

Dynamic Phase Transition,  
Enhanced Reaction Rate, and  
Decay of Metastable States in a Model of  
CO Oxidation with CO Desorption

*Per Arne Rikvold*

Florida State University, Tallahassee, Florida, USA

*Erik Machado and Gloria M. Buendía*

Universidad Simón Bolívar, Caracas, Venezuela

*Robert M. Ziff*

University of Michigan, Ann Arbor, Michigan, USA

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# Motivation

Nonequilibrium statistical models have a broad range of interest: chemical reactions, biological populations, growth-deposition, economics, etc.

**Catalytic processes** have many industrial and technological applications.

**Surface reaction models** : fruitful laboratory to explore out of equilibrium statistical physics

*The decay of metastable phases near non-equilibrium phase transitions lacks a well-established theoretical framework.*

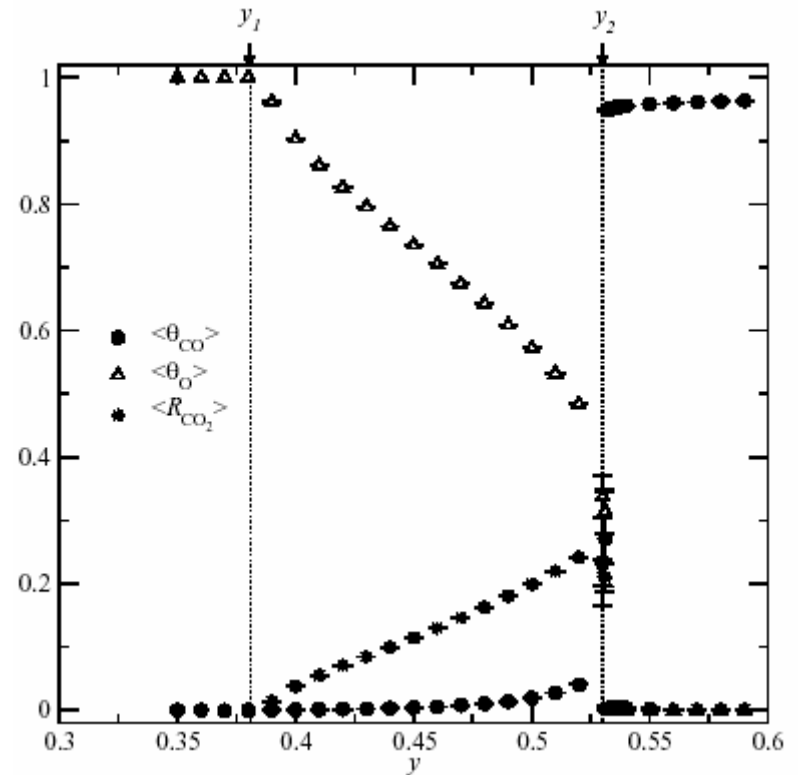
# Ziff-Gulari-Barshad (ZGB) Model

Lattice-gas adsorption-reaction model that describes kinetics aspects of the gas-phase catalytic oxidation of carbon monoxide on a crystal surface by Langmuir-Hinshelwood mechanism:



Process controlled by a single parameter  $y$ , which represents the probability that the next molecule arriving to the surface is CO. Proportional to **partial pressure of CO**.

- Two kinetic phase transitions: continuous at  $y_1$ ; discontinuous at  $y_2$ .
- $y < y_1$  : oxygen-poisoned state
- $y > y_2$  : CO poisoned state



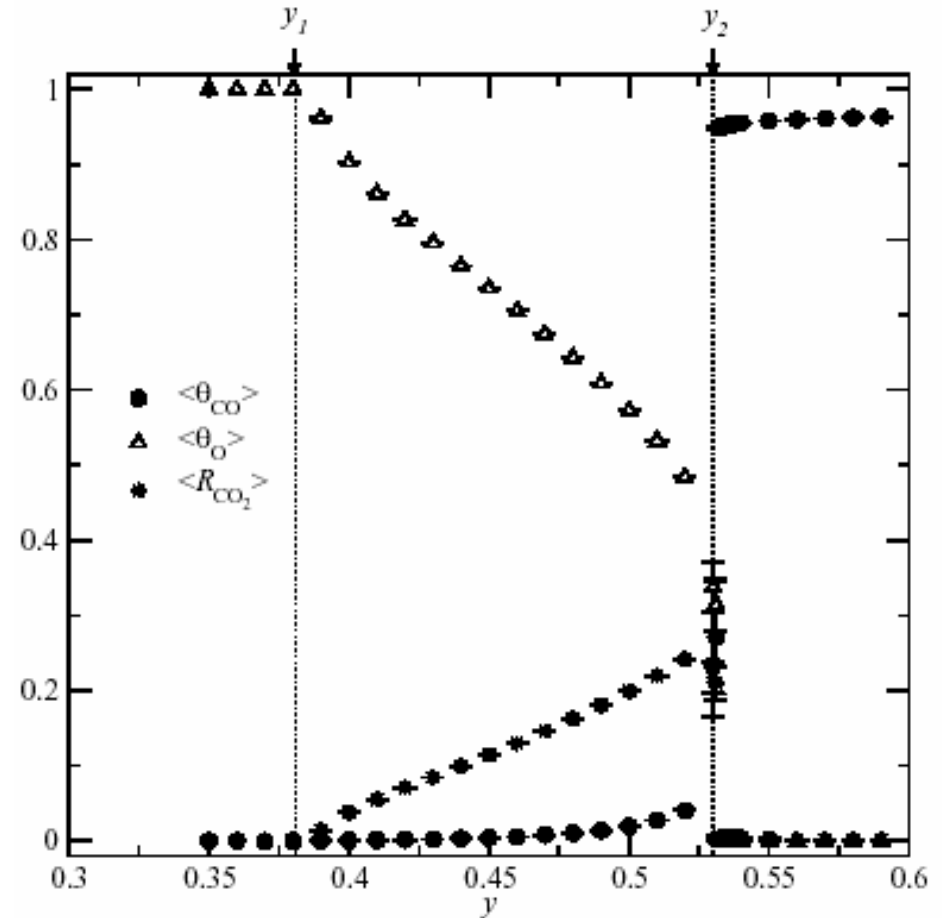
Real systems do not possess an oxygen-poisoned state.

Transitions between states of low and high CO coverage have been observed experimentally for high enough temperatures.

Add **CO desorption rate  $k$**  to mimic temperature effect

- Below  $k_c$ : distinct high and low coverage phases.
- Above  $k_c$ : the CO coverage varies smoothly with  $y \Rightarrow y_2(k)$ .
- ZGB-k model does not have a totally poisoned CO state. Hysteresis observed close to  $y_2(k)$ , associated with **metastable** states.

## ZGB-k model



# Purpose of this work

- Understand the dynamical response of the model near the discontinuous transition.
- Measure the lifetime of the metastable states. Explore mechanism of decay.
- How can these results be used to enhance the catalytic activity of the system?

# Simulations

- The ZGB- $k$  model is simulated on a square lattice of size  $L \times L$  that represents the catalytic surface.
- **Monte Carlo simulations:**

Desorption probability:  $k$    Adsorption probability:  $(1-k)$

Select a site  $i$

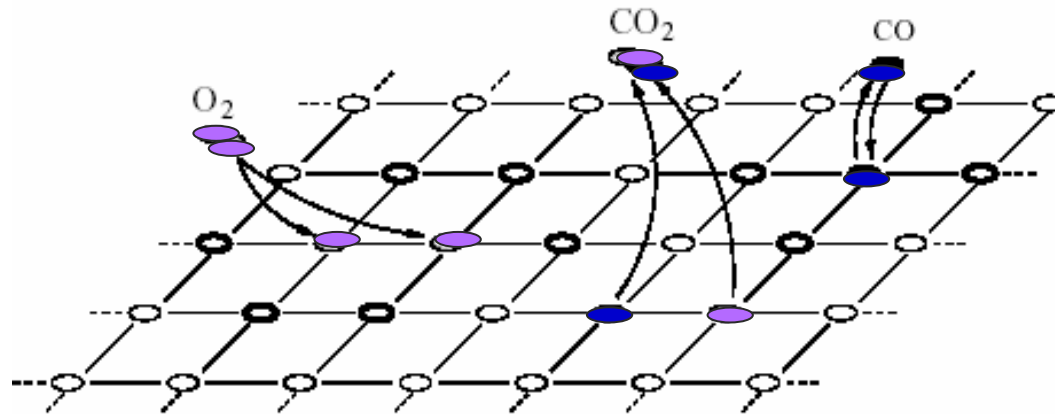
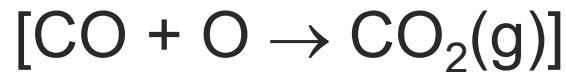
**Desorption:** If CO at  $i$ , desorb and end trial.  
If not, trial ends.

**Adsorption:** CO or O<sub>2</sub> selected with probability  $y$  and  $1-y$  respectively

**CO adsorption at  $i$ :** Adsorbed if no nn occupied by O. Otherwise, one of the nn O is removed



**O<sub>2</sub> Adsorption at  $i$ :** Needs 2 nn vacancies for  $\text{O}_2 \rightarrow 2\text{O}$ . If any nn of an O is a CO, they react



*These dynamical rules fully define the model.*

*Its properties are **not** derived from a Hamiltonian.*

- Use periodic boundary conditions.
- Time unit is one Monte Carlo step per site (MCSS), in which any site, on average is visited once.
- Averages taken over  $10^3$  independent runs.
- Define **coverage** as the fraction of the surface sites occupied by a molecule

$$\theta_{\text{CO}}, \theta_{\text{O}}, \theta_{\text{E}} \quad \theta_{\text{CO}} + \theta_{\text{O}} + \theta_{\text{E}} = 1$$

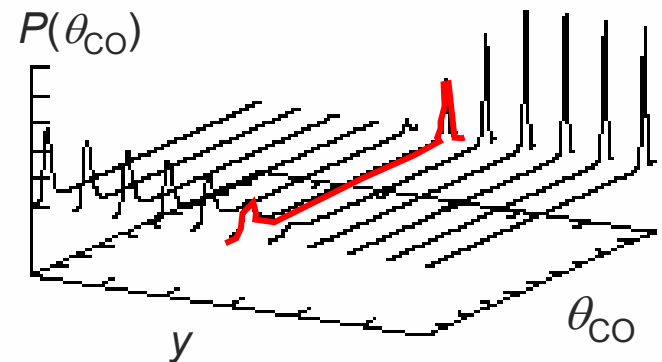
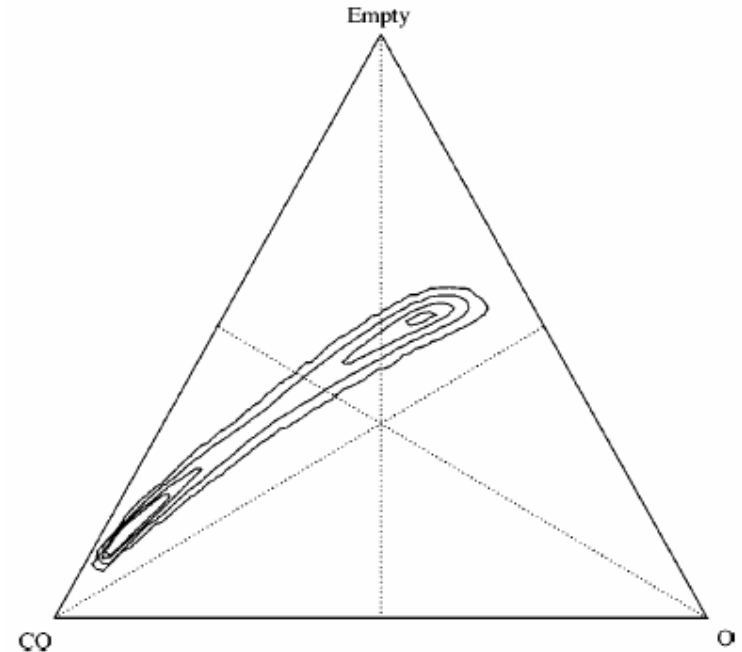
# Results -- Coexistence curve

- Estimate the probability distribution  $P(\theta_{CO})$
- Coverage fluctuations in  $L \times L$  system:

$$X_L = L^2(\langle \theta_{CO}^2 \rangle - \langle \theta_{CO} \rangle^2_L)$$

For a **discontinuous**  
phase transition:

$$X_L \sim L^d$$



# Finite-size scaling

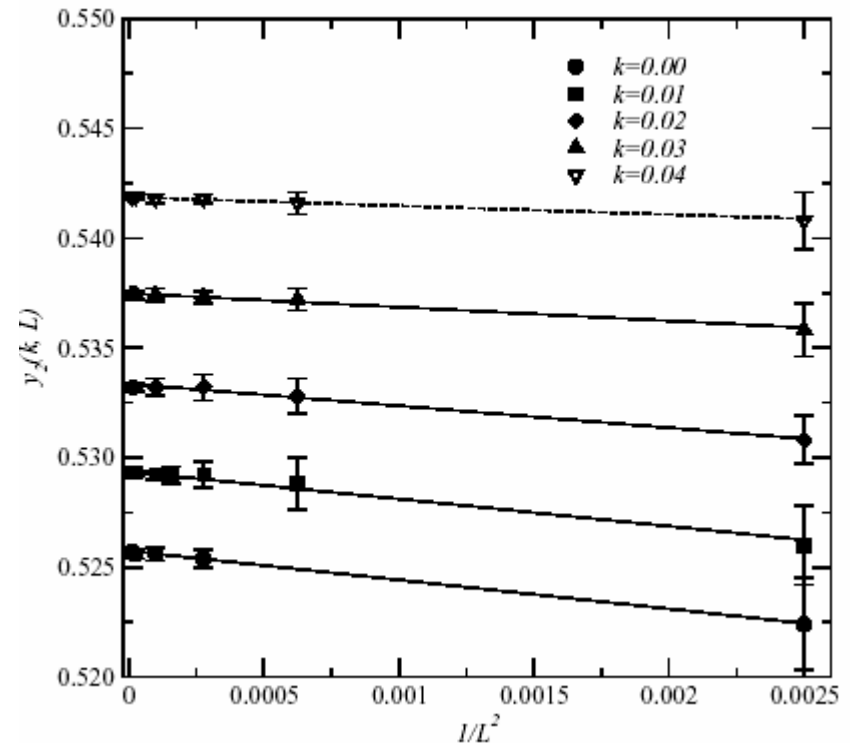
- Finite-size scaling indicates **discontinuous transition at  $y=y_2(k)$** , generating coexistence curve terminating at critical point

$$0.03 < k_c < 0.04 .$$

- Also calculate **fourth-order cumulant** of order parameter:

$$u_L = 1 - u_4 / 3u_2^2$$

$$u_n = \langle (\theta_{CO} - \langle \theta_{CO} \rangle)^n \rangle$$



## FSS equilibrium

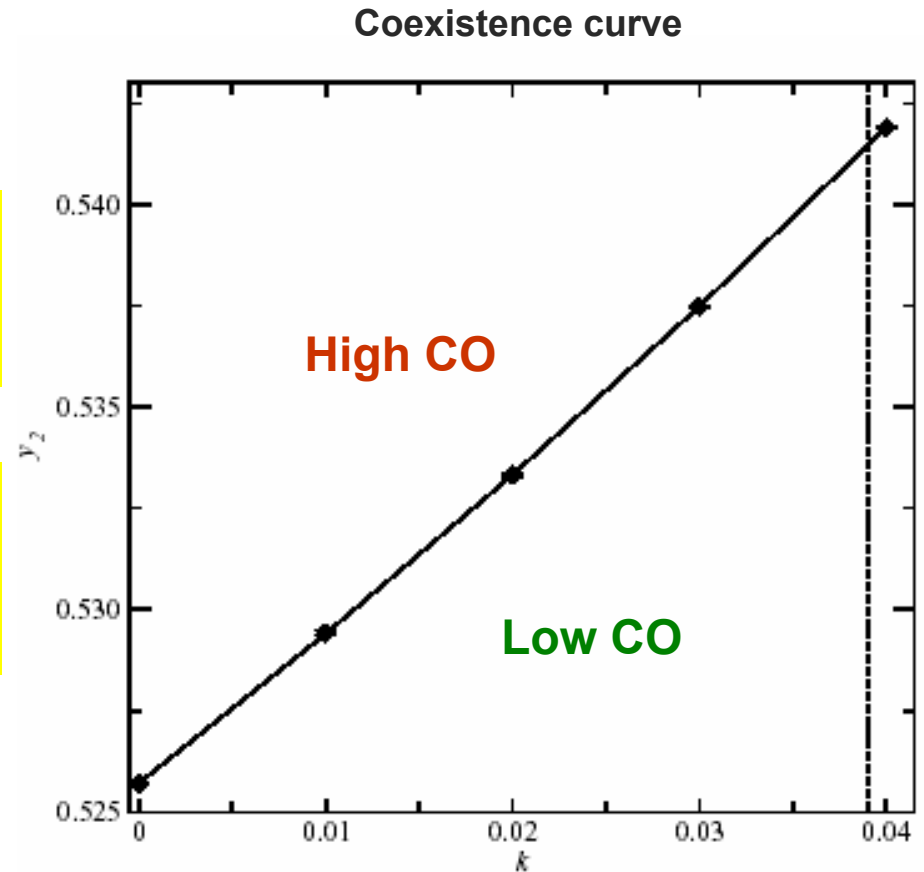
$$y_2(k,L) - y_2(k,\infty) \propto L^{-2}$$

$y_2(k,L)$  from the maximum of  $u_L$

$$y_2(0, L \rightarrow \infty) = 0.5257(3)$$

$$y_2(k_c, L \rightarrow \infty) = 0.542(3)$$

Consistent with previous results



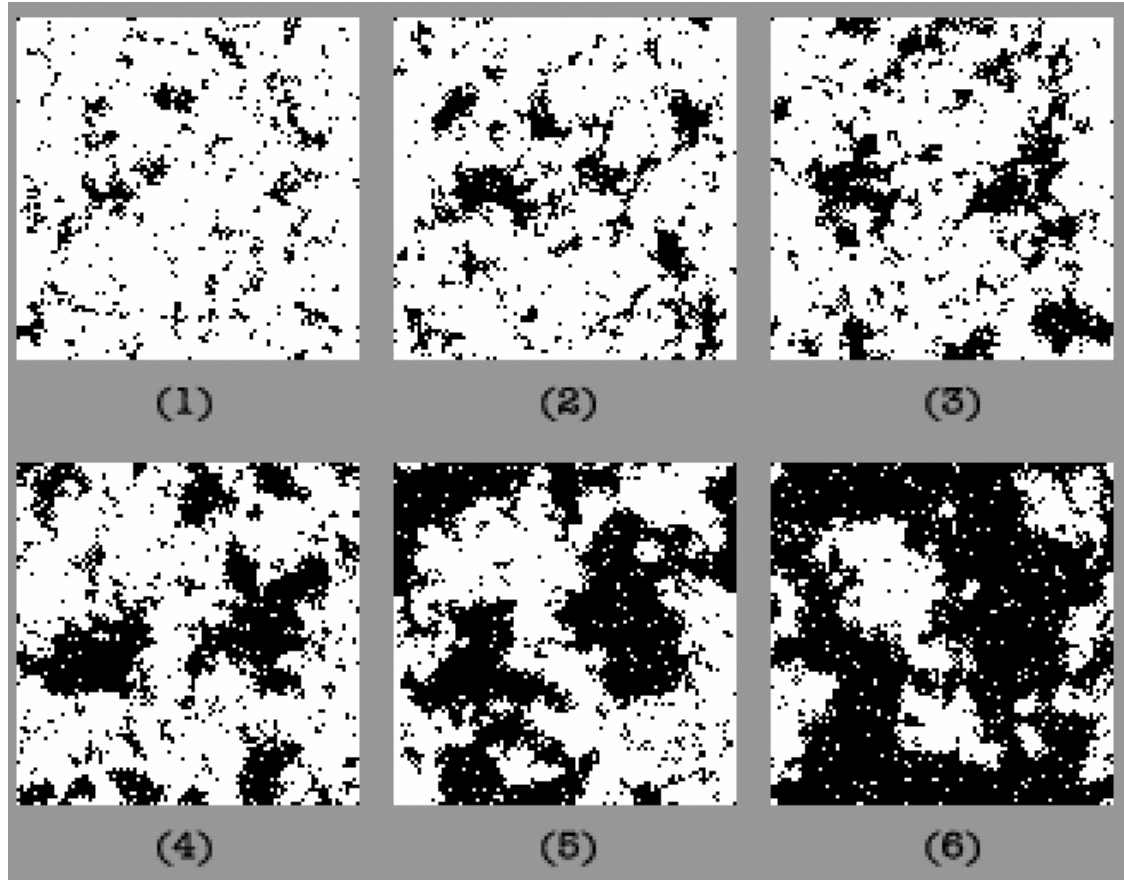
# Decay from the metastable phase

Define distance from coexistence curve:

$$\Delta(k,L) = |y - y_2(k,L)|$$

$\Delta^{-1}$  **small** (Far from coexistence)

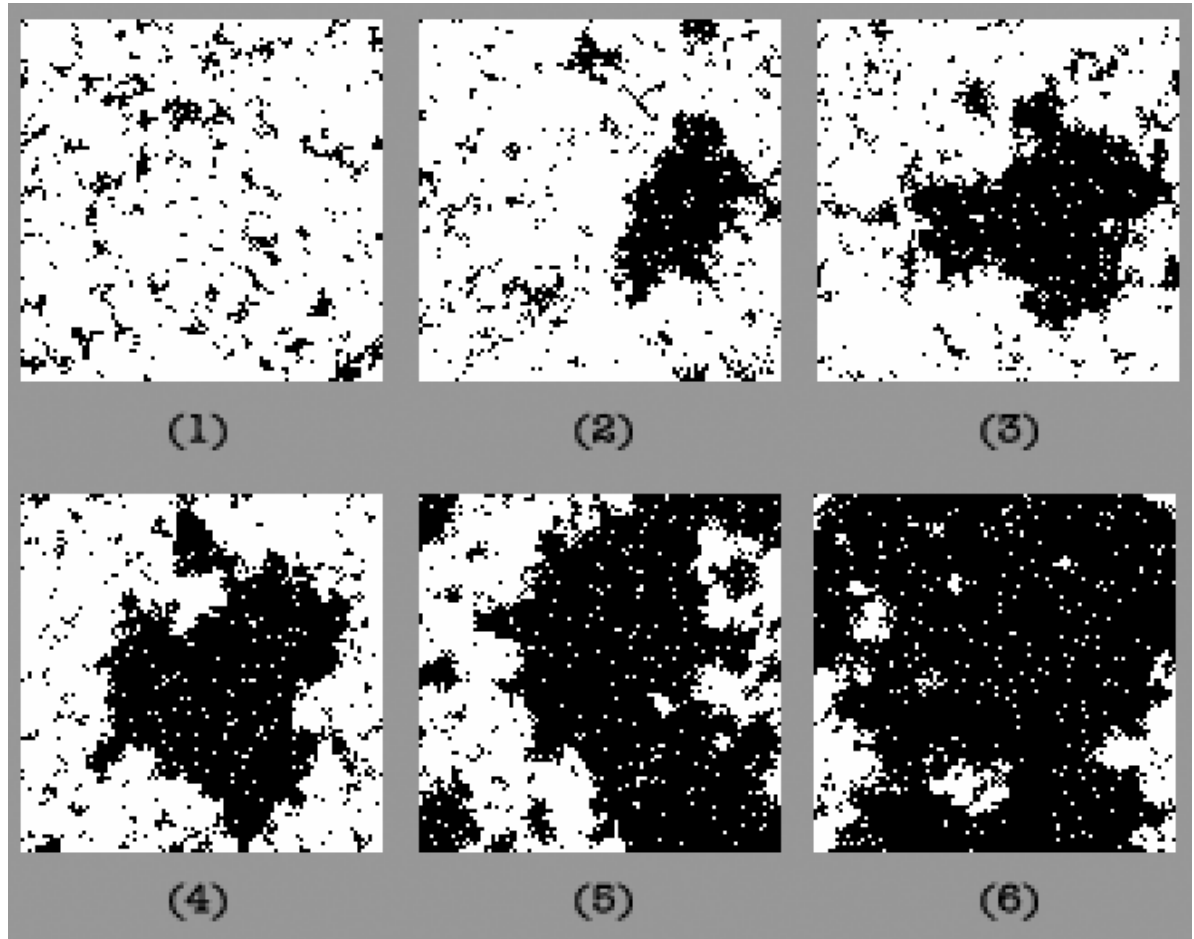
The system decays by nucleation and growth of **multiple droplets**



Low  $Q \rightarrow$  High  $Q$

$\Delta^{-1}$  large (close to coexistence curve)

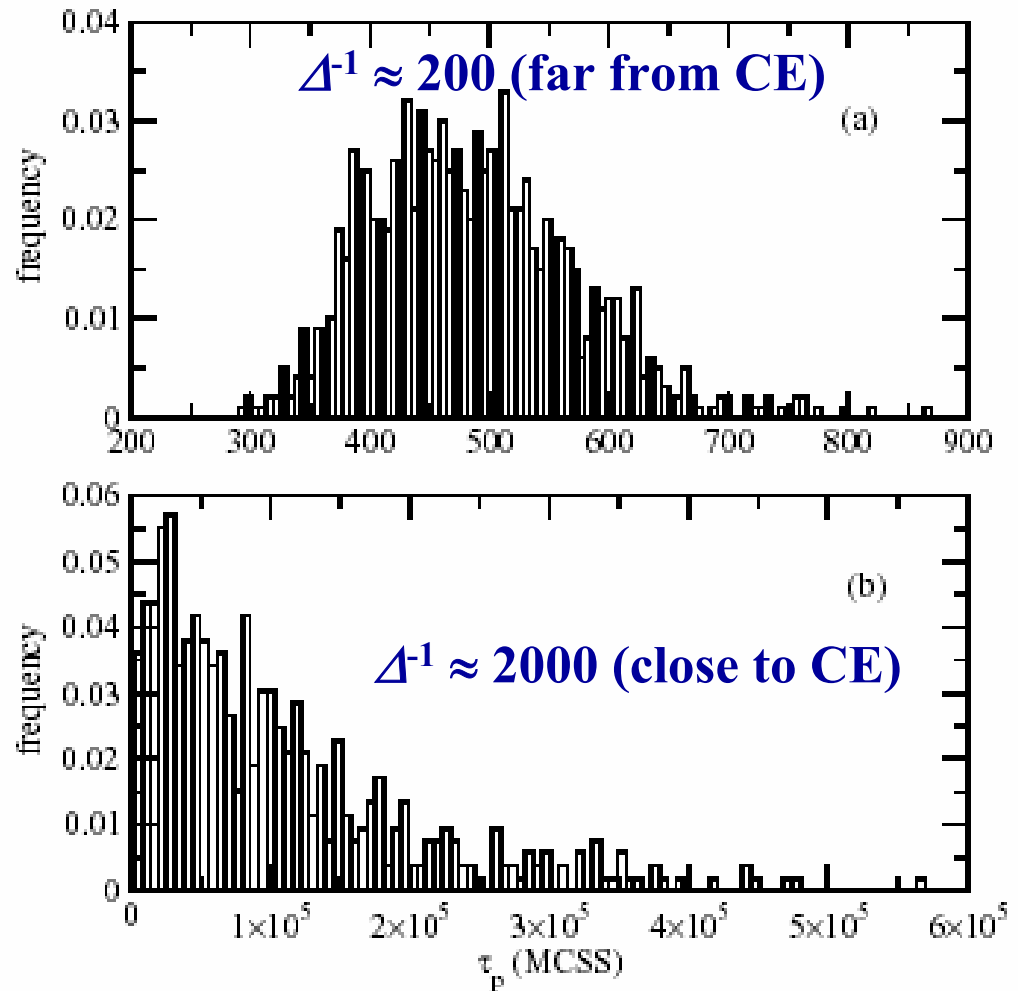
The system decays by nucleation and growth of a **single droplet** of the stable phase



Low Q → High Q

# Probability distributions of decay times

*The statistics of the lifetimes of this model are very similar to Hamiltonian systems that decay from a metastable phase associated with an equilibrium phase transition*



# Metastable decay of Hamiltonian system

(Equilibrium phase transition  
⇒ Kolmogorov-Johnson-Mehl-Avrami KJMA)

The decay occurs by nucleation and growth of droplets of the equilibrium phase. Described by the **KJMA** theory. **Single-droplet regime SD**  
- **Multidroplet regime MD**

**SD** if the 1<sup>st</sup> droplet grows fast enough to fill the system before another nucleates.

**MD** if the growth is slow, so many droplets can nucleate within the time it would take a single droplet to fill the system.

There is a competition between the nucleation rate  $I$  and the droplet growth velocity  $v$

⇒ **characteristic length**  $R_0 = (v/I)^3$

# KJMA Theory (equilibrium systems)

It is well known that the relative standard deviation of the lifetimes  $r$  satisfies

$$r = \frac{\sqrt{\langle \tau^2 \rangle - \langle \tau \rangle^2}}{\langle \tau \rangle} \approx \begin{cases} R_0 / L < 1 & \text{MD} \\ 1 & \text{SD} \end{cases}$$

The macroscopic parameters to study metastability in Hamiltonian system are the **chemical potential** and the **temperature**. In the present model the analogous quantities should be the distance from the coexistence  $\Delta$  and the desorption rate  $k$ .

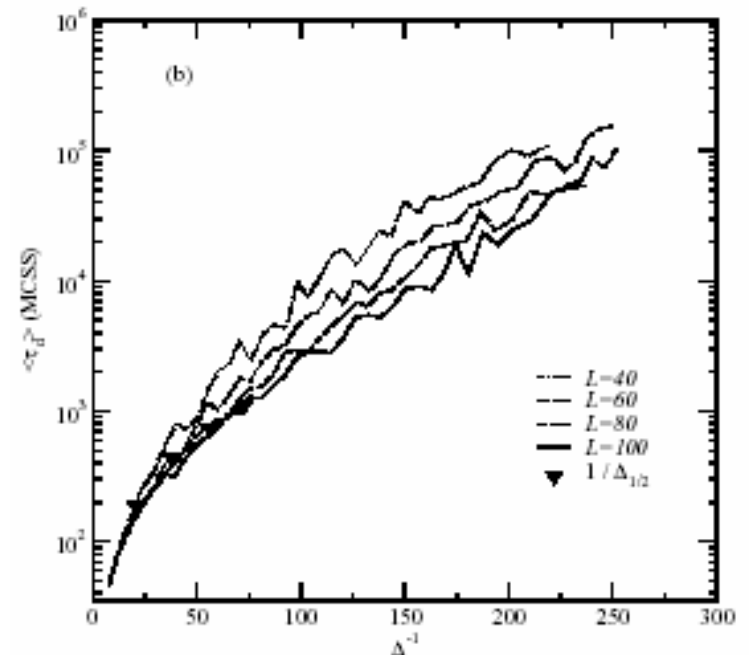
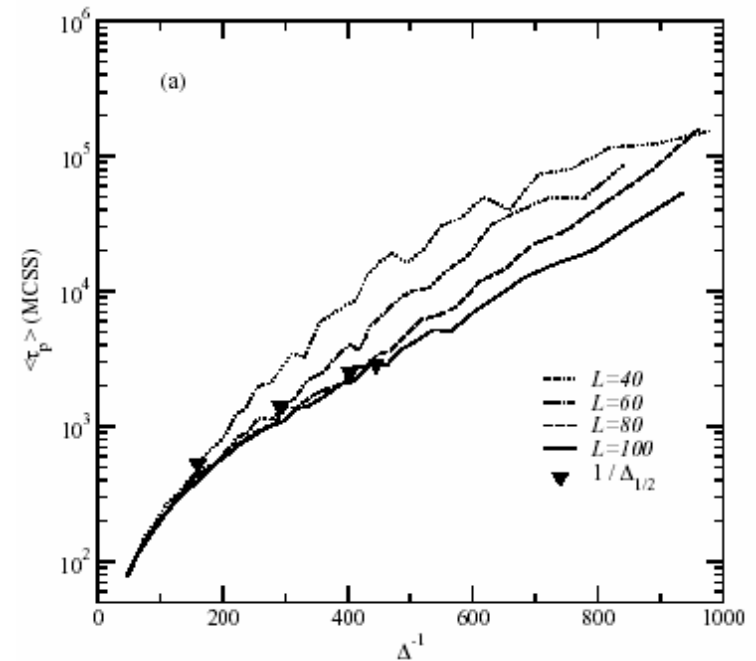
# Numerical results for the decay times

## General KJMA

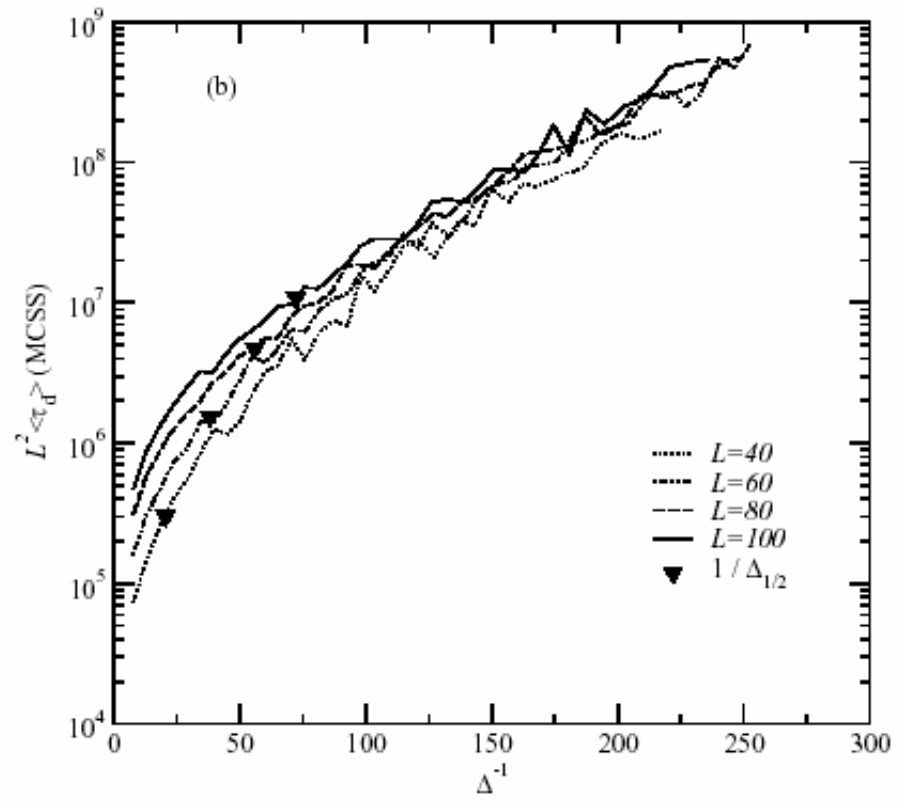
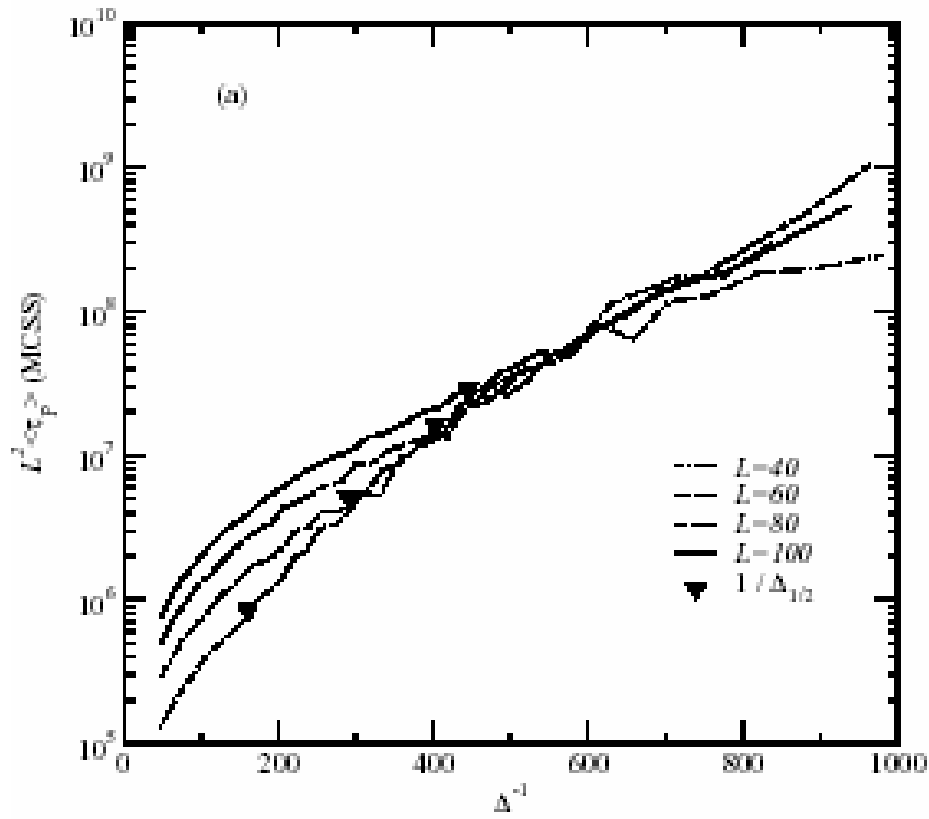
arguments indicate:

- Lifetimes independent of  $L$  in MD regime
- Lifetimes  $\propto L^{-2}$  in SD regime

For small  $\Delta^{-1}$  lifetime independent of  $L$



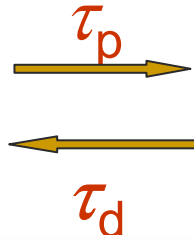
$\Delta^{-1}$  large:  $\langle \tau_p \rangle \propto 1/L^2$



- While a direct analog of the surface tension does not exist in the present system, *the results strongly suggest that it obeys a decay mechanism very similar to the one described by the standard KJMA theory of phase transformation by nucleation and growth*, which predicts well-defined single-droplet and multidroplet regimes.

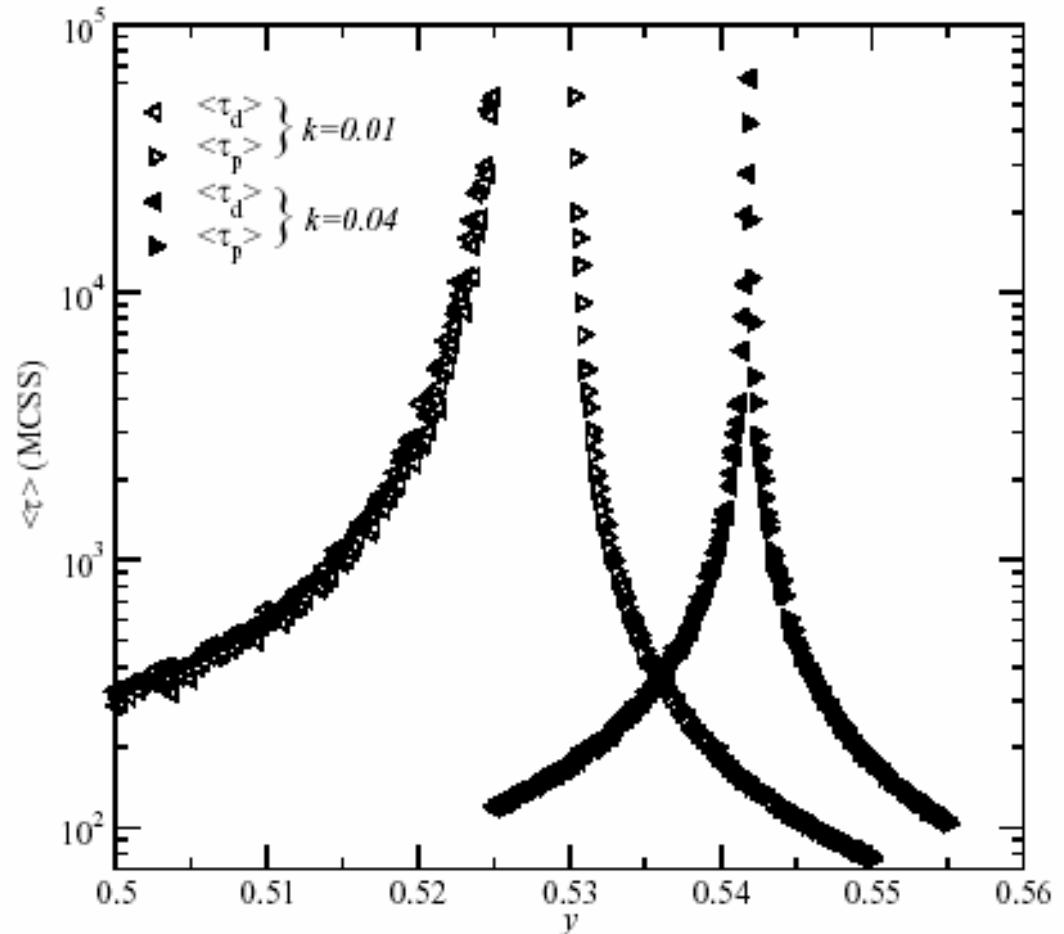
# Relaxation times

Low CO



High CO

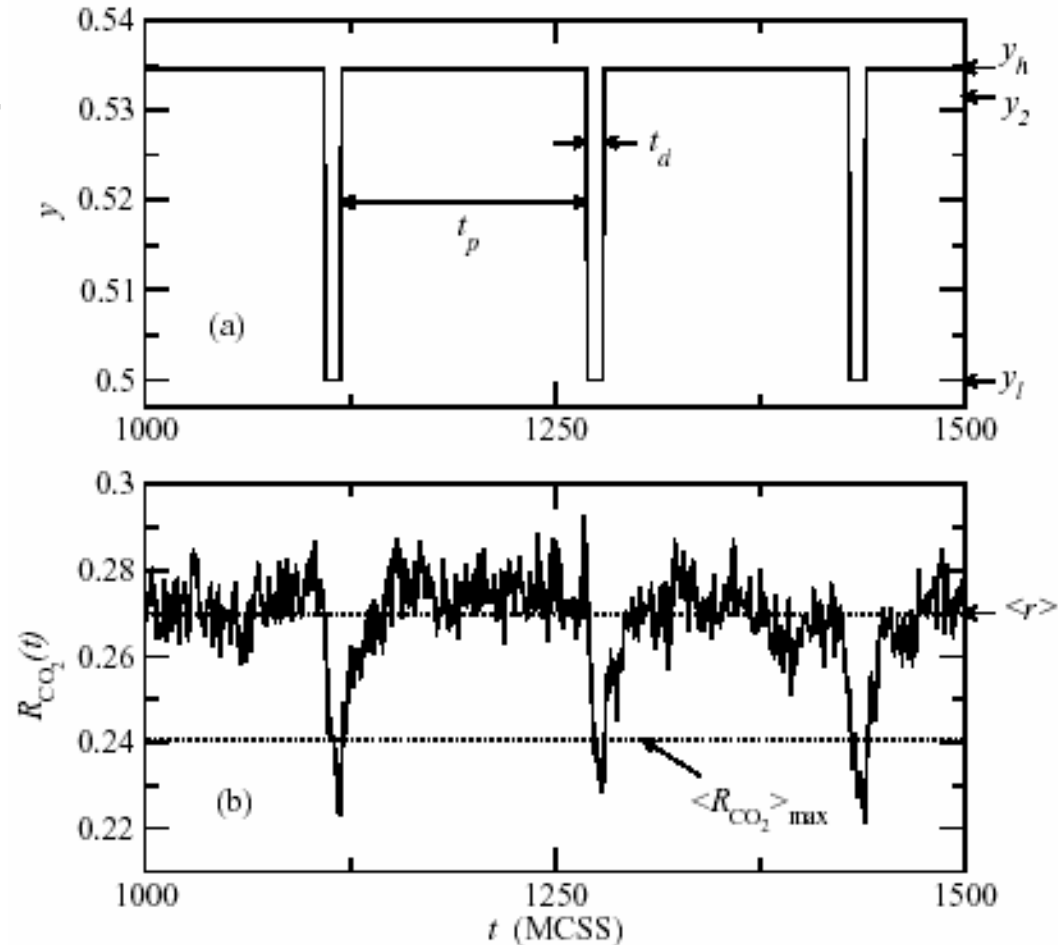
The lifetimes depend on the direction on the process. We exploit this fact perturbing the system by a square-wave periodic pressure variation with parameters that can be tuned to enhance the catalytic activity.



# Response to **periodic** CO pressure, $y(t)$

The average  $\text{CO}_2$  production rate,  $\langle R_{\text{CO}_2} \rangle$  increases compared with constant  $y$

The system undergoes a **dynamic phase transition** between a dynamic phase of high CO production, and a nonproductive one.



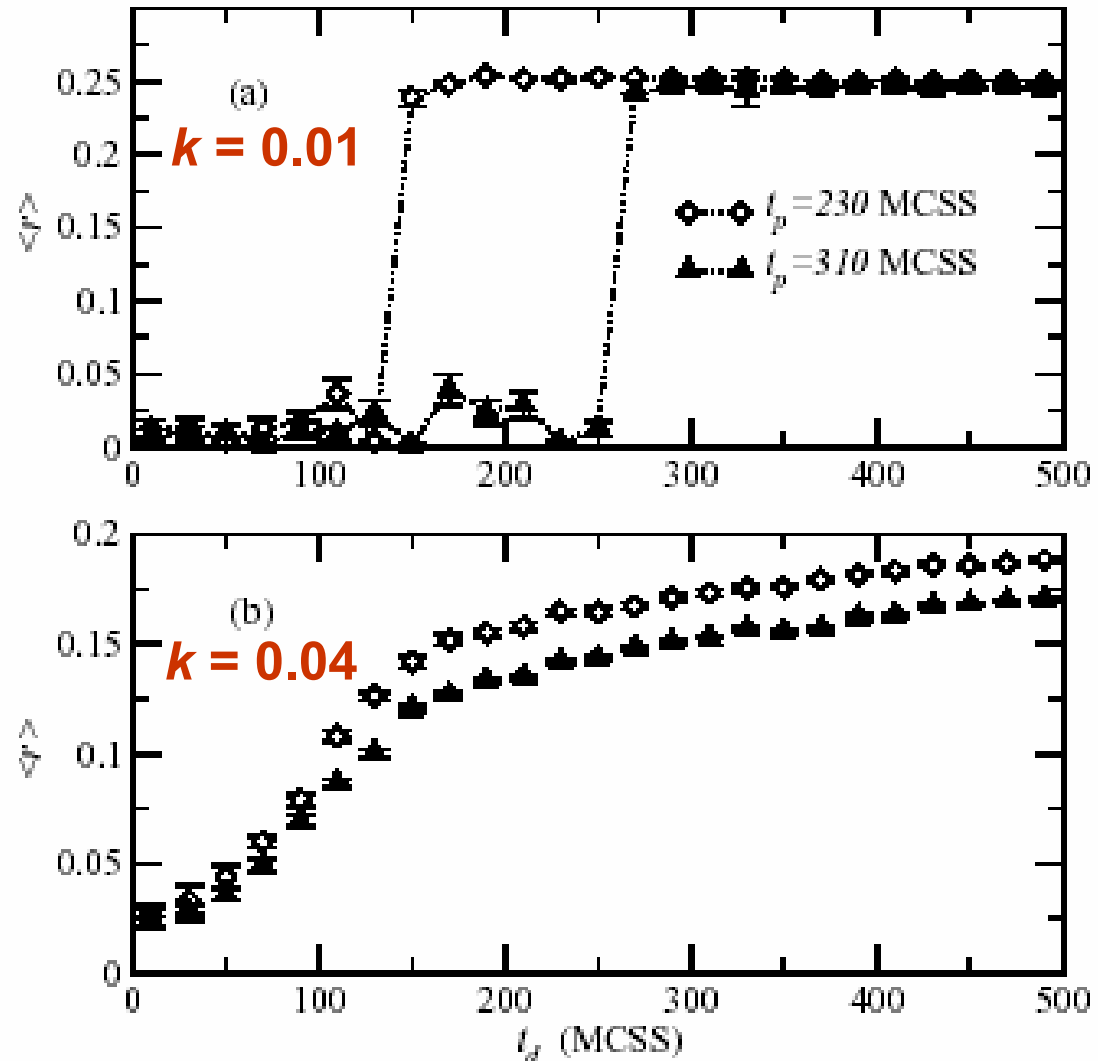
**Enhanced  $\text{CO}_2$  production!!**

# Dynamic phase transition (DPT)

Defining as an order parameter

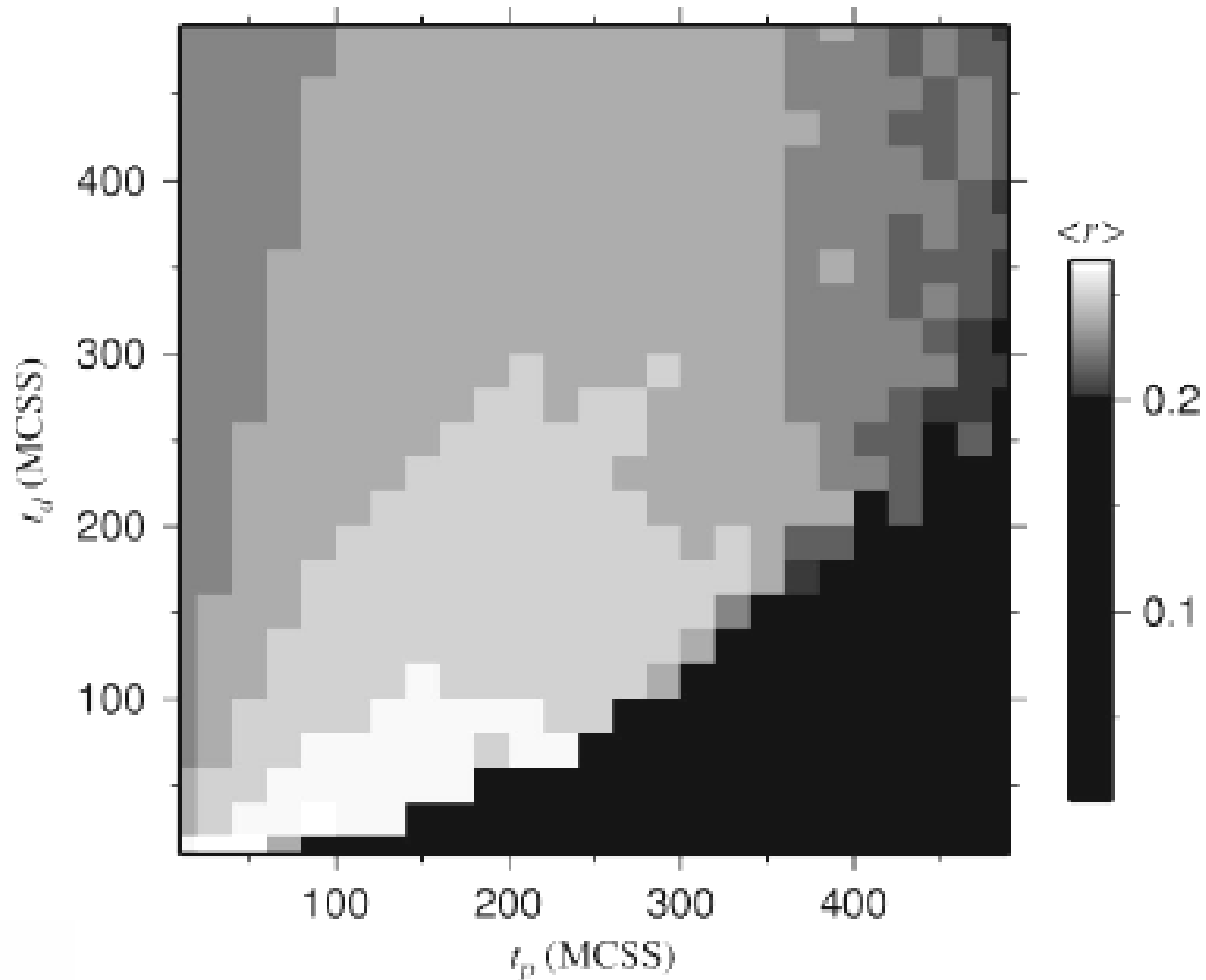
$$r = \frac{1}{T} \oint R_{CO_2}(t) dt$$

The system undergoes a dynamic phase transition between a productive phase  $\langle r \rangle > 0$  and a nonproductive one,  $\langle r \rangle = 0$ . ( $k < k_c$ )



$$y_l = 0.5 \text{ and } y_h = 0.535, L = 100$$

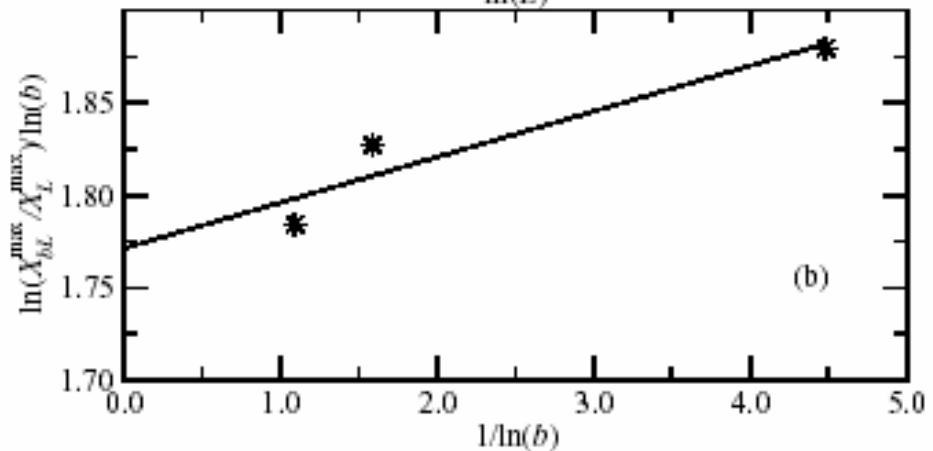
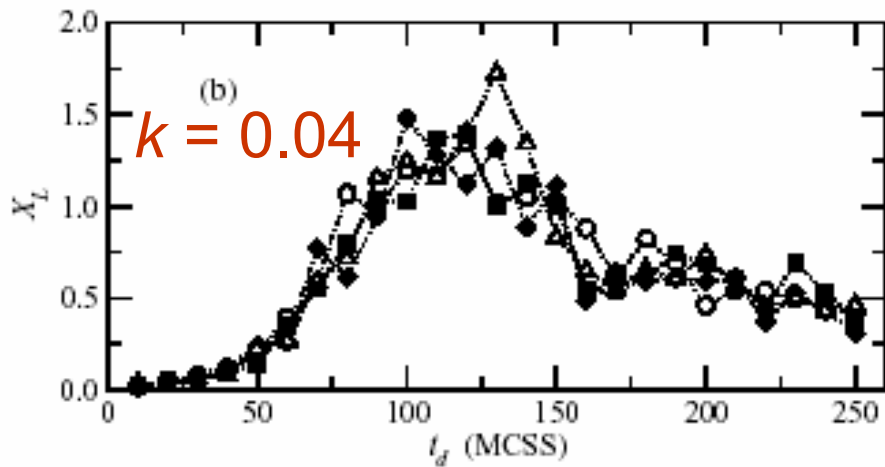
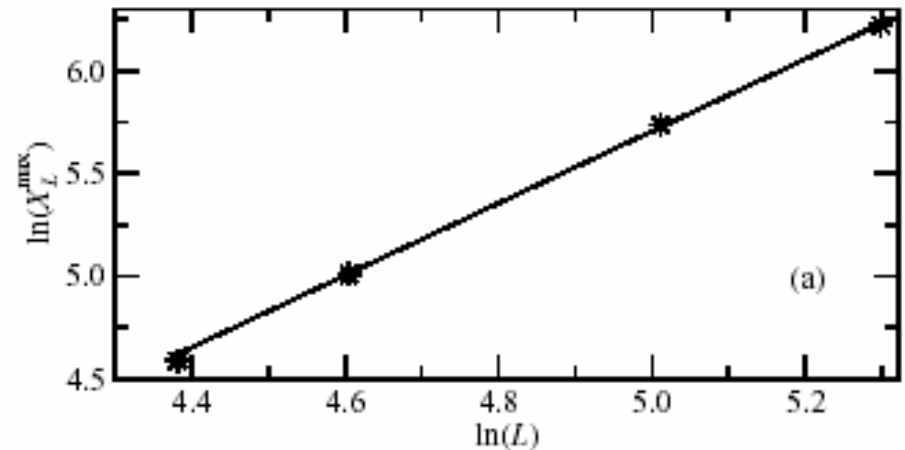
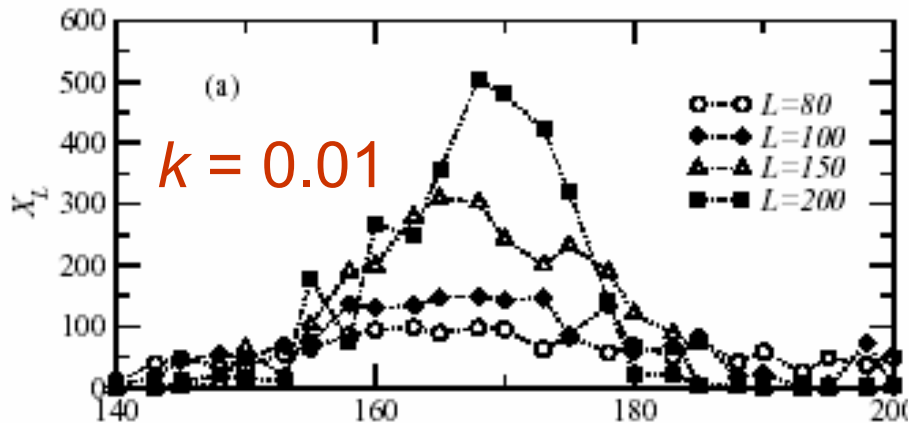
# Enhancement and DPT vs $t_p$ and $t_d$



$$y_l = 0.51, y_h = 0.535, k = 0.01, \text{ and } L = 100$$

Measure fluctuations in  $r$  :

$$X_L = L^2(\langle r^2 \rangle - \langle r \rangle^2)_L$$



$k = 0.01 \quad \chi \sim L^{\gamma/\nu}$

Analogous to a second order equilibrium phase transition the fluctuations and the  $n$ th moment of the order parameter present power law singularities

$$X_L^{max} \sim L^{\gamma/\nu}$$

$$\langle r^n \rangle_L \sim L^{-\nu\beta/\nu}$$

With  $\beta/\nu \approx 0.12$  (0.125 Ising)

and  $\gamma/\nu = 1.77$  (1.75 Ising)

**$\Leftrightarrow$  ZGB- $k$  has a DPT in the same universality class as the 2-D Ising model.**

# Conclusions

- \* Discontinuous, nonequilibrium phase transition between low and high CO-coverage phases for  $k < k_c$
- \* Metastable phases decay by KJMA mechanism:  
Near Coexistence  $\langle \tau \rangle \propto 1/L^2$  (**Single-droplet**)  
Far from Coexistence  $\langle \tau \rangle$  independent of  $L$  (**Multidroplet**).
- \* CO<sub>2</sub> production enhanced by oscillating CO pressure.

The decay mechanisms well described by the **classic KJMA theory**.

$k$  (desorption)  $\Leftrightarrow T$  (temperature)

$\Delta$  (distance to CEC)  $\Leftrightarrow \Delta\mu$  (electrochem. potential)

***Strong similarity between the dynamics of metastable decay in far-from equilibrium, non-Hamiltonian system of applied interest, and the well known behavior in Hamiltonian systems.***

Asymmetry between the lifetimes:  $\langle t_d \rangle \neq \langle t_p \rangle$

⇒ Select a square-wave periodic pressure  
CO  $y(t)$

that stays  $t_d$  in the high production region and  
 $t_p$  in the low production region.

Tune  $t_d$  and  $t_p$  to ***significantly enhance the catalytic activity*** of the system.

For low  $k$  this  $\rightleftharpoons$  driven nonequilibrium system  
undergoes a dynamic phase transition  
(high CO production                  non-production)  
consistent with an equilibrium second-  
order phase transition, that seems to  
belong to the ***same universality class as***  
***the equilibrium Ising model***

***Exciting and encouraging that this non-equilibrium system presents phase transitions that behave very similarly to equilibrium phase transitions.***

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Phys. Rev. E **71**, 031603 (2005)

## *Future*

- For a more realistic model of a catalyst surface
  - ⇔ Lateral diffusion of reactants
  - ⇔ Inhomogeneities in the surface