$ $\nu_{reac} = k_{reac} N_{A(s)} N_{B(s)} \frac{F_N}{S_p}$

[5] Molchanova, A. N., A. V. Kashkovsky, and Ye A. Bondar. "A detailed DSMC surface chemistry model." In AIP Conference Proceedings, vol. 1628, no. 1, pp. 131-138. AIP, 2014.

Scattering models

Current models in SPARTA

- Specular
- Diffuse – Maxwell's model

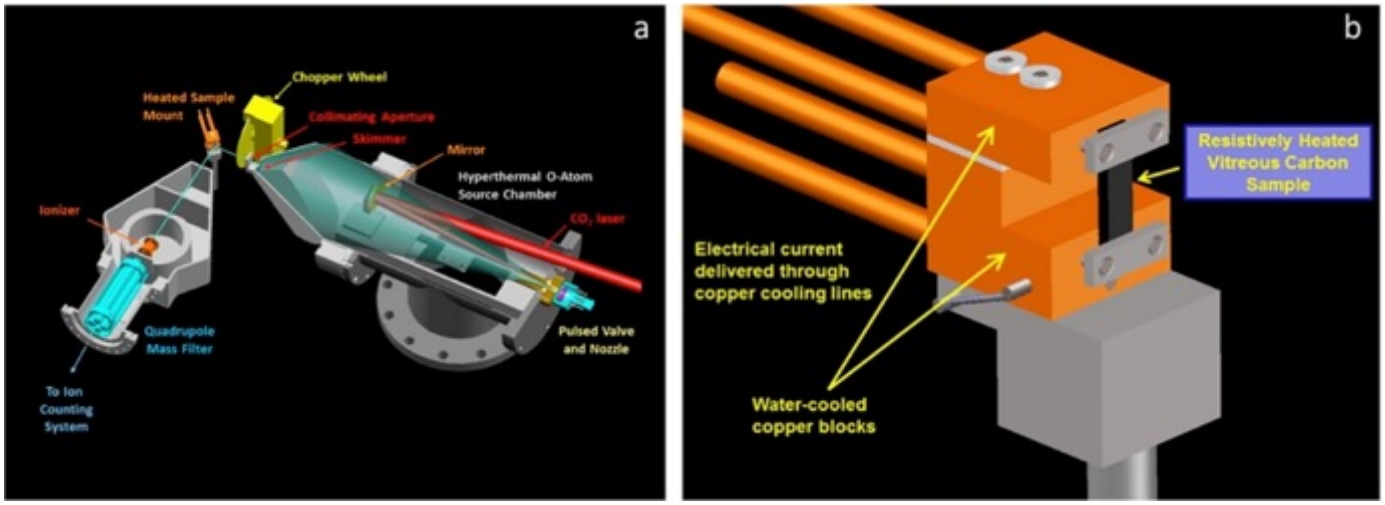
Additional models

- CLL model – Thermal regime scattering. Can capture full and partial energy and angular accommodation [6,7].
- Thermal – Thermally desorbing particles with options such as desorption barrier, additional energy transfer due to local hot-spots, etc.
- Impulsive – Structural regime scattering at hyperthermal energies.
- Non-thermal – Transition regime scattering at superthermal energies without full accommodation

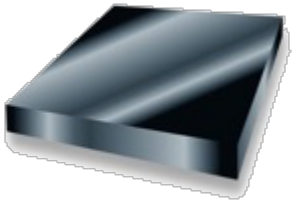
[6] Lord, R. G. (1991). Some extensions to the Cercignani–Lampis gas–surface scattering kernel. Physics of Fluids A: Fluid Dynamics, 3(4),706-710.
[7] Lord, R. G. "Some further extensions of the Cercignani–Lampis gas–surface interaction model." Physics of Fluids 7, no. 5 (1995): 1159-1161.

Application: Simulating Beam Experiments

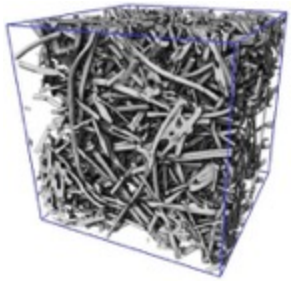
- Perform DSMC simulations of the molecular beam experiments of oxygen beam on Vitreous Carbon and Fiberform – Murray *et al* [8].
- Used to construct a finite rate surface oxidation model for carbon.



Murray *et al* [1]



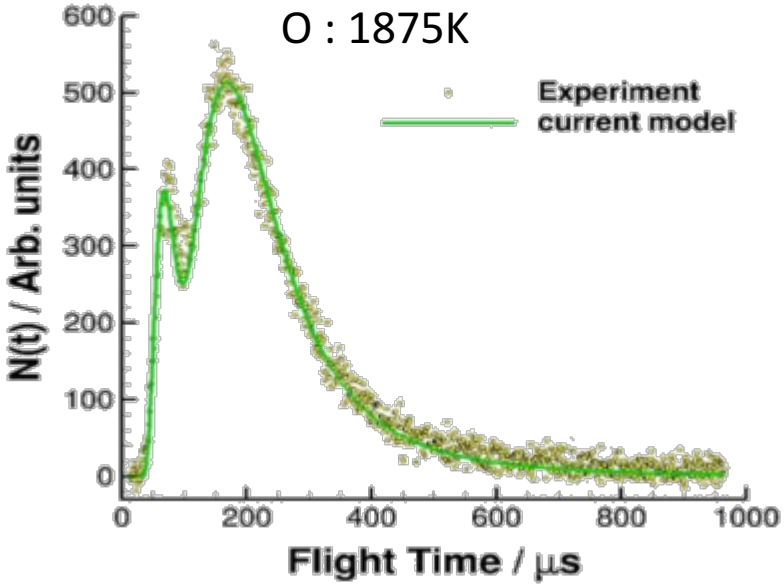
Vitreous carbon
SPI Supplies

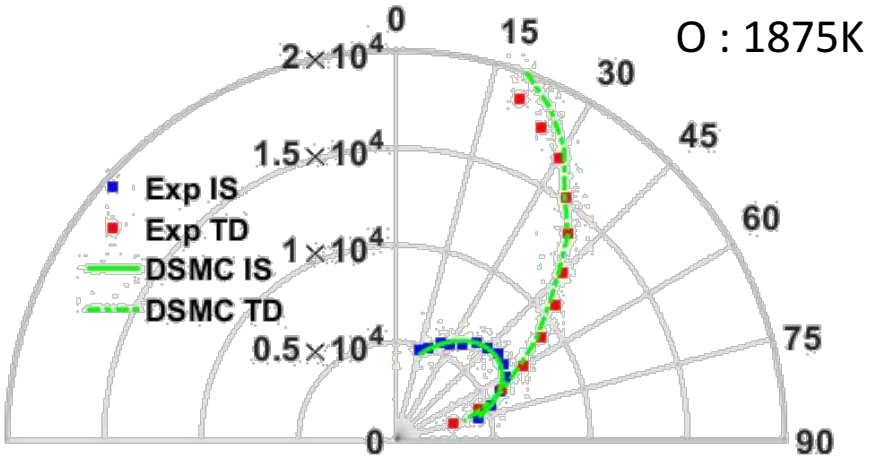


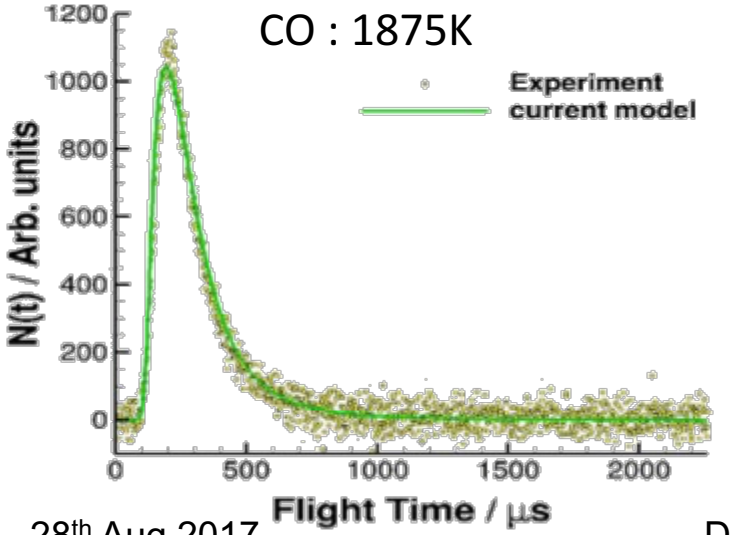
FiberForm®

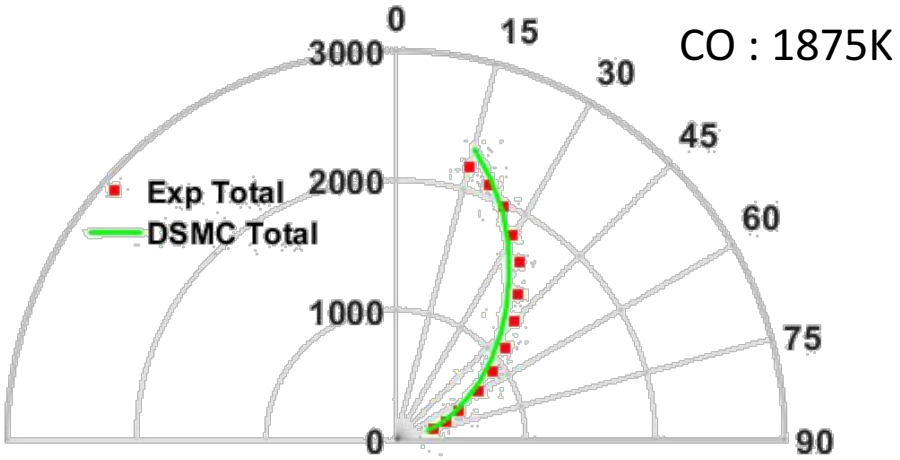
[8] Murray, V J., et al. "Inelastic and Reactive Scattering Dynamics of Hyperthermal O and O2 on Hot Vitreous Carbon Surfaces." *The Journal of Physical Chemistry C* 119.26 (2015): 14780-14796.

Application: Vitreous Carbon Oxidation Model









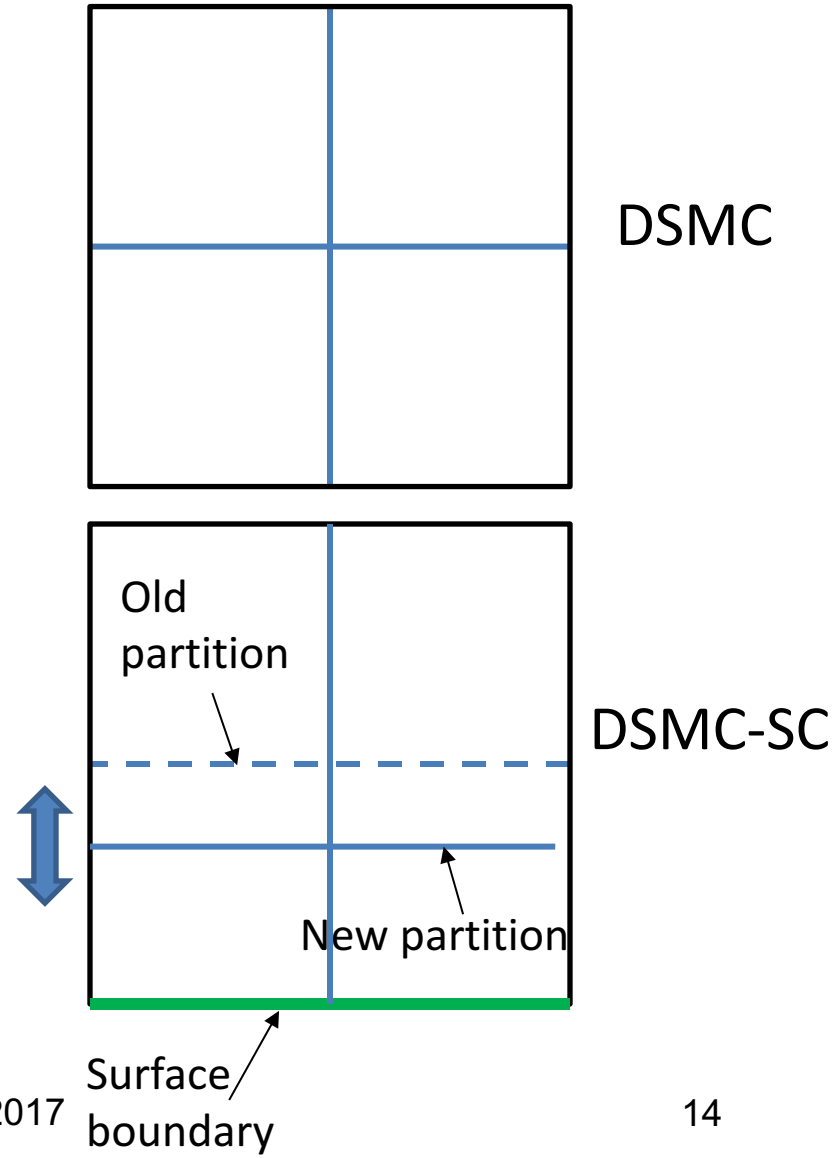
Application: Vitreous Carbon Oxidation Model

Mechanisms	Reaction	Rate constant (k)
Adsorption	$O + (s) \longrightarrow O(s)$	$\frac{1}{4\Phi}\sqrt{\frac{8k_bT_g}{\pi m}} * 0.87$
LH3 CO{a} formation	$O + (s) + O'(s) + C(b) \longrightarrow CO\{a\}(s) + O'(s)$	$\frac{1}{4\Phi}\sqrt{\frac{8k_bT_g}{\pi m}} * 3.8027\ exp(-\frac{4243.3}{T_s})$
LH3 CO{b} formation	$O + (s) + O'(s) + C(b) \longrightarrow CO\{b\}(s) + O'(s)$	$\frac{1}{4\Phi}\sqrt{\frac{8k_bT_g}{\pi m}} * 8.7351\ exp(-\frac{1468.2}{T_s})$
LH1 O formation	$O(IS) + (s) \longrightarrow O(TD) + (s)$	$\frac{1}{4\Phi}\sqrt{\frac{8k_bT_g}{\pi m}} * 3.0237\ exp(-\frac{3034.5}{T_s})$
LH1 CO formation	$O + (s) + O'(s) + C(b) \longrightarrow CO + (s) + O'(s)$	$\frac{1}{4\Phi}\sqrt{\frac{8k_bT_g}{\pi m}} * 73.006\ exp(-\frac{5978.8}{T_s})$
LH1 CO_2 formation	$O + O(s) + 4O'(s) + C(b) \longrightarrow CO_2 + (s) + 4O'(s)$	$\frac{1}{4\Phi}\sqrt{\frac{8k_bT_g}{\pi m}} * 53.097\ exp(-\frac{231.41}{T_s})$
Desorption	$O(s) \longrightarrow O + (s)$	$270567.8\ exp\left(-\frac{5275.6}{T_s}\right)$
LH3 CO{a} desorption	$CO\{a\}(s) \longrightarrow CO\{a\} + (s)$	$8573.7\ exp\left(-\frac{2375.8}{T_s}\right)$
LH3 CO{b} desorption	$CO\{b\}(s) \longrightarrow CO\{b\} + (s)$	$0.70598\ exp\left(-\frac{1743.1}{T_s}\right)$

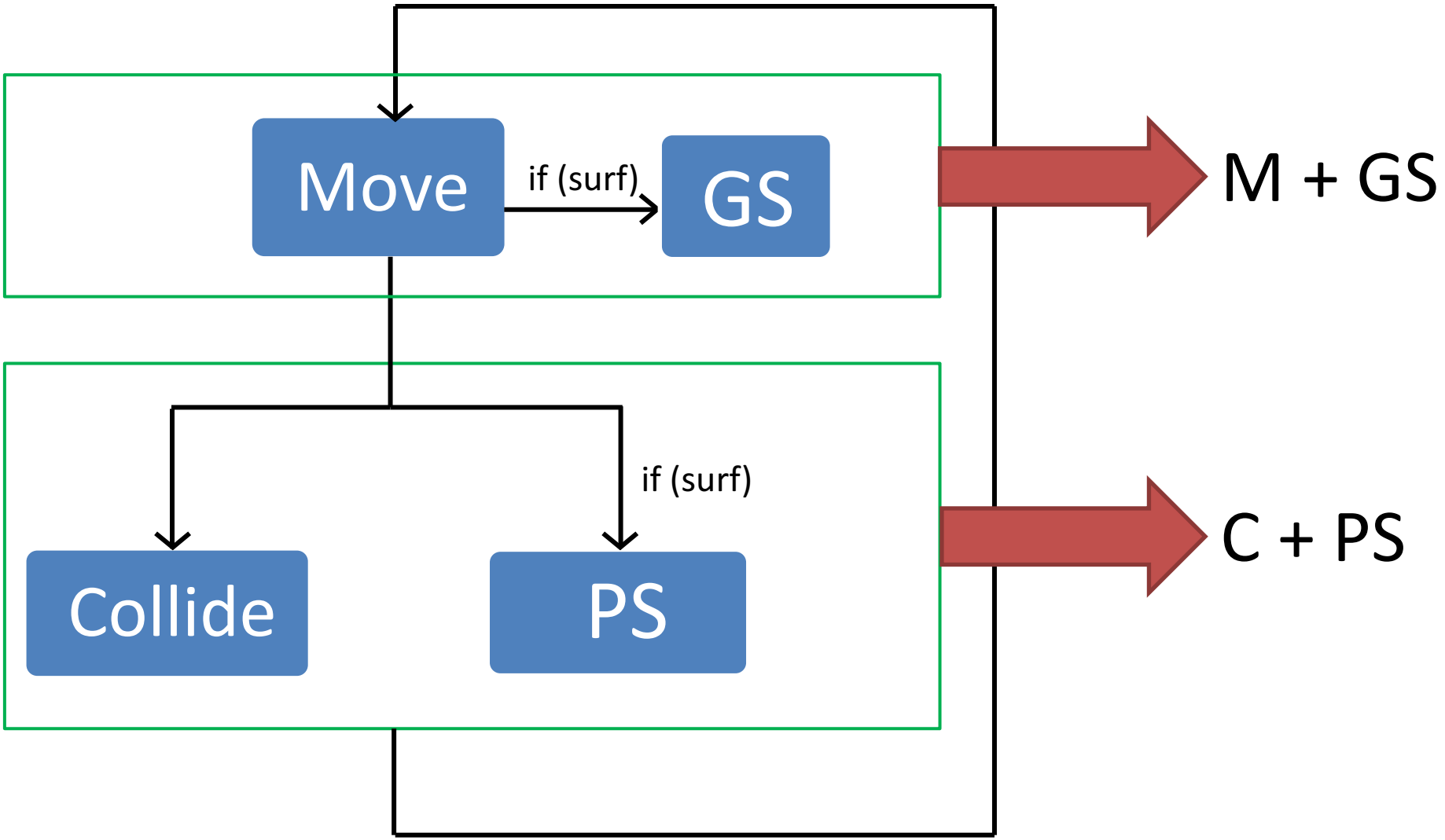
Parallelization in DSMC with surface chemistry

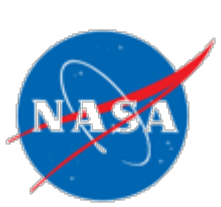
- Particle on the surface is not stored anymore (only its information).
- Parallelization based on the number of (gas-phase) particles will not work in DSMC-SC
- Two additional kernels in DSMC-SC – GS and PS reactions.

- **Move**
- **Collide**
- **GS (Gas-Surface) reactions**
- **PS (Pure-Surface) reactions**



Flowchart for DSMC-SC





Parallelization in DSMC with surface chemistry

Two strategies

1. Keep track of the computer time taken for each cell for a length of time. Use this information to partition the domain.
   - Works well for steady flows

2. Do approximate calculation of the computer time based on the information and the algorithms used.

Parallelization in DSMC with surface chemistry

- $t_{move} = O(n_p * n_{steps})\{moving\} + O(n_p * n_{steps})$ {boundary/surface/cell exit check}
- $t_{GS} = O(n_{surf\text{-}elem} * n_{surf\text{-}coll} * n_{GS\text{-}rxns})$
- $t_{collide} = O\left(\frac{0.5 * n_p^2}{V_c}\right)$ {assuming temperature and cross sections are constant}
- $t_{PS} = O(n_{surf\text{-}elem} * n_{PS\text{-}rxns\text{-}occur} * n_{PS\text{-}rxns})$ $\quad n_{PS\text{-}rxns\text{-}occur} = \frac{dt}{-\log(0.5)} \sum_{i=1}^{n_{rxn}} \nu_i$
  - ν_i α Rate(k, n_{ad}, order)

$$t_{C+PS} = t_{collide} + t_{PS} \qquad t_{M+GS} = t_{move} + t_{GS}$$

Summary and Future Work

Summary

- A general, detailed, physics-based surface chemistry framework implemented in SPARTA.
- Includes physical models with wide range of options and parameters to capture all/several experimental details.
- Capability to model various types of surface reactions accommodating user specified reaction rates, surface properties and parameters.

Future Work

- Further develop and implement parallelization strategies.
- Extension to ionization and plasma chemistry.
- Inclusion of internal energy scattering details.

Acknowledgements

- This work was performed under the Entry System Modeling Project (M. J. Wright Project Manager) at the NASA Game Changing Development (GCD) Program and supported by NASA Grant NNX15AU92A.

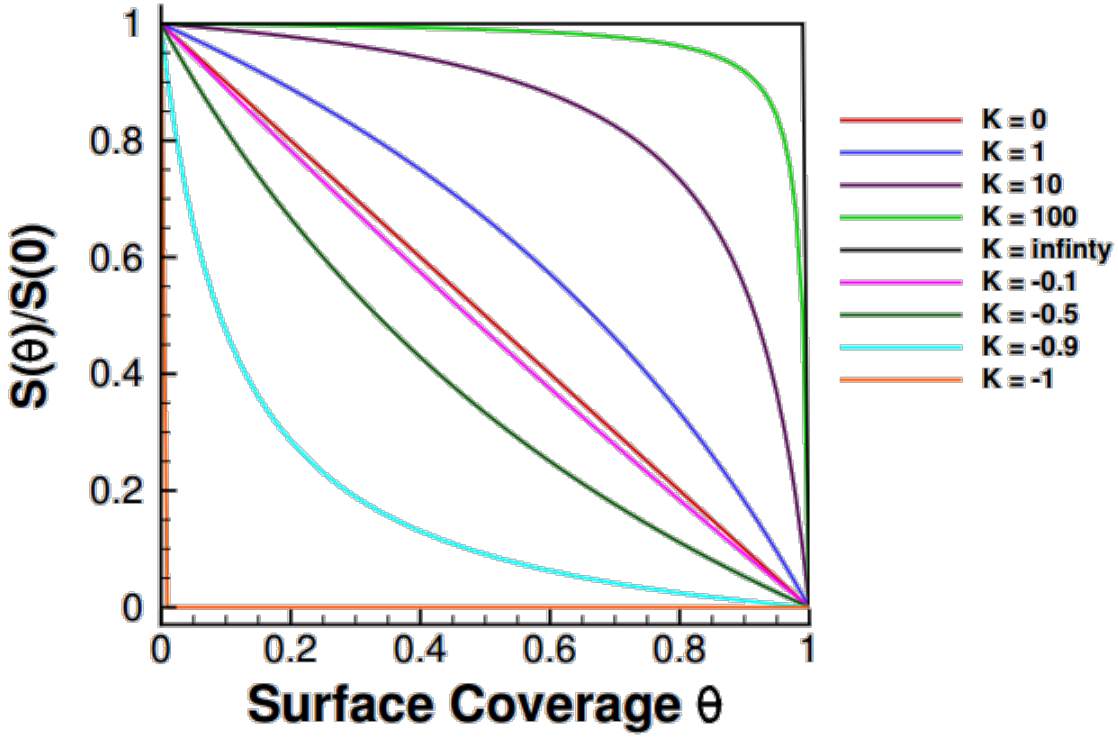
Backup Slides

Adsorption modeling

- Adsorption: direct and indirect pathways.
- Direct adsorption captured using the Langmuir model.
- Kisliuk model[4] used to capture the indirect adsorption pathway.
- K_{eq} is an additional parameter – K_{eq}=0 gives the Langmuir model.

$$\frac{S(\theta)}{S(0)} = \frac{(1+K_{eq})(1-\theta)^{\alpha}}{1+K_{eq}(1-\theta)^{\alpha}}$$

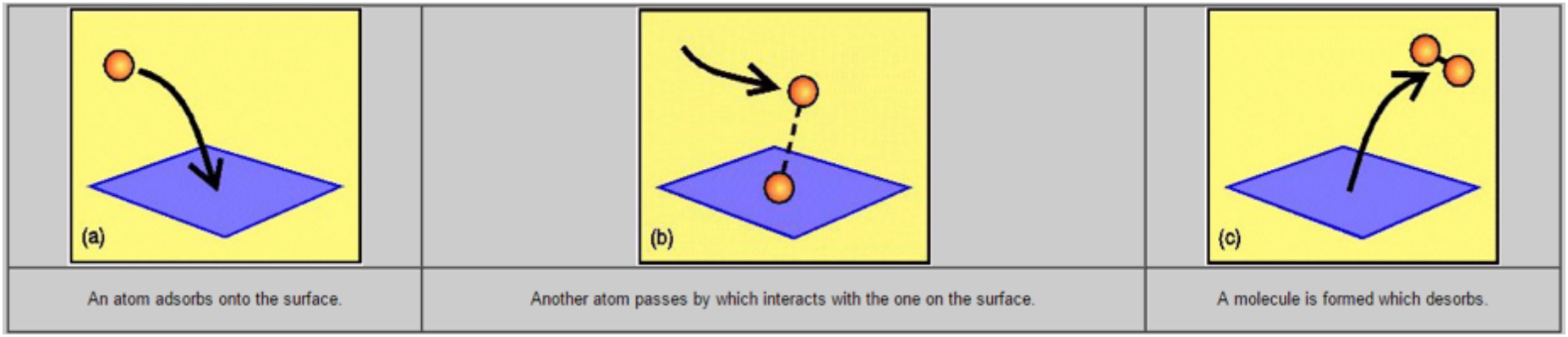
$$K_{eq} = \frac{k^*_{ads}}{k^*_{des}}$$



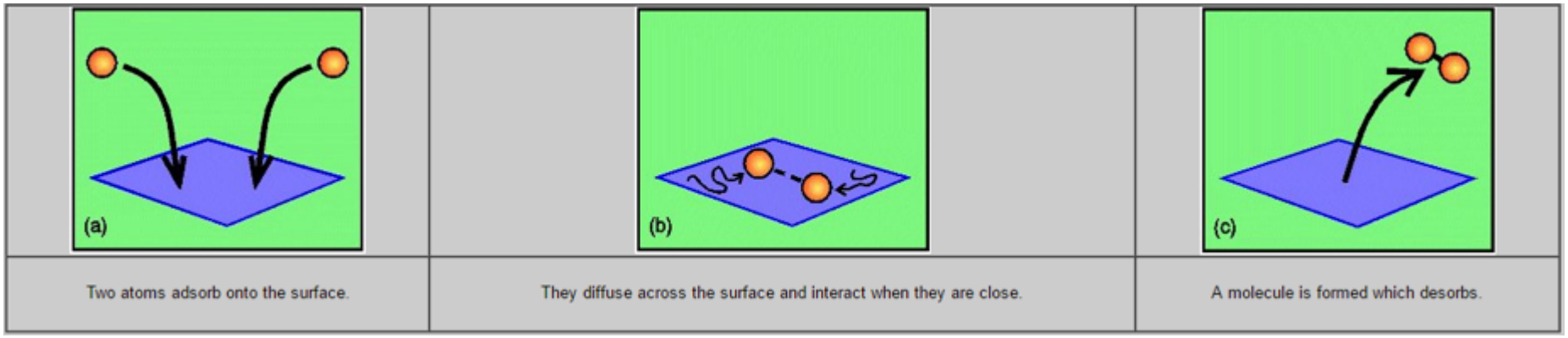
[4] Kisliuk, P. "The sticking probabilities of gases chemisorbed on the surfaces of solids." Journal of Physics and Chemistry of Solids 3, no. 1-2 (1957): 95-101.

Surface Reaction Mechanisms

Eley-Rideal (ER) mechanism : A(s) + B → AB + (s)



Langmuir-Hinshelwood (LH) mechanism : A(s) + B(s) → AB + 2(s)



From: UCL Center for Cosmic Chemistry and Physics

Different Types of LH Mechanisms

The Langmuir-Hinshelwood mechanism has two steps – Formation
Desorption

$$O(g) + (s) \rightarrow O(s)$$

$$O(s) + C(b) \rightarrow CO(s) \quad (1) - t_f$$

$$CO(s) \rightarrow CO(g) + (s) \quad (2) - t_d$$

$$O(g) + C(b) \rightarrow CO(g) \quad (3)$$

$O(s)$ – Reactant
$CO(s)$ – Intermediate
$CO(g)$ – Product

Time scale of interest = τ

Based on time scale arguments 4 types of LH mechanisms can be defined

1. $t_f << \tau$ $t_d << \tau$ - Prompt thermal mechanism
2. $t_f \sim \tau$ $t_d << \tau$ - LH limited by formation
3. $t_f << \tau$ $t_d \sim \tau$ - LH limited by desorption
4. $t_f \sim \tau$ $t_d \sim \tau$ - LH limited by both desorption and formation