Modeling of Fronts and Patterns at the Atomic level for Surface Reactions

CO oxidation on metals (100) surfaces

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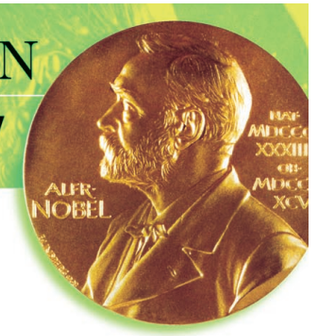
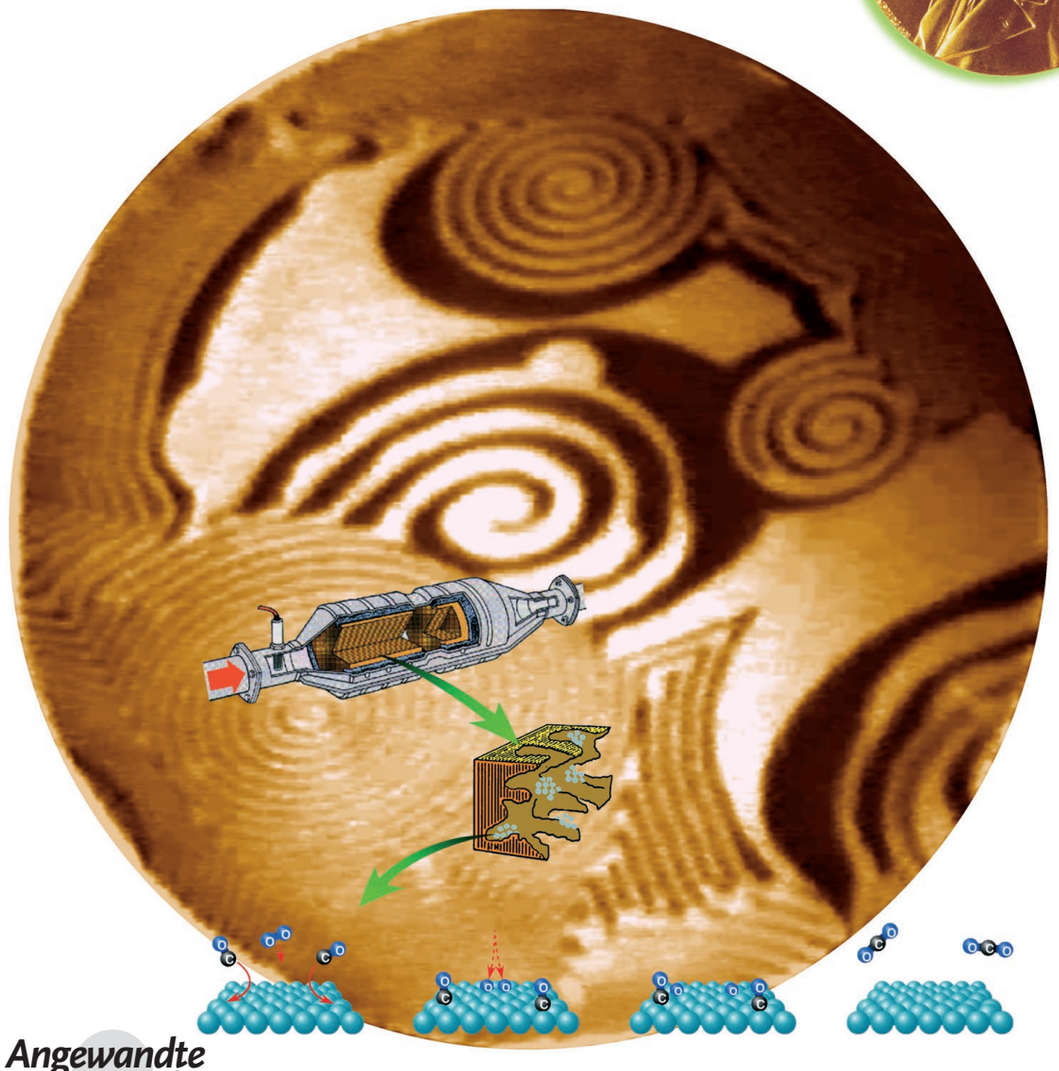
March 23, 2017
KI-Net Conference

Pattern Formation in Surface Reactions

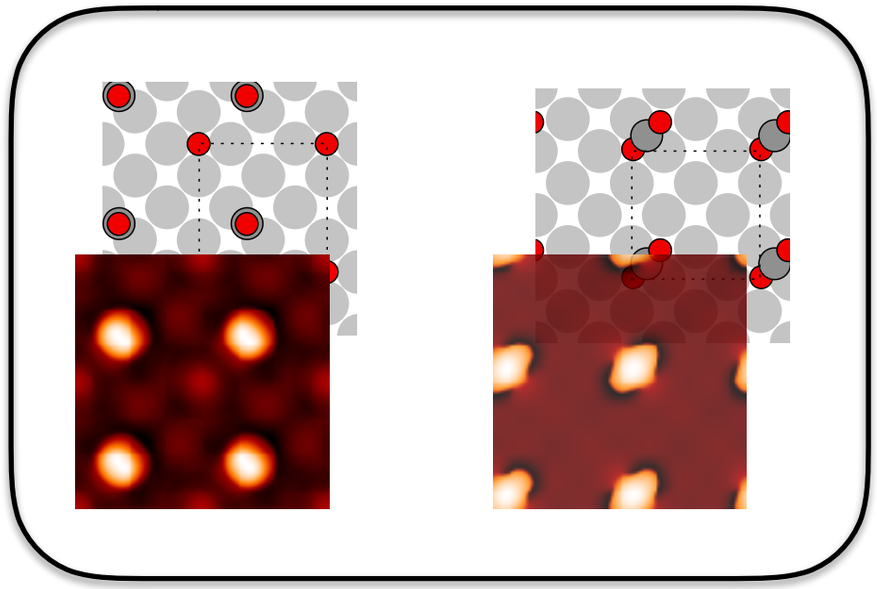
PEEM of CO oxidation on Pt(110) (Rotermund, Ertl 1993)

THE NOBEL PRIZE IN CHEMISTRY 2007

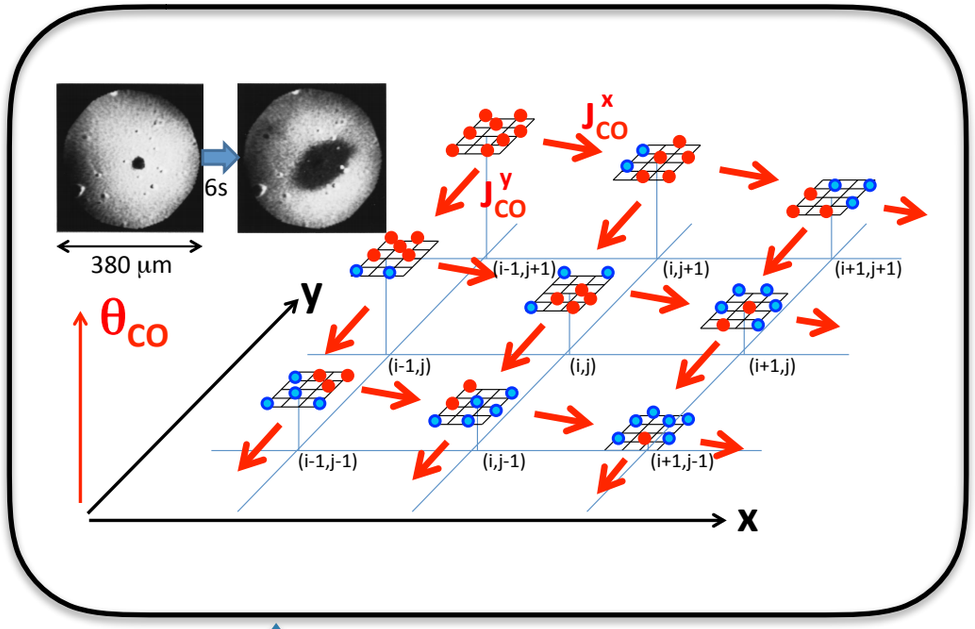




Electronic level: DFT (PW and GTO) → CCSD(T) → QMC(?) (Zahariev, Gordon, Ames Lab)



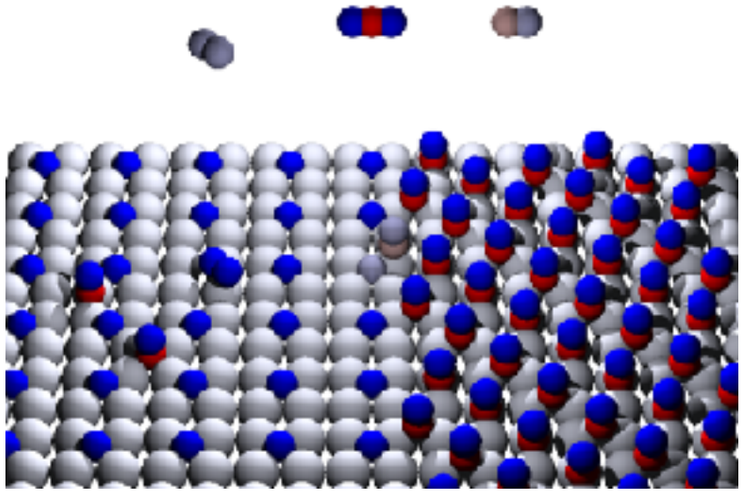
Phenom. → Cluster Expansion → machine learning(?)



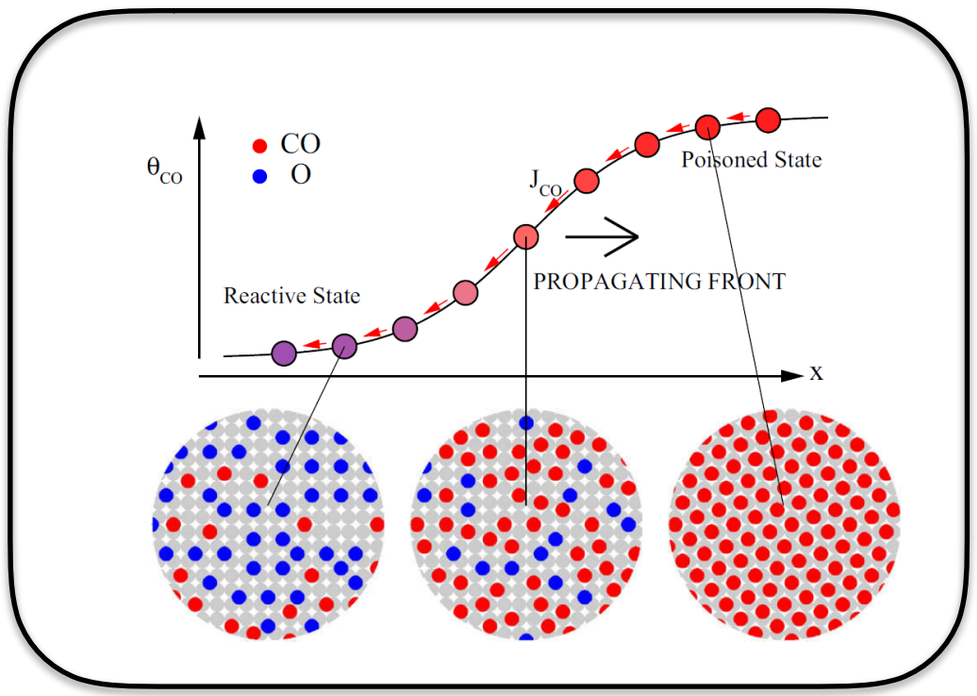
massively parallel kMC simulations (Xeon-Phi, GPU)(?)

Heterogenous coupled lattice-gas model (HCLG)

Multi-site Lattice-Gas model



Multi-species transport Onsager theory



Electronic Level

DFT (at the GGA level) is very good in determining interaction between species

- but not very good at site preference, diffusion barrier
- Inadequate for adsorption and reaction energies.

Chemical bond on metal surfaces: adsorbate interacts with whole surface rather than their nearest neighbors; single calculation using model system (periodic or cluster geometry) is not reliable

Averaging technique: varying slab thicknesses, for (100) surfaces, L=7 to 12 layers.

Multisite Lattice-Gas Model

For homogenous surfaces:

$$H = \sum_{i,\alpha} n_i^{\alpha} \epsilon_i^{\alpha} + \sum_{i<j} \sum_{\alpha,\beta} n_i^{\alpha} n_j^{\beta} \omega_{i,j}^{\alpha,\beta}(d)$$

- α denotes various species at different adsorption sites, e.g. CO(br), O(h), …
- i and j denotes various lattice sites
- Pairwise interactions only
- ω determined directly from DFT (PBE); ε from DFT corrected by CCSD(T) value of CO triplet-singlet gap.

CO-CO interactions

substrate	d/a	top-top	br-br	4fh-4fh	mixed
Pd(100)	1	0.285	0.301	0.447	
	$\sqrt{5}/2$				0.141
	$\sqrt{2}$	0.000	0.006	0.065	
	3/2				0.005
	$\sqrt{5/2}$	−0.004	0.011	−0.004	
	2	0.019	0.020	0.020	
	$3/\sqrt{2}$		0.003		
	$\sqrt{5}$		0.006		
Rh(100)	1	0.289	0.172	0.317	
	$\sqrt{5}/2$				0.109
	$\sqrt{2}$	−0.001	0.023	0.038	
	$\sqrt{5/2}$	0.009	0.009	0.009	
	2	0.016	0.027	0.024	
Pt(100)	1	0.314	0.273	0.454	
	$\sqrt{5}/2$				0.146
	$\sqrt{2}$	−0.012	0.017	0.059	
	$\sqrt{5/2}$	−0.002	0.024	−0.002	
	2	0.035	0.031	−0.002	
Ir(100)	1	0.288	0.143	0.356	
	$\sqrt{5}/2$				0.084
	$\sqrt{2}$	−0.008	0.020	0.047	
	$\sqrt{5/2}$	0.006	0.004	0.006	
	2	0.005	0.012	0.009	

CO-O interactions

substrate	d/a	top	br	4fh	mixed
Pd(100)	1	0.106	0.208	0.438	
	$\sqrt{5}/2$				0.172
	$\sqrt{2}$	−0.003	0.032	0.078	
	3/2				0.020
	$\sqrt{5/2}$	0.003	0.021	0.003	
Rh(100)	1	0.164	0.149	0.370	
	$\sqrt{5}/2$				0.154
	$\sqrt{2}$	−0.001	0.038	0.044	
	3/2				0.020
	$\sqrt{5/2}$	0.010	0.021	0.010	
Pt(100)	1	0.088	0.192	0.370	
	$\sqrt{5}/2$				0.159
	$\sqrt{2}$	−0.024	0.033	0.109	
Ir(100)	1	0.130	0.113	0.361	
	$\sqrt{5}/2$				0.129
	$\sqrt{2}$		0.023		

O-O interactions

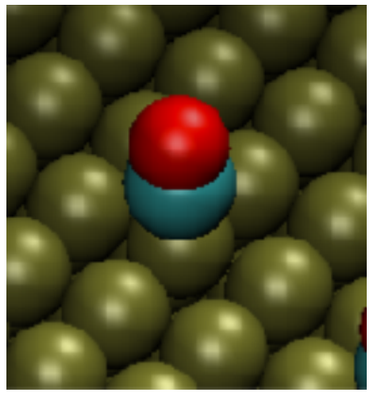
substrate	d/a	top	br	4fh	mixed
Pd(100)	1	0.142	0.219	0.368	
	$\sqrt{5}/2$				0.247
	$\sqrt{2}$	0.058	0.086	0.132	
	3/2				0.047
	$\sqrt{5/2}$	0.017	0.054	0.017	
	2		0.013	−0.036	
	$\sqrt{5}$			−0.002	
Rh(100)	1	0.148	0.238	0.464	
	$\sqrt{5}/2$				0.214
	$\sqrt{2}$	0.028	0.056	0.141	
	$\sqrt{5/2}$	0.013	0.037	0.014	
	2		0.012	−0.005	
	$\sqrt{5}/2$			0.001	
Pt(100)	1	0.045	0.208	0.339	
			−0.107(v), 0.341(g)		
	$\sqrt{5}/2$				0.188
	$\sqrt{2}$	−0.016	0.014	0.180	
	$\sqrt{5/2}$	0.003	0.015	0.003	
	2		0.060	0.003	
			0.071(v), 0.017(g)		
	$\sqrt{5}/2$		0.023		
Ir(100)	1	0.050	0.162	0.378	
			−0.077(v), 0.390(g)		
	$\sqrt{5}/2$				0.194
	$\sqrt{2}$	−0.008	0.010	0.124	
	$\sqrt{5/2}$	−0.002	0.044	−0.002	
	2		0.025	0.005	
			0.030(v), −0.020(g)		
	$\sqrt{5}/2$		−0.005		

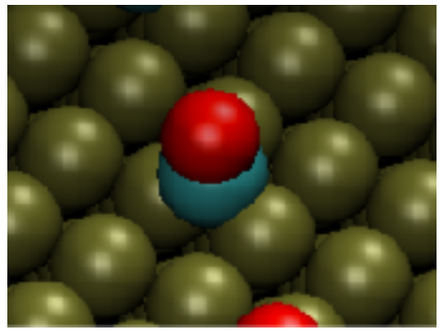
adsorption energy

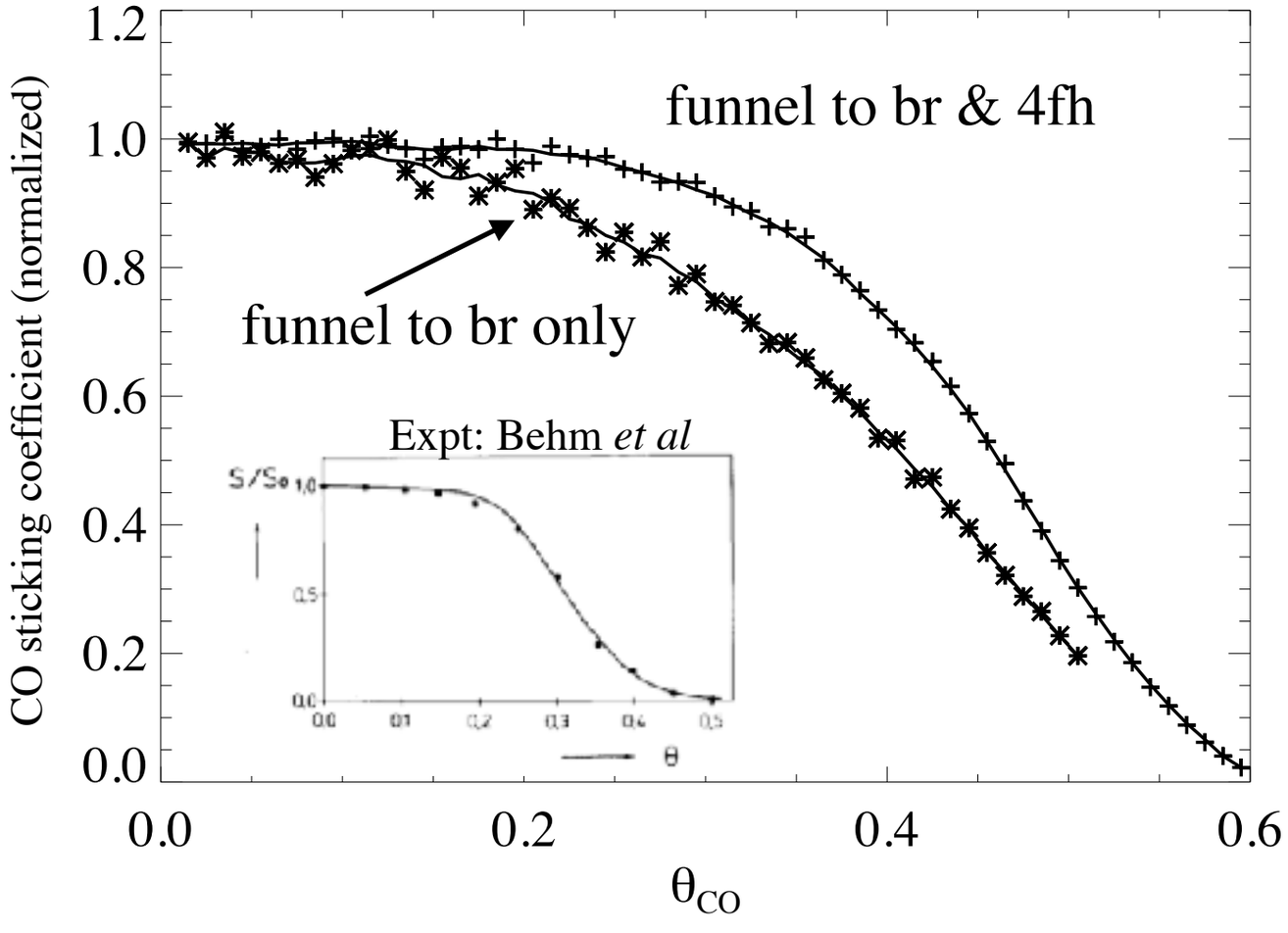
M	Pd	Rh	Pt	Ir
br CO	1.644	1.708	1.854	1.741
4fh CO	1.426	1.420	1.154	1.216
top CO	1.344	1.726	1.904	2.033
br O	0.940	1.840	1.231	1.960
4fh O	1.220	2.020	0.719	1.641
top O	−0.220	0.085	0.100	1.184

CO Adsorption Kinetics:

CO steered to top site first, then funnel to a nearby bridge site

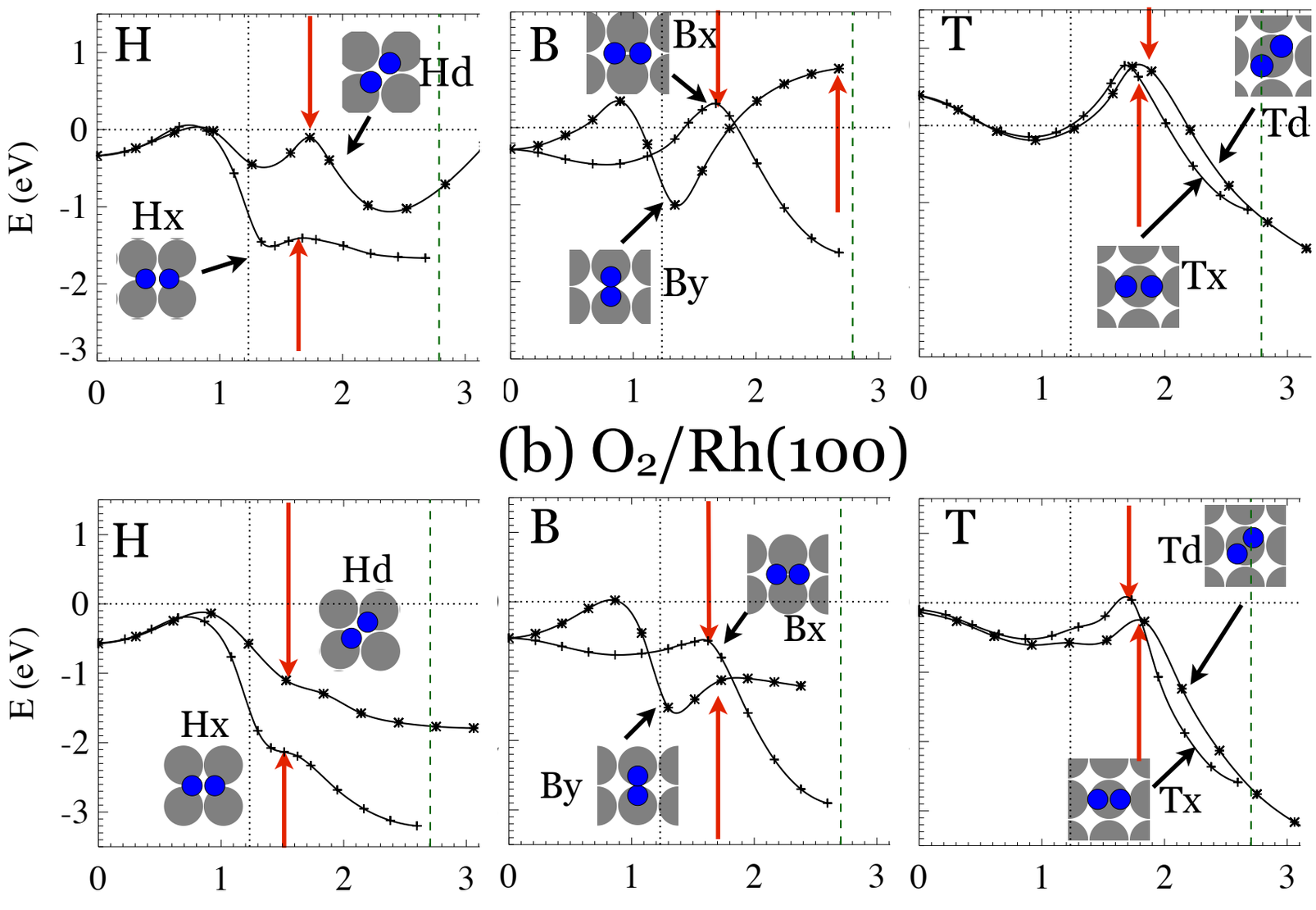






O_2 Dissociation Kinetics:

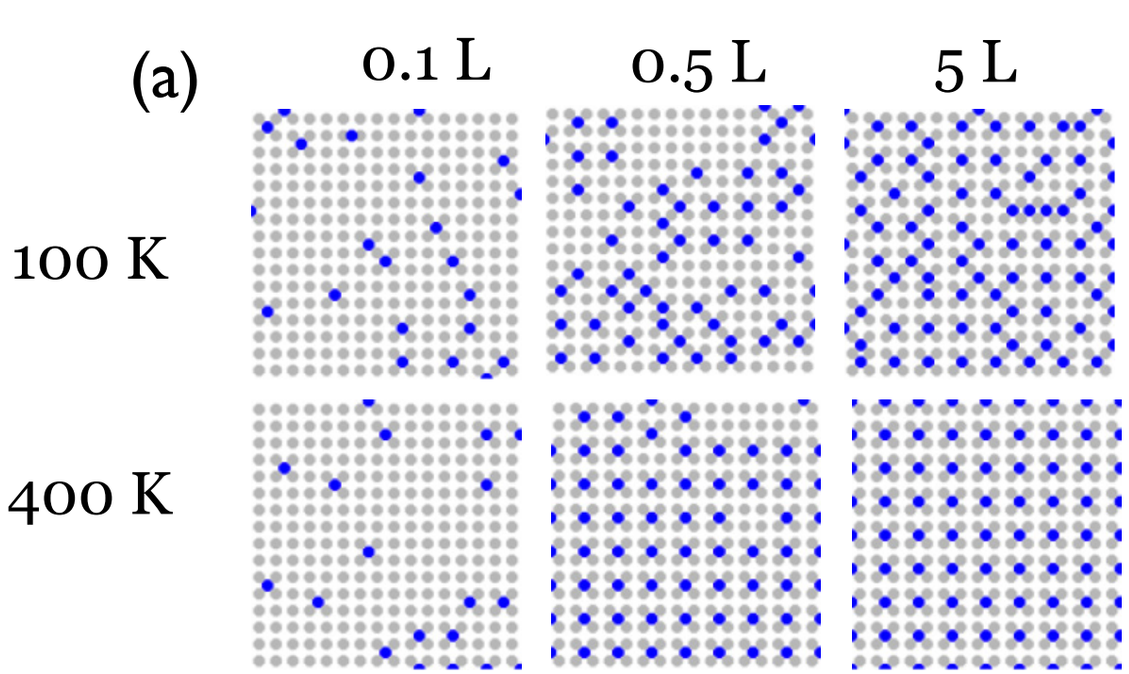
Constrained minimal energy path from DFT

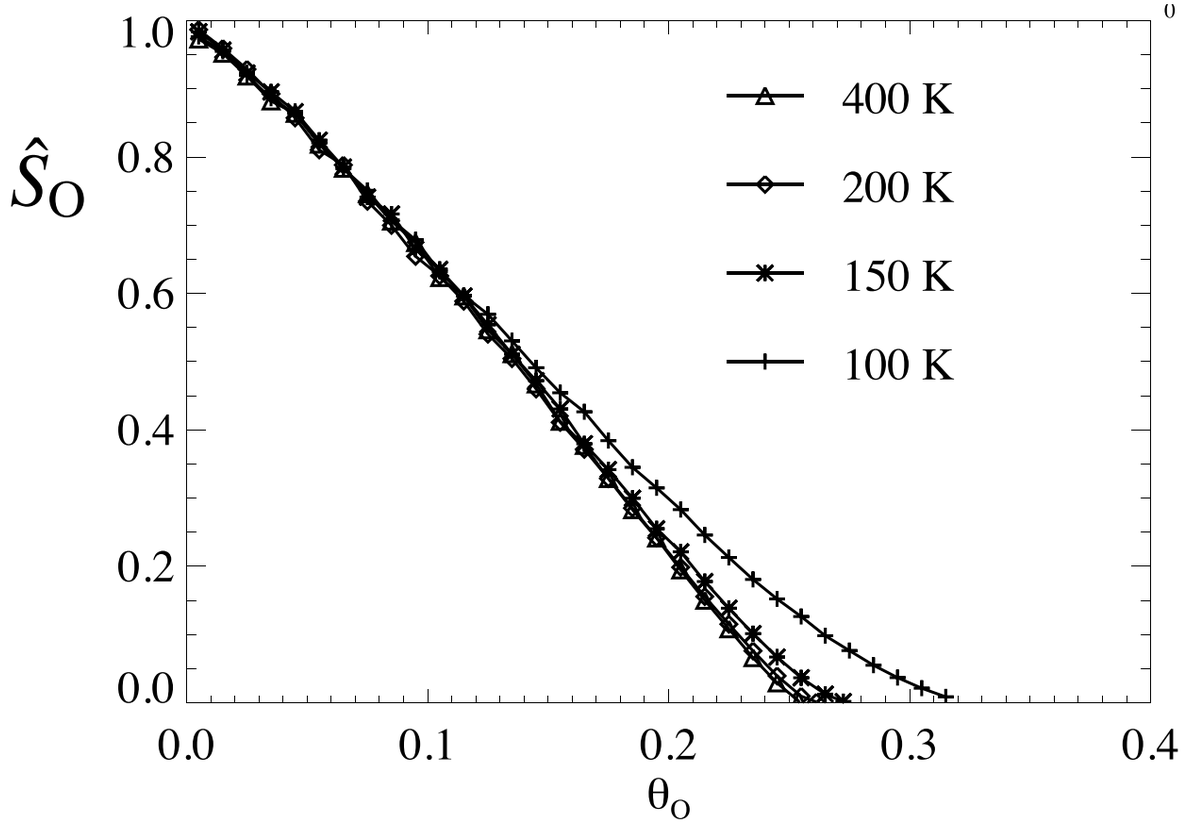


A General LG Model for O_2 Dissociation

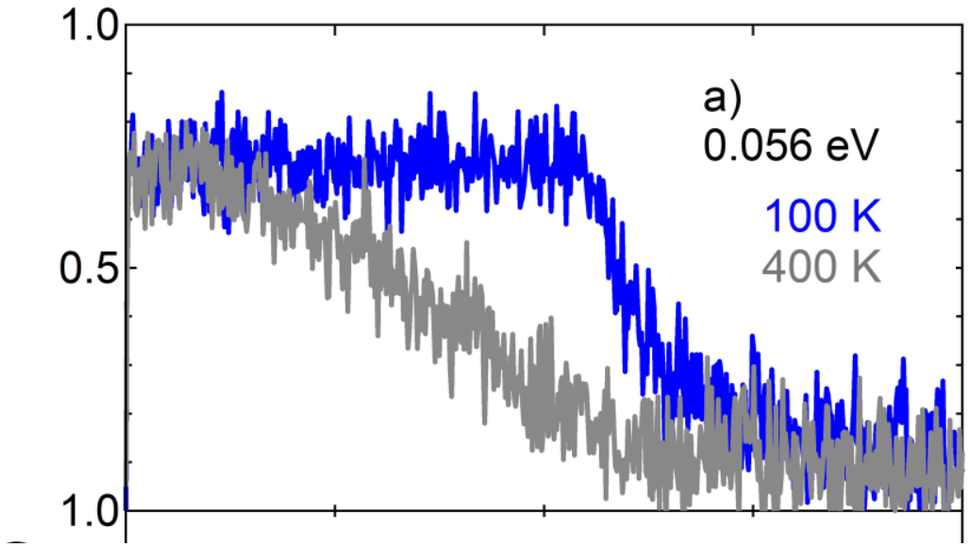
$$E_{\mathrm{act}} = E_{\mathrm{ads}} + \Delta E_{\mathrm{TS}},$$

E_{ads}: Adsorption energy of 2 O(ads) as NN, including lateral interactions
ΔE_{TS}: Extra barrier to the transition state energy for them to truly dissociate, not sensitive to environment, only as function of the pathway.

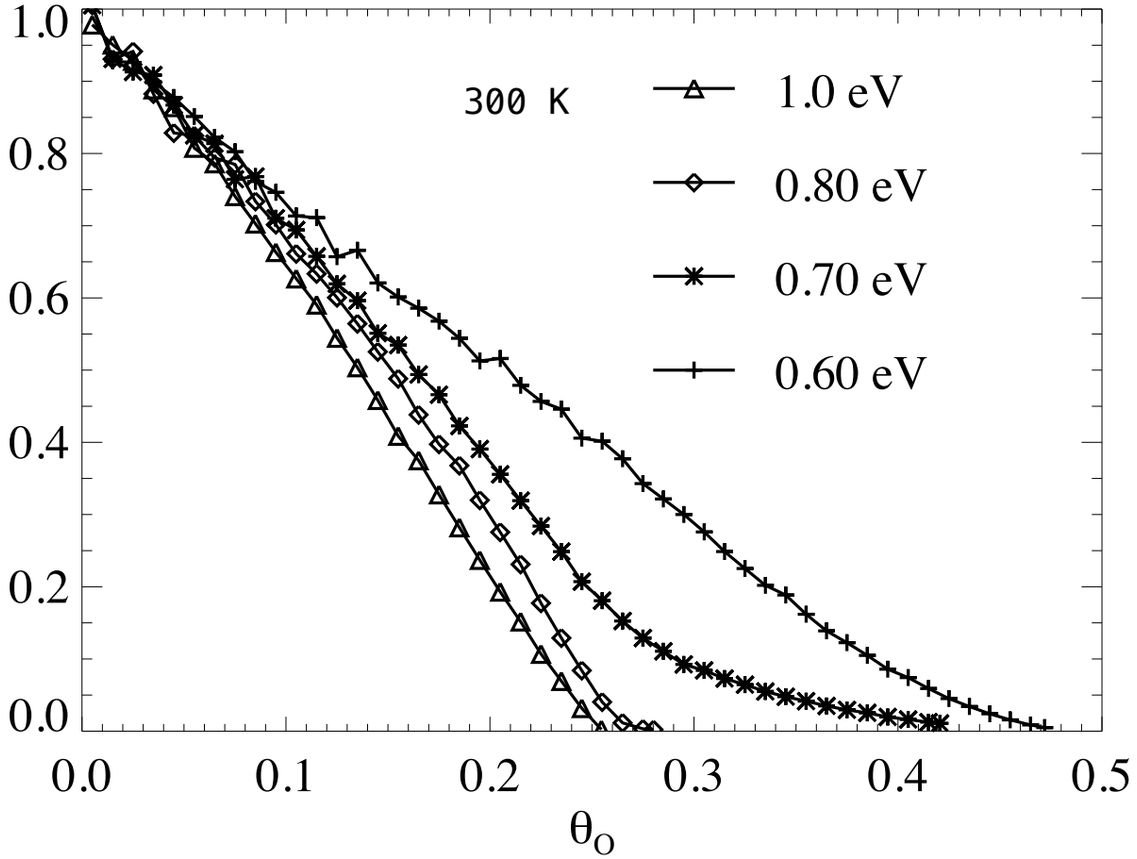




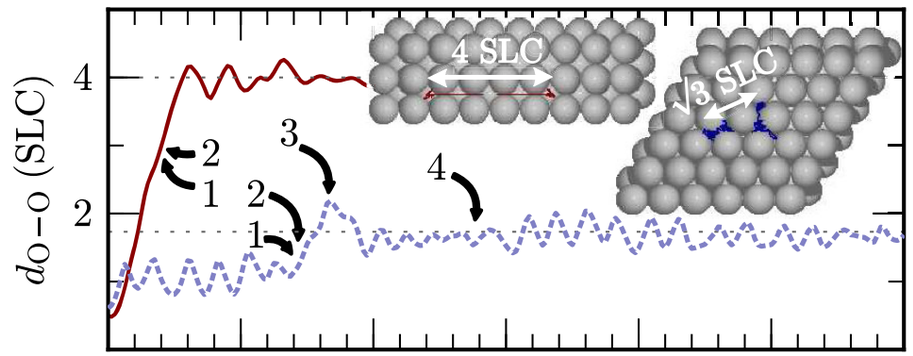
den Dunnen *et al.* J. Chem. Phys. **144**, 244706 (2016)

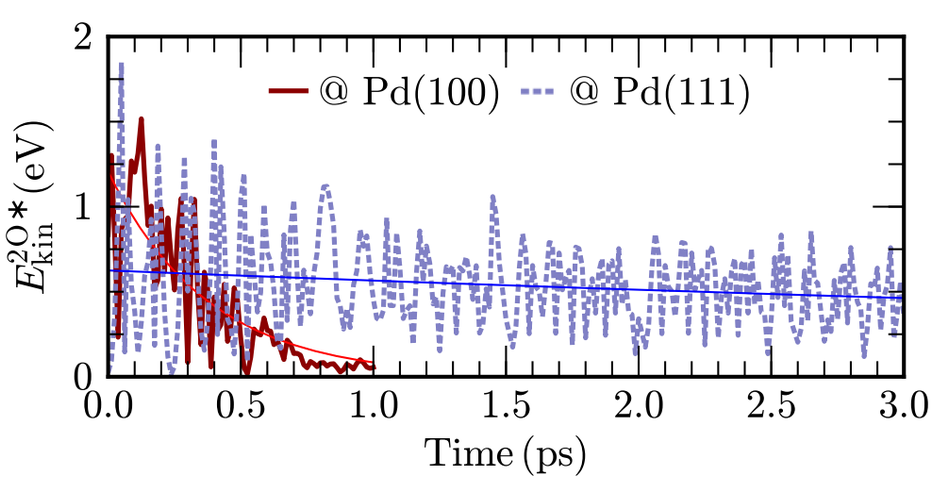


Normalized O_2 Sticking on Pd(100)
Refined model with different ΔE_{TS} for Hx pathway

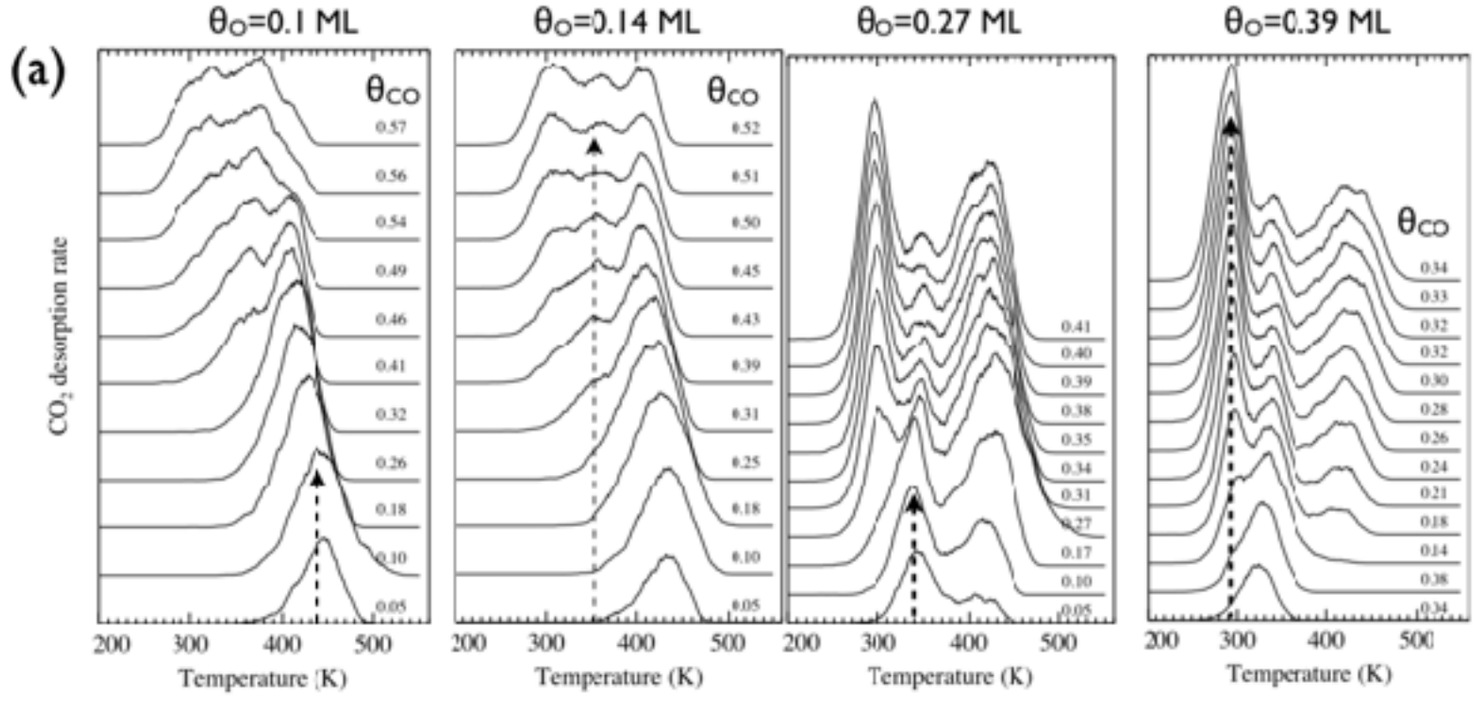


Hot adatom diffusion
Bukas and Reuter, PRL **117**, 146101 (2016)



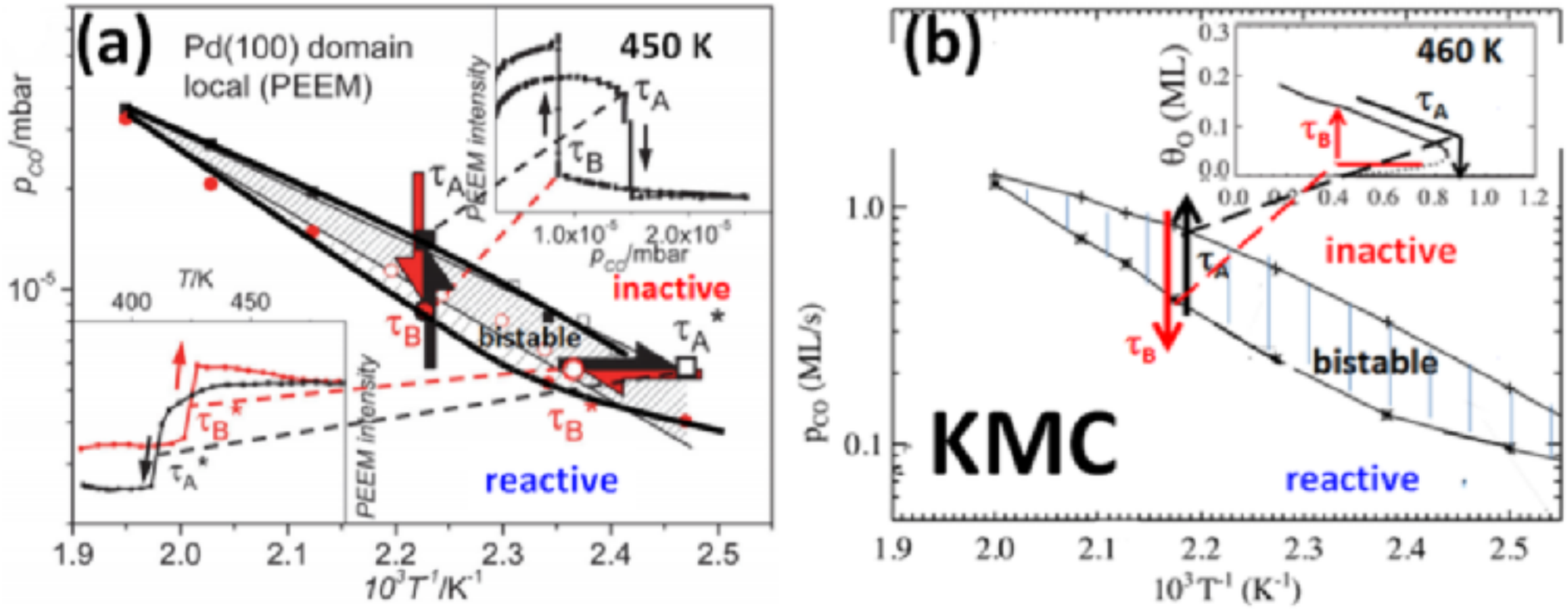


Temperature-Programmed Reaction Spectra CO+O/Rh(100)



Hopstaken and Niemantsverdriet (2000)

Bifurcation Diagram
CO Oxidation on Pd(100)



Vogel *et al*

Tailored Model for CO Oxidation on Pd(100)

CO on bridge sites only; O on 4fh sites only
No neighboring pairs with $d \leq a$.
No interaction between reactants with $d > a$.
Dissociative adsorption of O_2 satisfying the above prescription of interaction.
CO desorption with activation barrier E_{CO}
CO+O reaction at 2NN 4fh-bri pair with E_{react}
Very fast CO diffusion, moderately fast O diffusion

Almost as simple, but more physical than the widely studied Ziff-Gulari-Barshad (ZGB) model for CO oxidation

Only two parameters needed, unfortunately DFT not reliable for neither of them.

Kirkwood-type Approx. of the Tailored Model

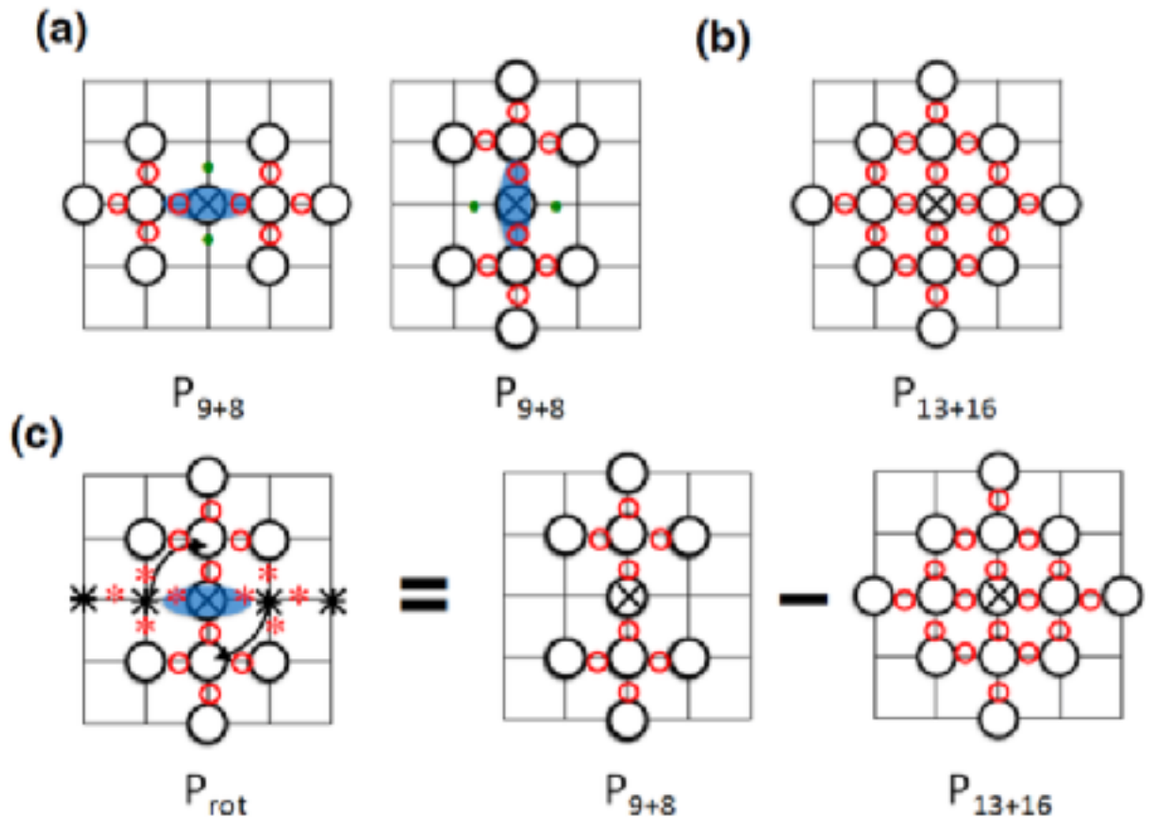
O_2 dissociation

9 4fh + 8 bri blocking, reorientation

$$S_{CO} = [1 - 2\theta_{CO} - 2\theta_O][1 - \alpha\theta_{CO}{}^4] \\ /[1 - 2\theta_{CO} - 2\theta_O + 9.5\theta_{CO}{}^3 + \theta_{CO}{}^2\theta_O + 2\theta_O{}^6]$$

$$S_{O_2} = 2P_{9+8} - P_{13+16}, \quad \text{where} \quad P_{9+8} = Q_{8|9}P_9$$

$$\text{and} \quad P_{13+16} = Q_{16|13}P_{13}$$



Kirkwood approximations:

$P_9 = P_2^8 / P_1^8$

$P_{13} = P_2^{16} / P_1^{19}$

$P_1 = 1 - \theta_O$

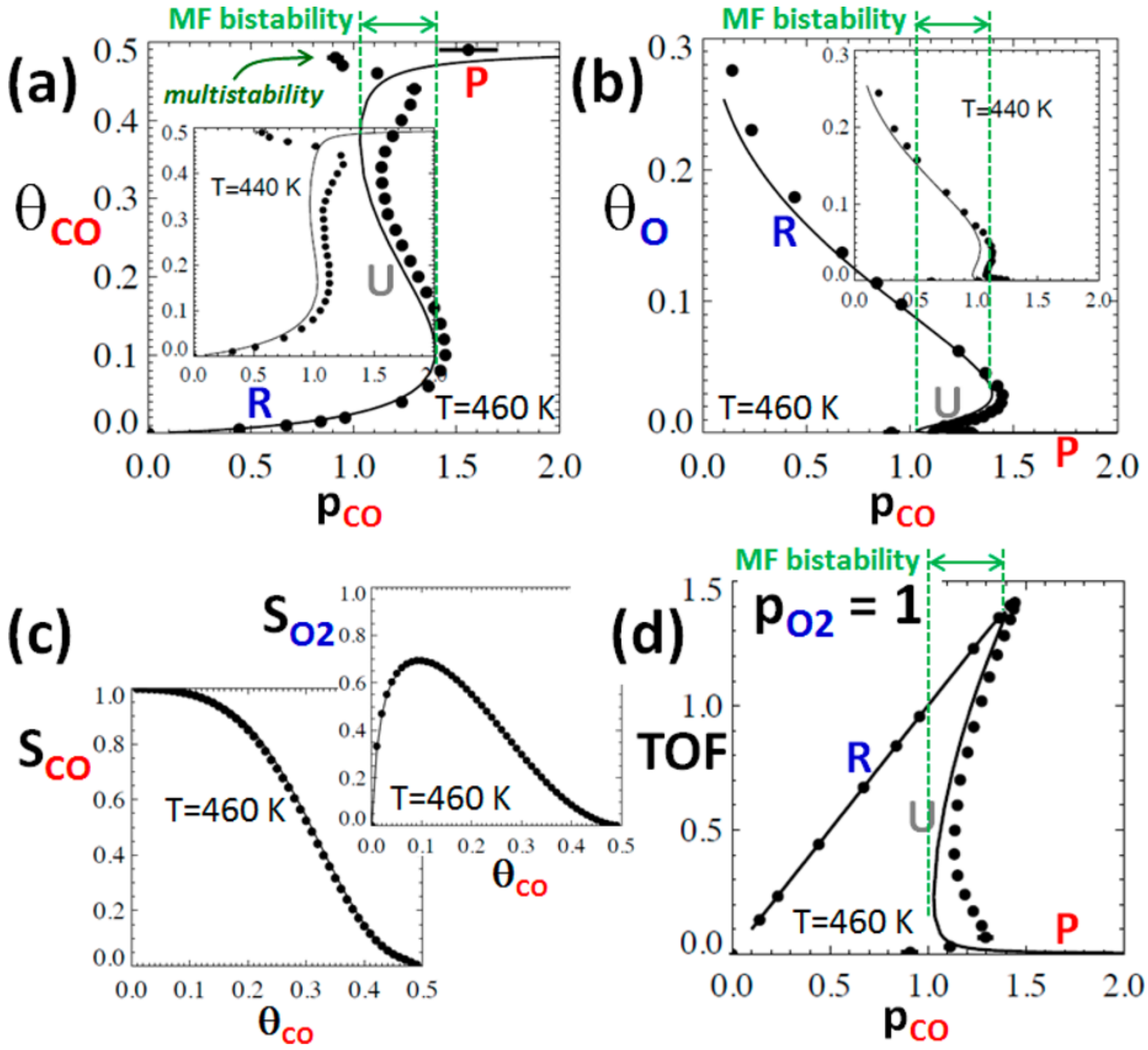
$P_2 = 1 - 2\theta_O$

$Q_{8|9} = Q_4^2 Q_2 / Q_1^2$

$Q_n = 1 - n\theta_{CO}^{br}(\text{loc})$

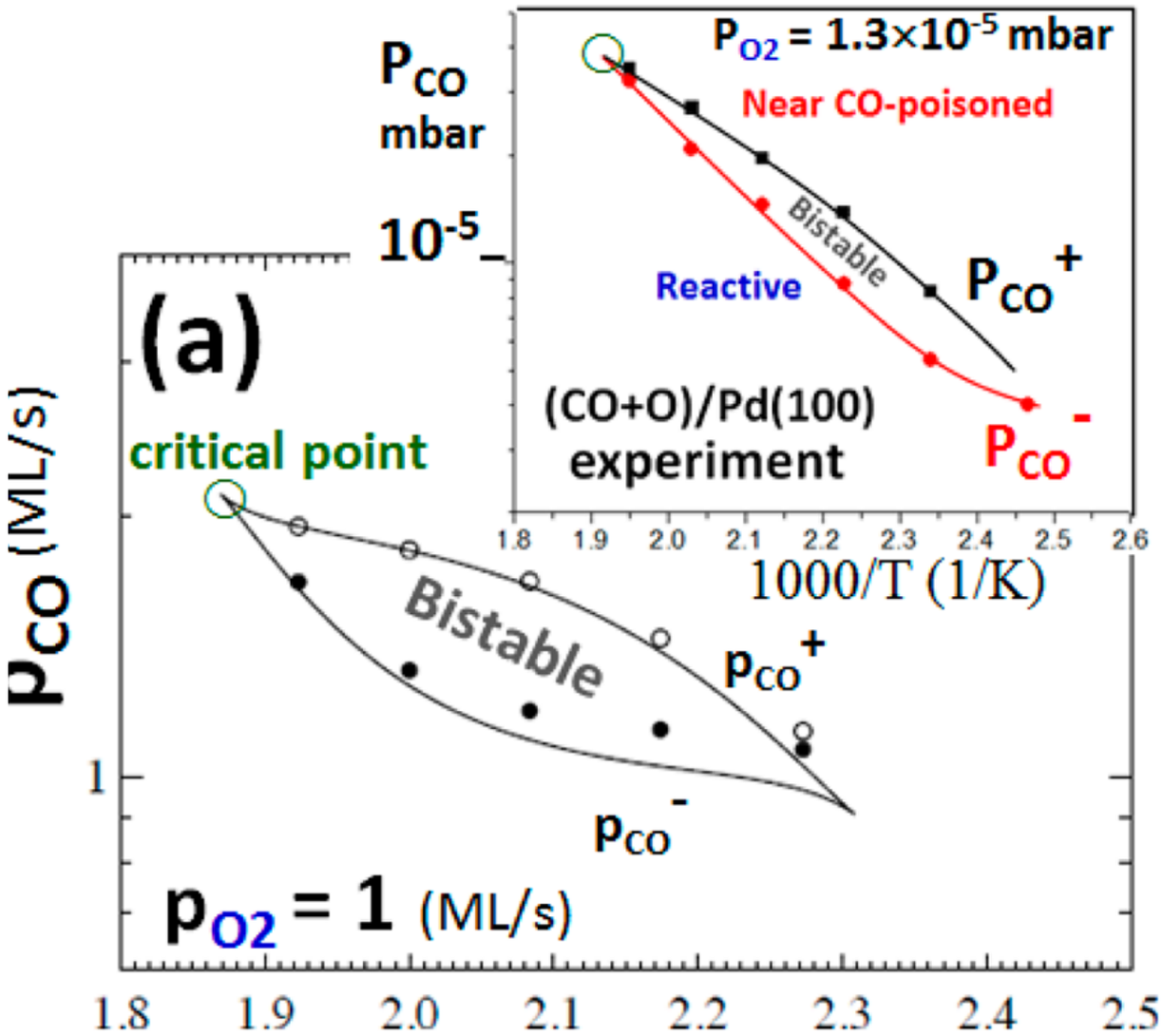
$\theta_{CO}^{br}(\text{loc}) = \theta_{CO}^{br} / (1 - 2\theta_O)$

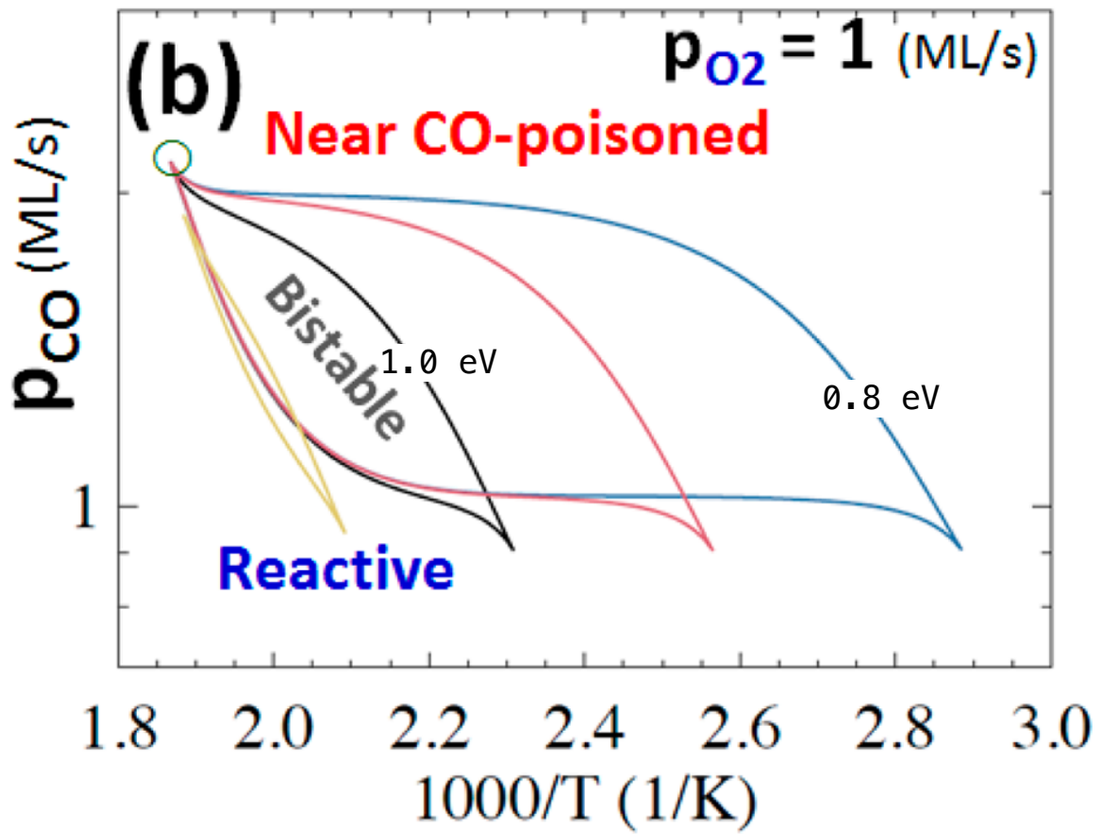
Bistability in the Tailored Model



Phase diagram of the Tailored Model

Numerical Continuation (Homotopy) Method





Reaction-Diffusion Equation of Mixed Reactants

Revised Fick's Laws of Diffusion

$$\frac{\partial \theta_{\mathrm{CO}}}{\partial t} = R_{\mathrm{CO}}(\theta_{\mathrm{CO}}, \theta_{\mathrm{O}}) - \nabla \cdot \mathbf{J}_{\mathrm{CO}},$$

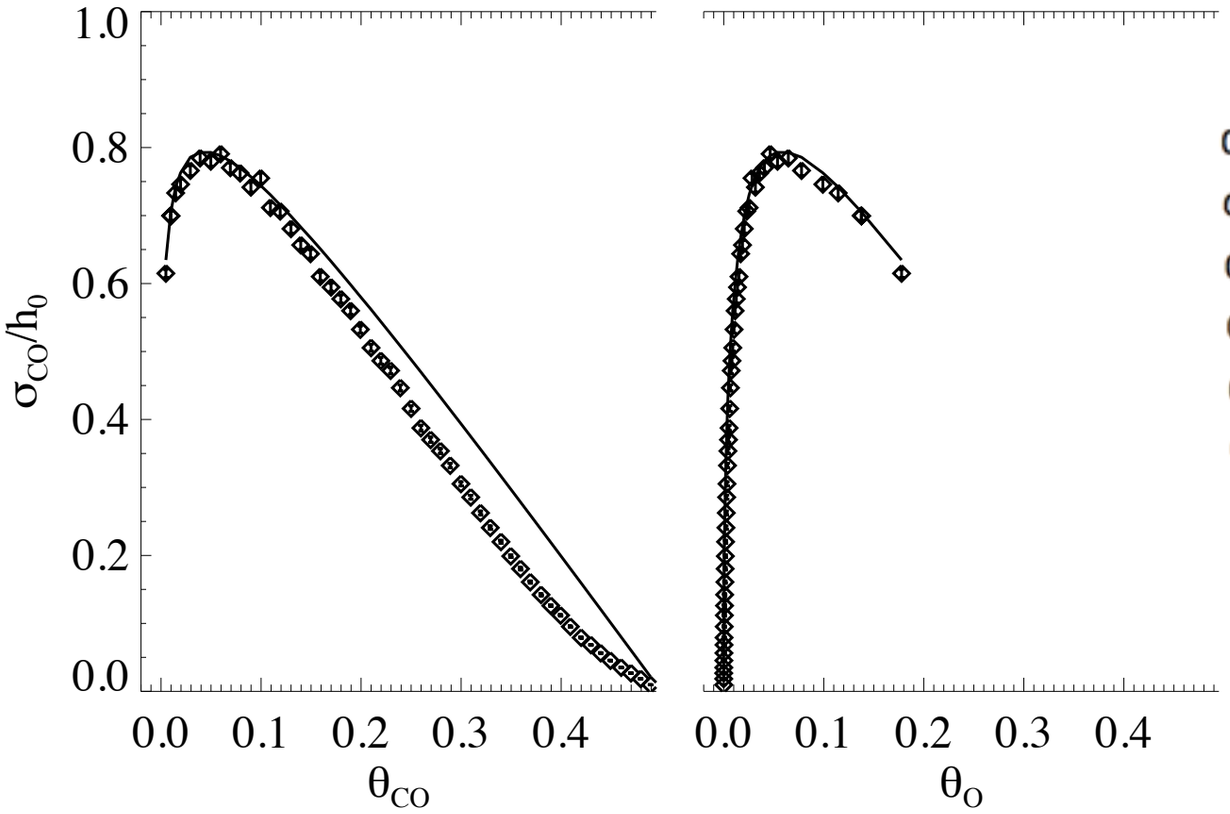
$$\frac{\partial \theta_{\mathrm{O}}}{\partial t} = R_{\mathrm{O}}(\theta_{\mathrm{CO}}, \theta_{\mathrm{O}})$$

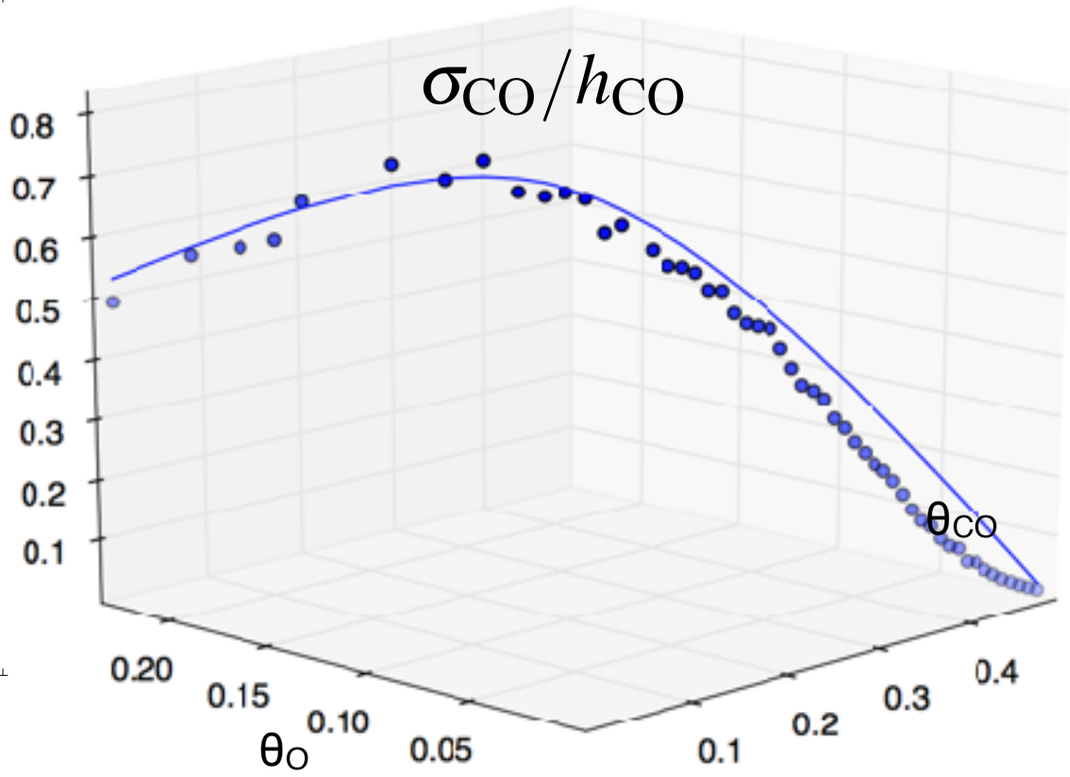
$$\mathbf{J}_{\mathrm{CO}} = -D_{\mathrm{CO,CO}} \nabla \theta_{\mathrm{CO}} - D_{\mathrm{CO,O}} \nabla \theta_{\mathrm{O}}$$

Onsager theory:

$$J_{\mathrm{CO}} = -\Lambda_{\mathrm{CO}} \nabla \mu_{\mathrm{CO}}$$

The mobility of CO in mixed layers

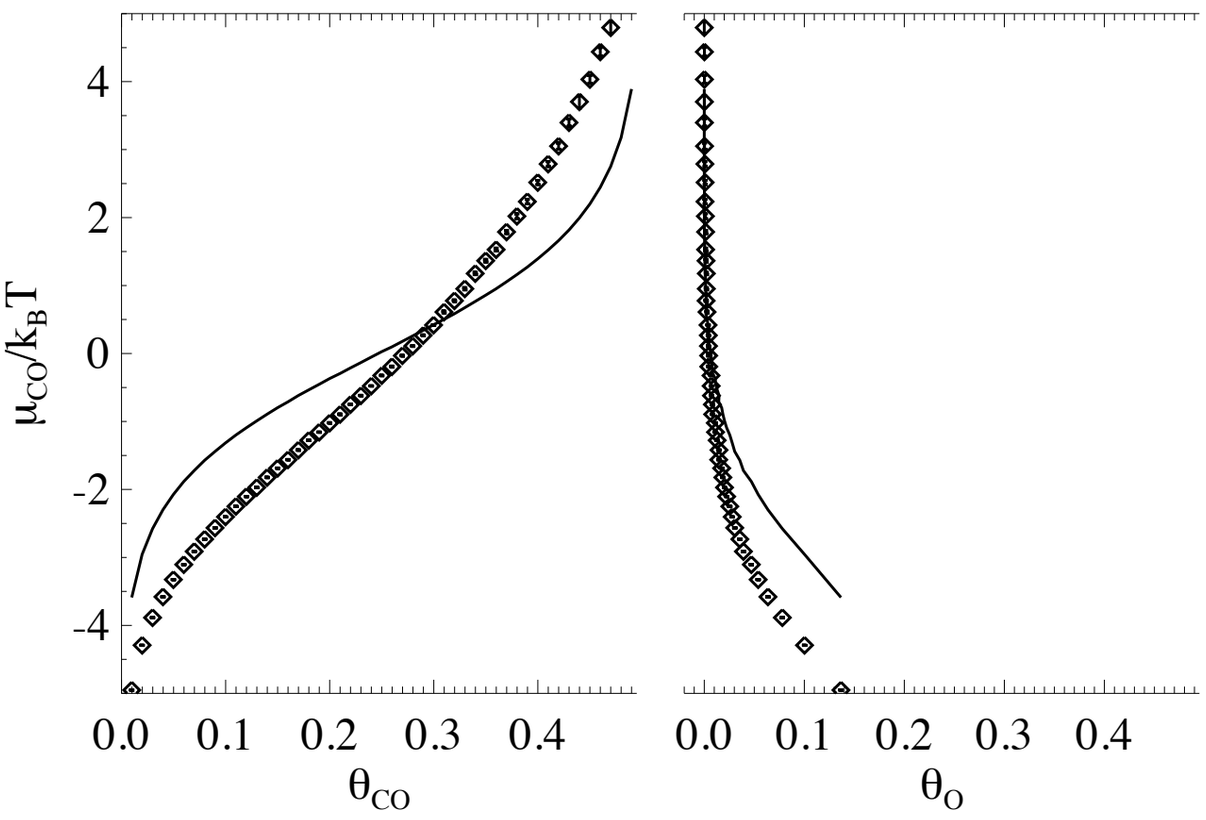


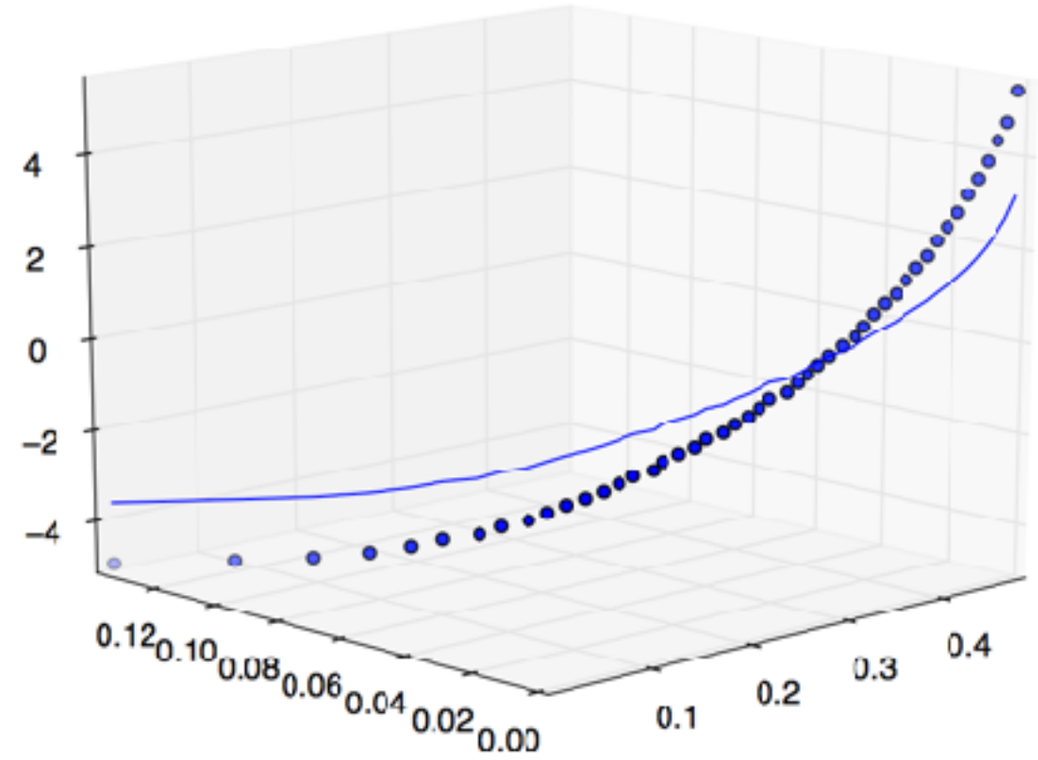


$$\sigma_{\mathrm{CO}} = \lim_{t\to\infty} (2dt)^{-1} |R_{\mathrm{CO}}(t) - R_{\mathrm{CO}}(0)|^2$$ from KMC, Einstein's relation

$$\sigma_{\mathrm{CO}}/h_{\mathrm{CO}} = 1 - 2\theta_{\mathrm{CO}} - 2\theta_{\mathrm{O}}$$ analytic approximation

The chemical potential of CO in mixed layers



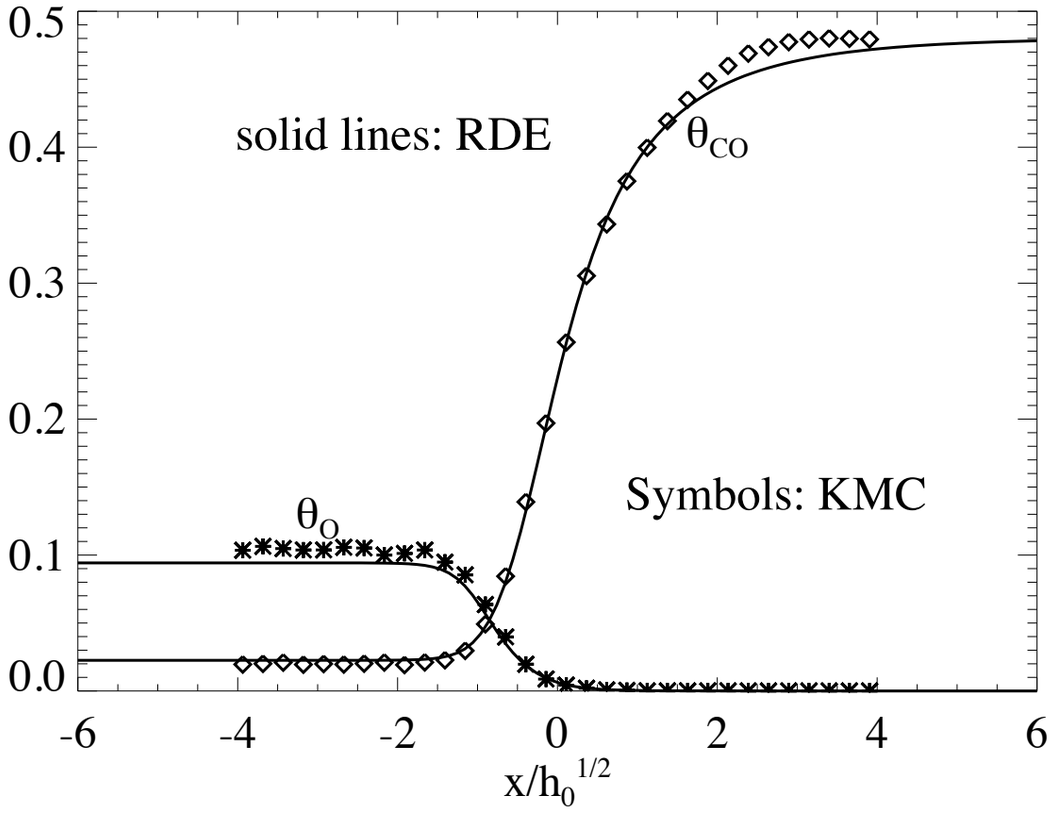


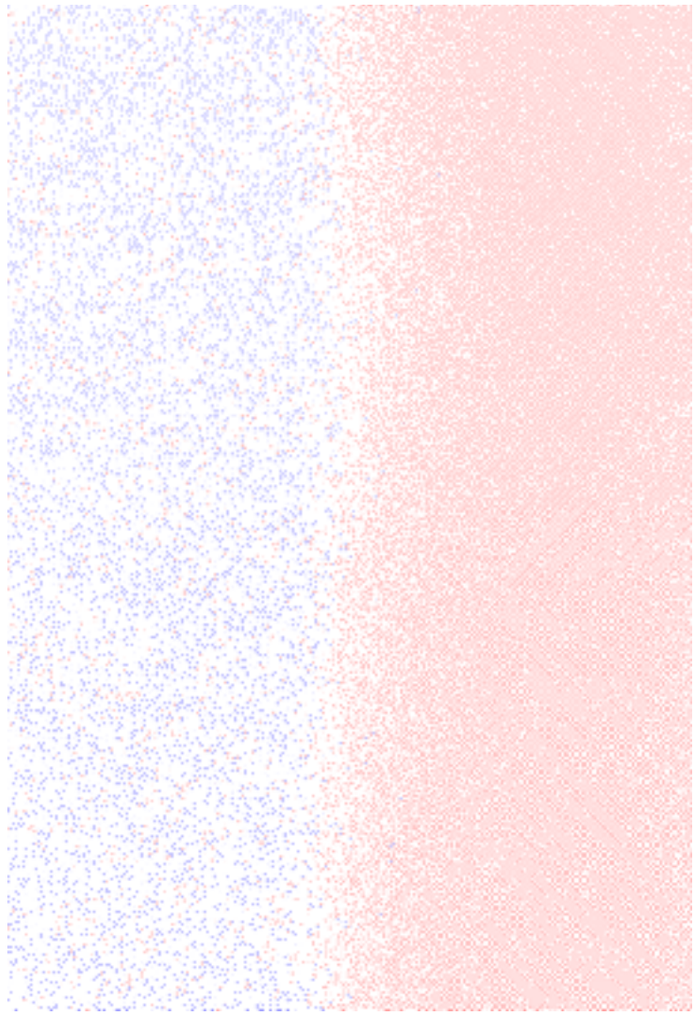
$$\mu_{CO}/(k_BT) = \ln\theta_{CO} - \ln\left[\langle\exp(-\delta E/(k_BT))\rangle\right]$$ from KMC, Widom's insertion method

$$\mu_{CO}/(k_BT) = \ln[2\theta_{CO}/(1-2\theta_{CO}-2\theta_O)]$$ analytic approximation

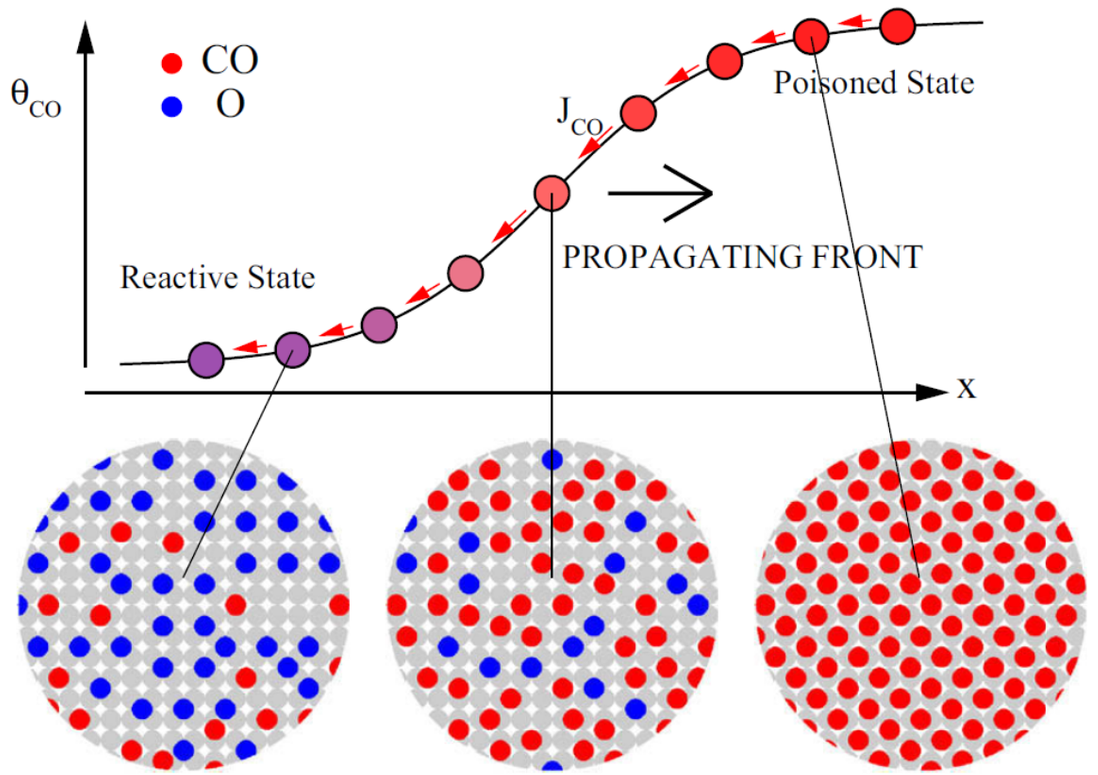
Profile of a chemical Wave

Reaction-Diffusion Eq. vs. Kinetic MC Simulations





Heterogeneous Coupled Lattice Gas Model



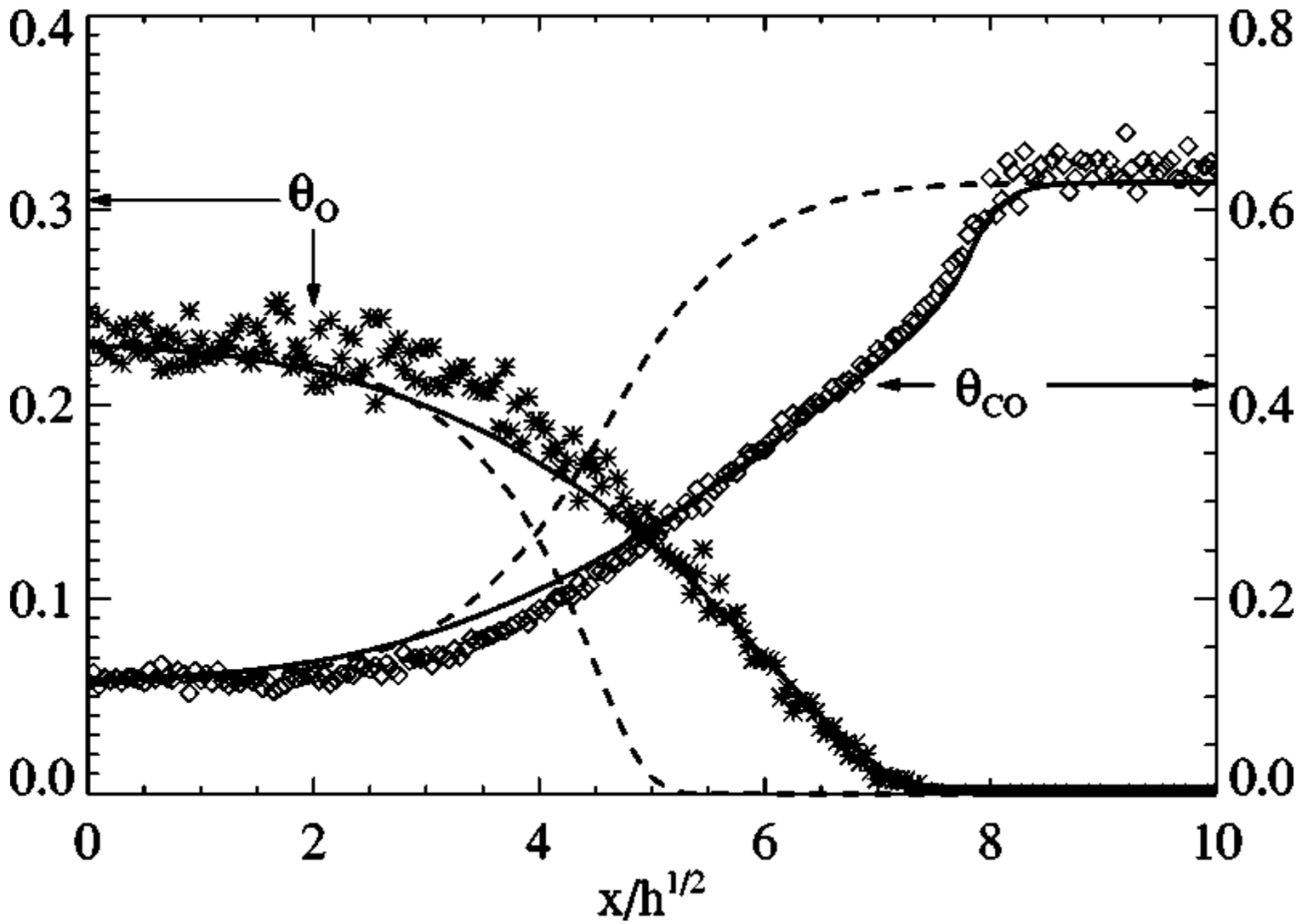
$$\partial\,\theta_{\mathrm{CO}}/\partial\,t = R_{\mathrm{CO}}(\theta_{\mathrm{CO}},\{\mathrm{O}\}) - \nabla\cdot\boldsymbol{J}_{\mathrm{CO}}$$

$$\boldsymbol{J}_{\mathrm{CO}} = -(kT)^{-1}\sigma_{\mathrm{CO}}\theta_{\mathrm{CO}}\,\nabla\,\mu_{\mathrm{CO}}(\theta_{\mathrm{CO}},\{\mathrm{O}\})$$

Applications requires:
Availability of massively parallel processors
Ab initio calculations of diffusion barriers

Profile of Stationary Chemical Wave

Realistic Model with Metropolis-like rates for diffusion

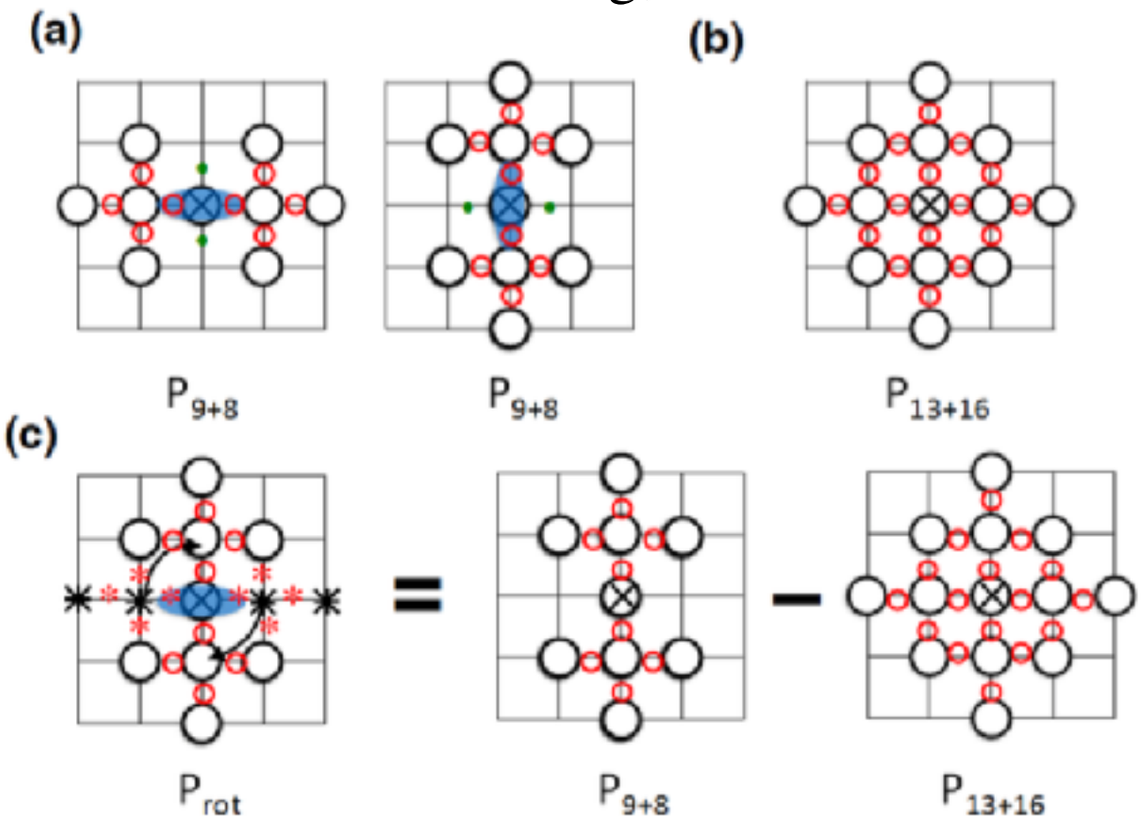


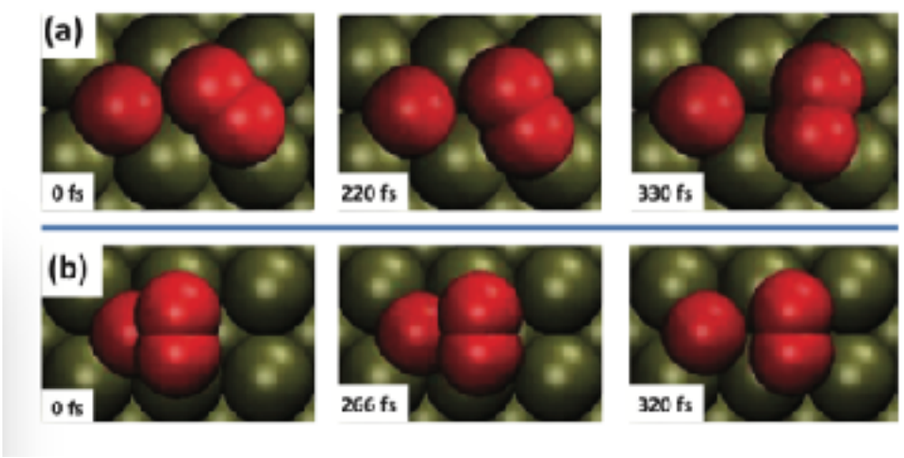
Summary

- First-principle derived model for surface reaction.
- Multi-site Lattice-gas model, with efficient algorithms and capping technique, 10^6 adsorption sites, 10^3 seconds.
- Homogenous properties, stationary patterns can be simulated with single processor.
- Spatial-temporal behavior more challenging, HCLG most suitable for massively parallel computer (GPU, Xeon Phi)

O_2 dissociation

9 4fh + 8 bri blocking, reorientation





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$$\text{and} \quad P_{13+16} = Q_{16|13}P_{13}$$

Kirkwood approximations:

$$P_9 = P_2^8/P_1^8$$
$$P_{13} = P_2^{16}/P_1^{19}$$
$$P_1 = 1 - \theta_O$$
$$P_2 = 1 - 2\theta_O$$
$$Q_{8|9} = Q_4^2 Q_2/Q_1^2$$
$$Q_n = 1 - n\theta_{CO}^{br}(\text{loc})$$
$$\theta_{CO}^{br}(\text{loc}) = \theta_{CO}^{br}/(1 - 2\theta_O)$$