

Non-equilibrium correlations in stochastic (interacting-particle) reaction-diffusion models with inhibited "stirring"

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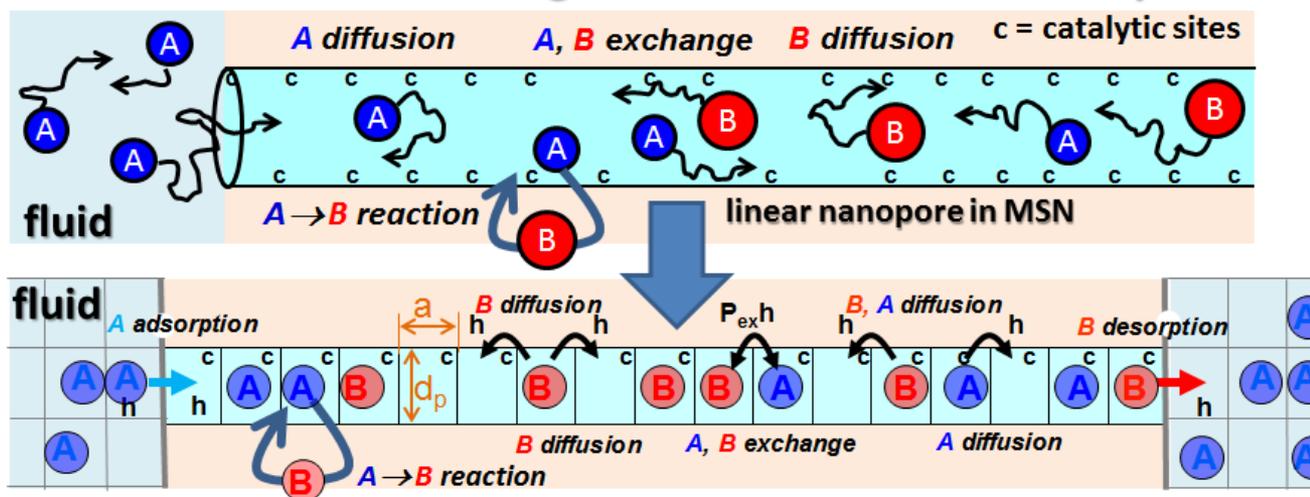
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\$\$\$ USDOE
 Basic En. Sci.
 Chemical
 Sciences

CG Stochastic Modeling: $A \rightarrow B$ reaction in nanopores



OUTLINE / OVERVIEW

Examples: Catalytic rxn in porous materials with narrow 1D pores
Catalytic reaction (rxn) on crowded 2D surfaces (for high P)

Traditional modeling: “mean-field” continuum reaction-diffusion eqn
“Well-stirred” randomly-distributed reactants...**neglects spatial correlations***
Treatment of diffusion neglects complications for mixed reactant systems

**spatial correlations come from thermodynamics (molecular interactions) and kinetics (e.g., low mobility with rxn)*

Analysis of spatially-discrete stochastic molecular-level models:
Heterogeneous Master Equations (lattice differential type equations)
...precise model analysis generally requires **Kinetic Monte Carlo simulation**



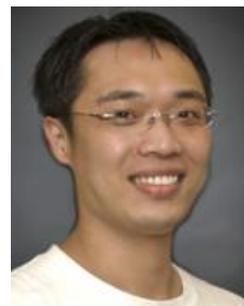
Andres Garcia



David Ackerman



Jing Wang



Chi-Jen Wang



Da-Jiang Liu

1D nanoporous systems

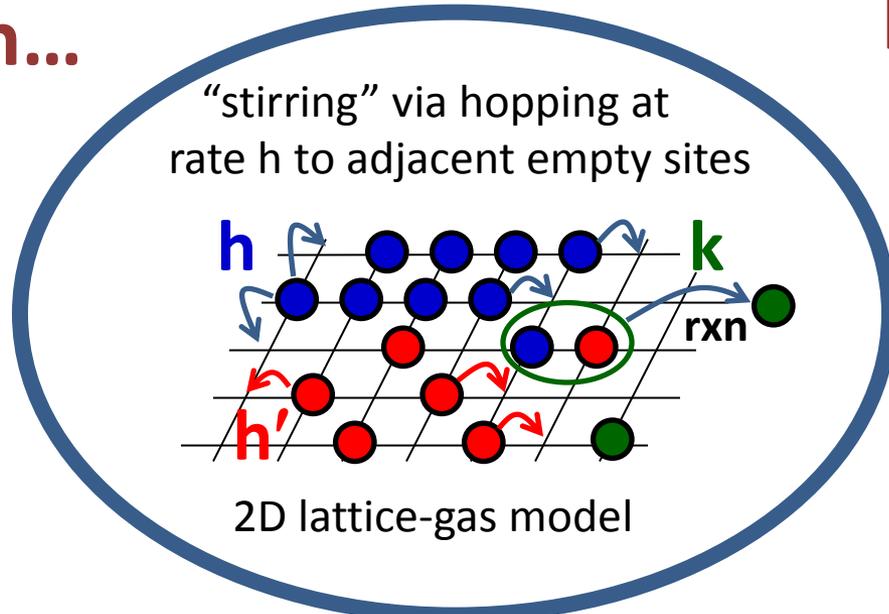
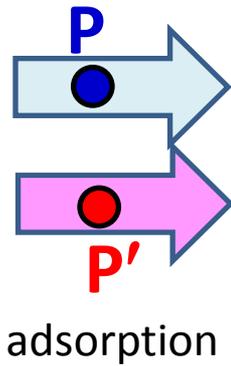
2D surface systems

Spatially-discrete (lattice-gas) stochastic catalytic reaction-diffusion models

Catalytic system

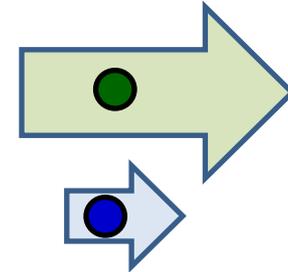
1D, 2D or 3D lattice-gas model

Reactants in...

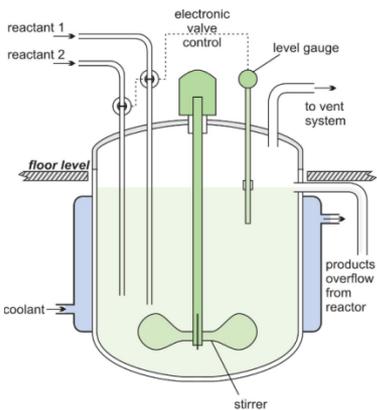


Products out...

reaction (rxn)



non-reactive desorption



Rapid stirring ($h \gg P, k$)

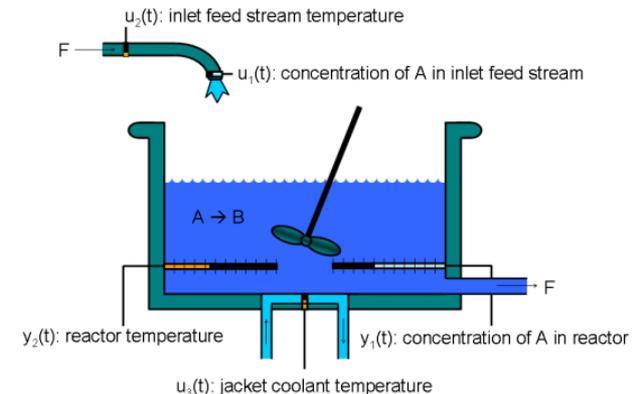
\Rightarrow catalytic system **equilibrated**

\Rightarrow species randomized if no interactions between them

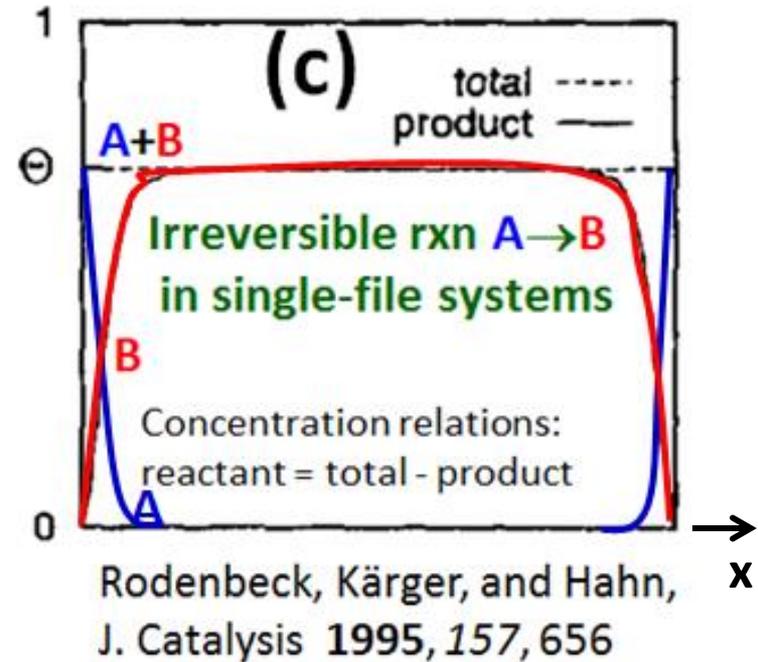
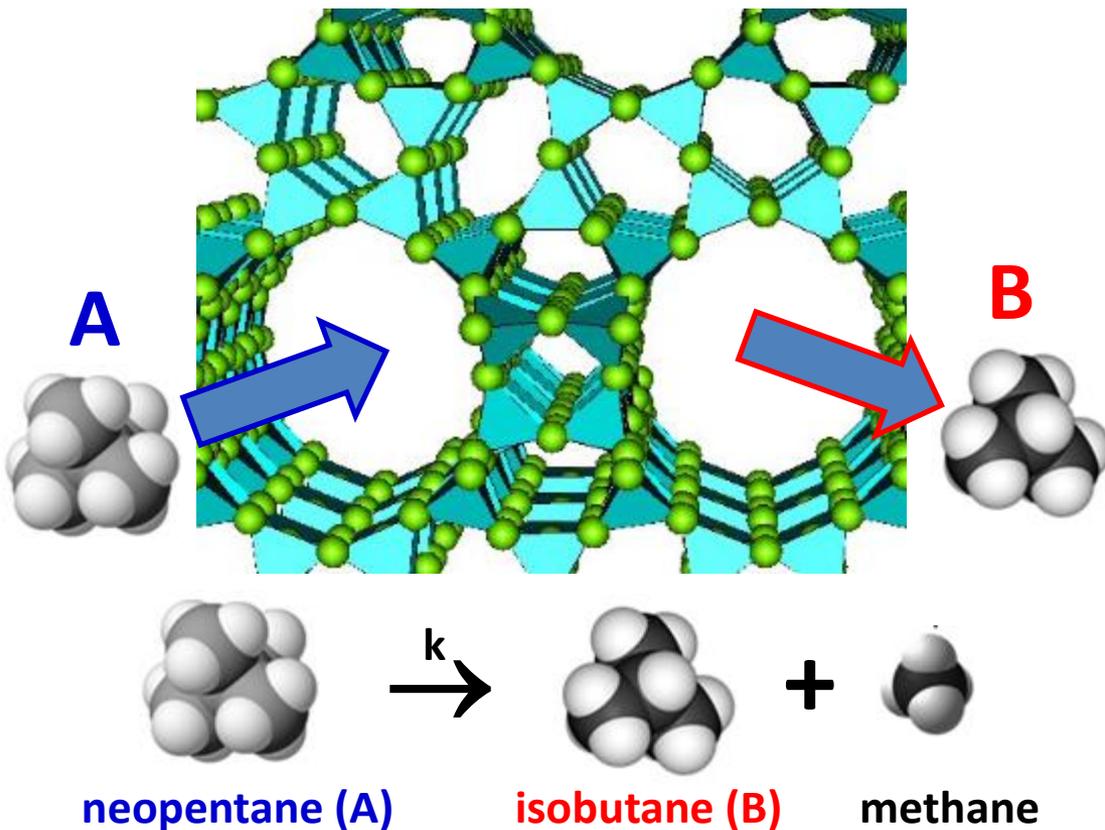
$$\Rightarrow \text{rxn rate} = k [\bullet\bullet] = k[\bullet][\bullet]$$

Inhibited stirring \Rightarrow spatial

correlations $\Rightarrow [\bullet\bullet] \neq [\bullet][\bullet]$



CATALYTIC CONVERSION A → B IN ZEOLITES WITH INHIBITED TRANSPORT



Zeolite = nanoporous aluminosilicate

Mean-field (MF) reaction-diffusion eqns (RDE): A → B @ rxn rate k

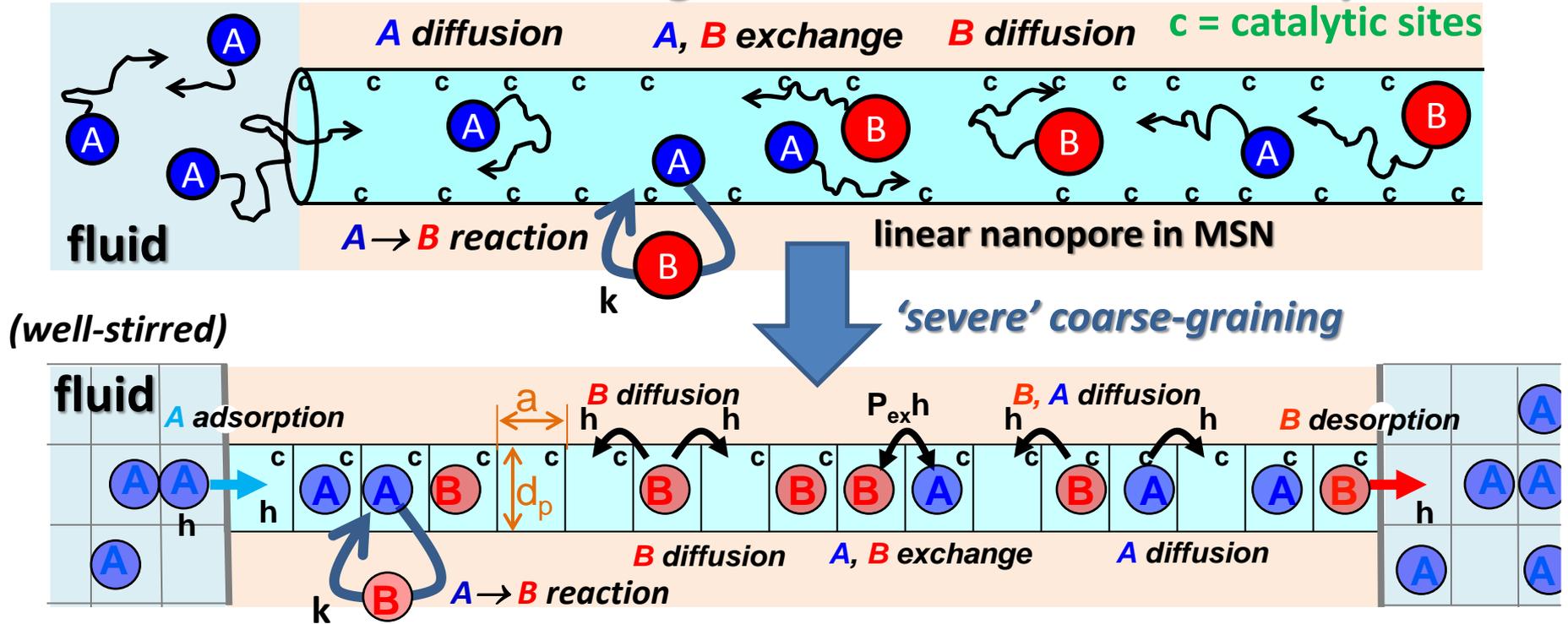
$$\frac{\partial}{\partial t} [A] = -k [A] - \frac{\partial}{\partial x} J_A; \quad \frac{\partial}{\partial t} [B] = +k [A] - \frac{\partial}{\partial x} J_B \dots \text{with } J_A = -D_A \frac{\partial}{\partial x} [A], \text{ etc. } ??$$

+ appropriate adsorption-desorption boundary conditions @ pore openings

CATALYTIC CONVERSION REACTION $A \rightarrow B$ WITH INHIBITED TRANSPORT

Fig. 2.3 Chemical Reviews 115 (2015) 5979

CG Stochastic Modeling: $A \rightarrow B$ reaction in nanopores

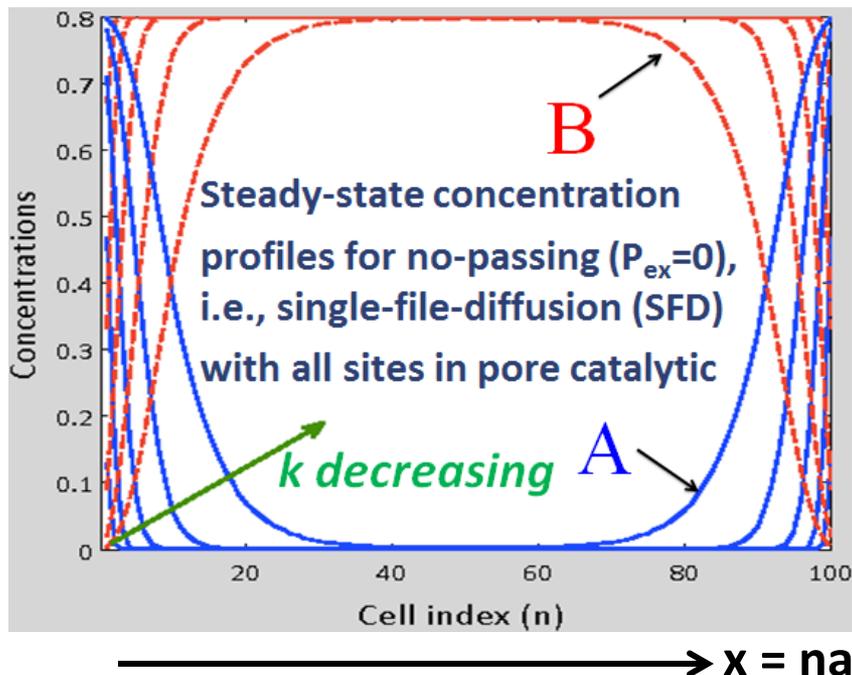
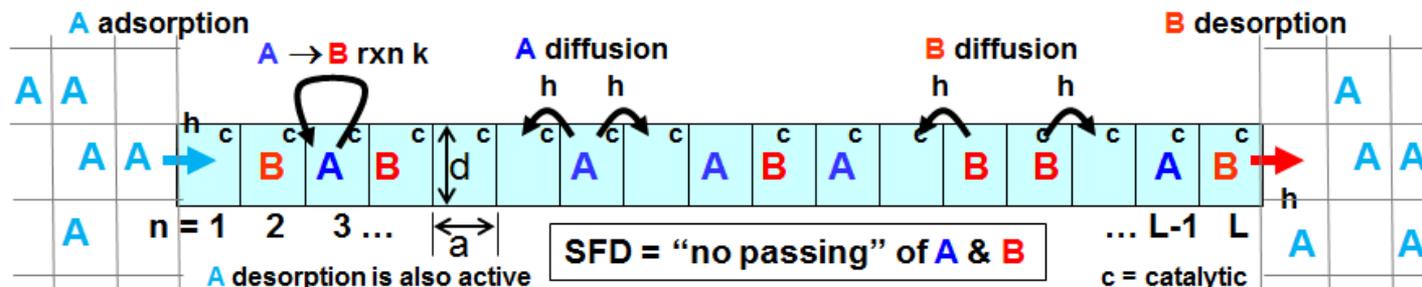


If "color blind", so A & $B \rightarrow X$, then model becomes a simple diffusion problem for X w/o reaction \Rightarrow total steady-state concentration is uniform

History: Wei et al. Chem Eng Sci (1991); Kärger et al. J. Catal. (1992) (1995); PRE (1997); Okino et al. JCP (1999); Nedeá et al. PRE (2002) (2003)

ISU group: J Chem Phys 134 (2011) Ed. Choice; 138 (2013); ACS Catal 1 (2011); Phys Rev Lett 108 (2012); 113 (2014); Chem. Rev. 115 (2015)

IRREVERSIBLE REACTION $A \rightarrow B$ with SINGLE-FILE DIFFUSION (SFD): Dependence of behavior on the “microscopic” conversion rate k (relative to h)



BASIC QUESTIONS:

Reactant (A) penetration depth into pore

$L_p \sim a(h/k)^n$ What is n ? MF theory says $\frac{1}{2}$.

Total reactivity/yield: $R_{tot} \sim k L_p \sim k^{1-n}$

Shape of reactant concentration profile:

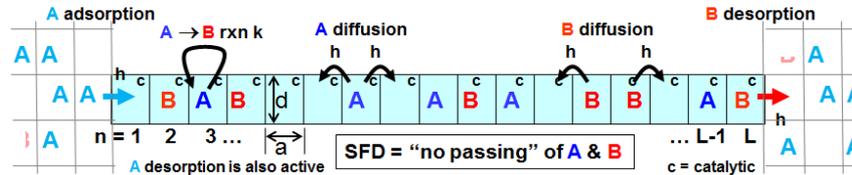
MF theory predicts exponential decay at left end of the form $\langle A(x) \rangle \sim \exp(-x/L_p)$? where $x = na$ ($\ll L/2$) distance into pore

J Chem Phys (2011); ACS Catal. (2011); PRL (2012)

$k/h = 1, 0.1, 0.01, 0.001, 0.0001$ gives...

$L_p = 1.10, 1.47, 2.64, 5.21, 10.50$ in units of 'a'

CATALYTIC CONVERSION REACTION $A \rightarrow B$ WITH INHIBITED TRANSPORT: EXACT FORMULATION FOR SPATIALLY DISCRETE STOCHASTIC MODEL



$[A_n]$ = concentration of A on cell n (i.e., probability that cell n is occupied by A), etc.

Also if $[X_n] = [A_n] + [B_n] = \text{tot. conc.}$, then $[E_n] = 1 - [X_n] = \text{prob. cell n is empty}$.

$$d/dt [A_n] = -k [A_n] - \nabla_n J_A(n \rightarrow n+1); \quad d/dt [B_n] = +k [A_n] - \nabla_n J_B(n \rightarrow n+1)$$

where $J_A(n \rightarrow n+1) = h([A_n E_{n+1}] - [E_n A_{n+1}]) + p_{\text{ex}} h([A_n B_{n+1}] - [B_n A_{n+1}])$, etc.

and $\nabla_n K_n = K_n - K_{n-1}$ is the discrete gradient (discrete first-order difference)

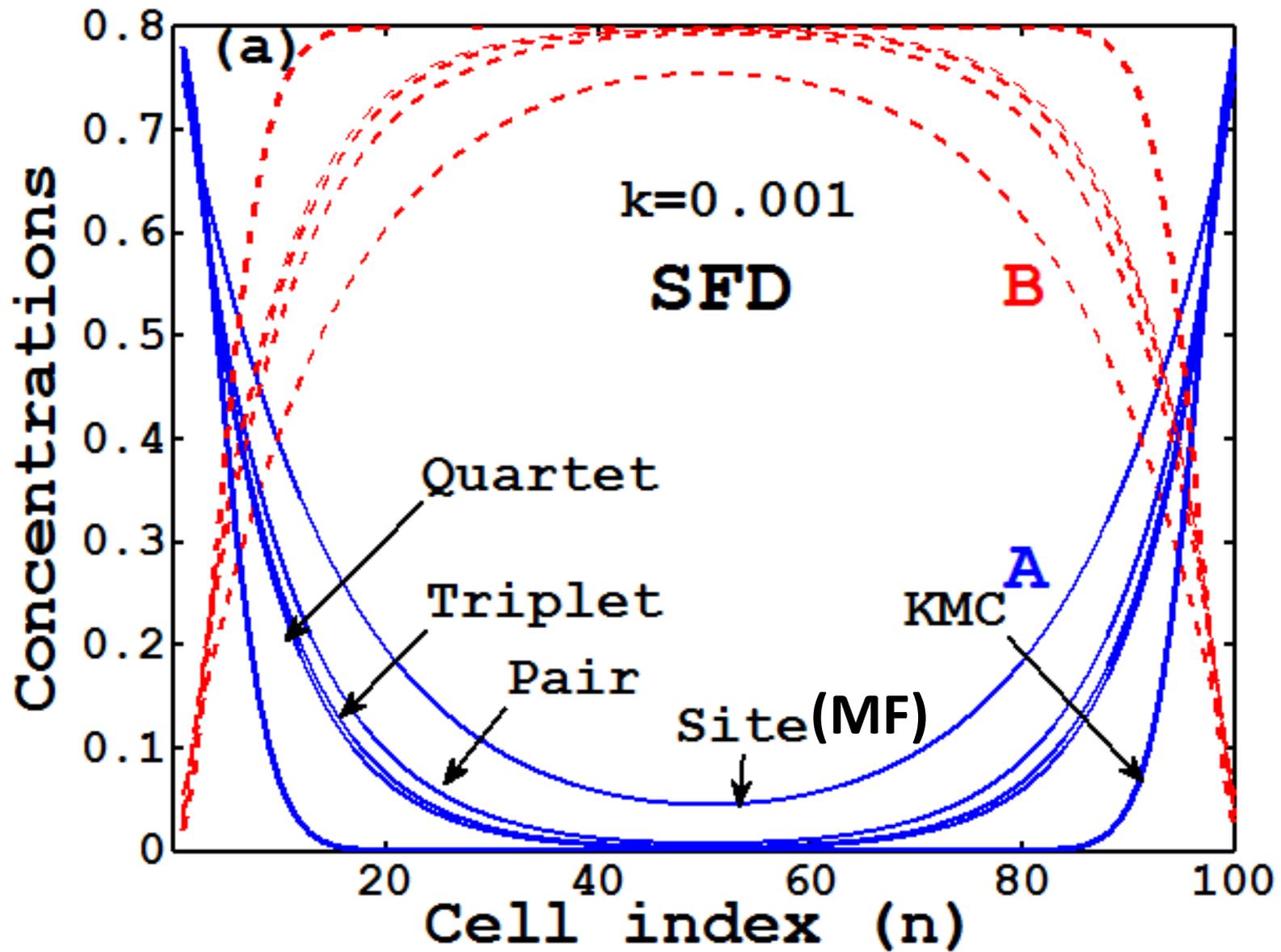
These equations are not closed. Can add equation $d/dt [A_n E_{n+1}] = \dots$ etc. which couple to triple cell quantities like $[A_n E_{n+1} B_{n+2}]$ etc. Generates infinite coupled hierarchy...

Approximate hierarchical truncation treatments (cf. Boltzmann's truncation of BBGKY hierarchy):

Mean-field 'site' approx. (neglects spatial correl.): $[A_n E_{n+1}] = [A_n][E_{n+1}]; [A_n B_{n+1}] = [A_n][B_{n+1}];$ etc. produces a closed set of discrete RDE also described as lattice differential equations.

'Pair' approximation: $[A_n E_{n+1} B_{n+2}] = [A_n E_{n+1}][E_{n+1} B_{n+2}]/[E_{n+1}]$, etc. 'Triplet' approximation:...

CATALYTIC CONVERSION REACTION $A \rightarrow B$ WITH INHIBITED TRANSPORT

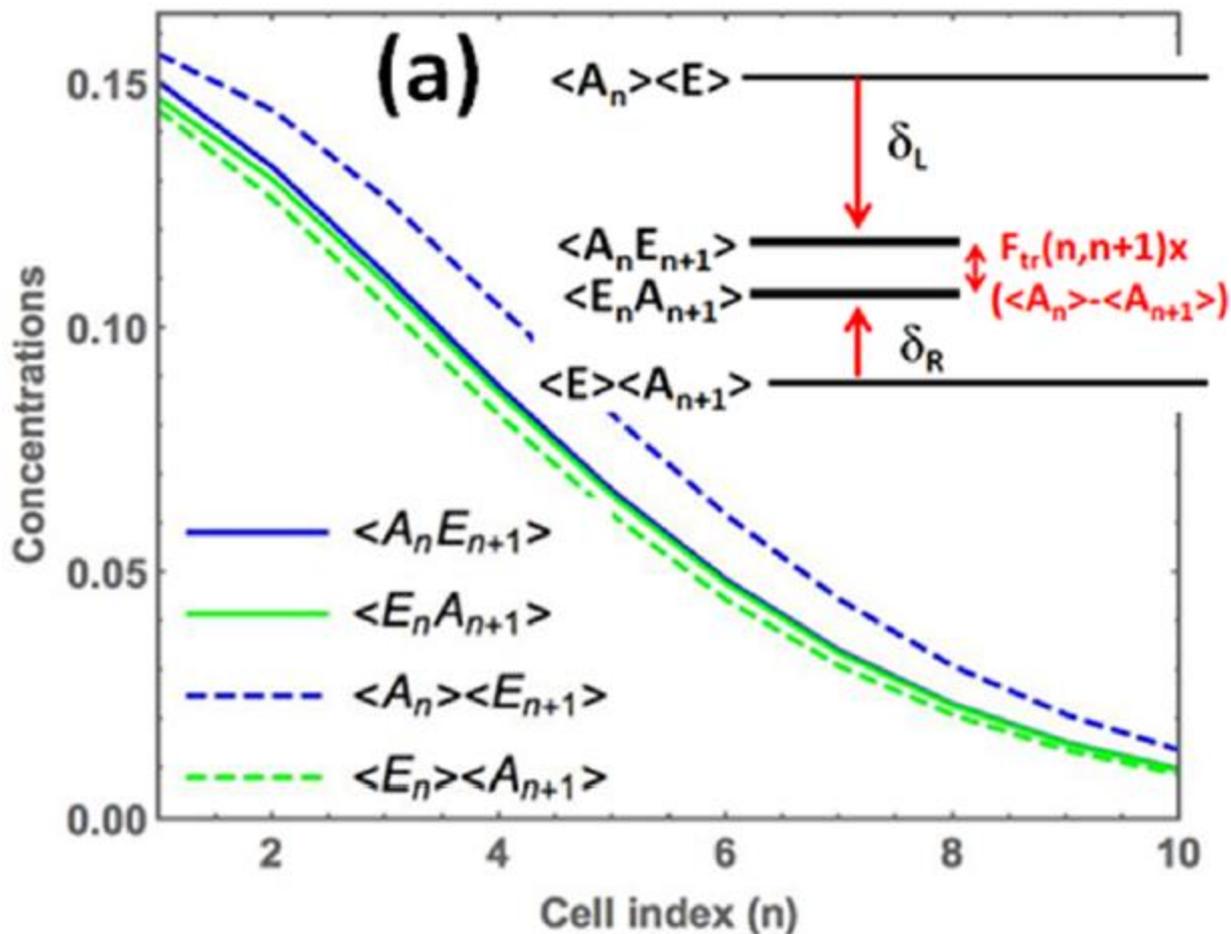


CATALYTIC CONVERSION REACTION $A \rightarrow B$: SPATIAL CORRELATIONS

Garcia, Wang, Sadow, Windus, Evans PRE 93 (2016) 052137; also Chem Rev (2015)

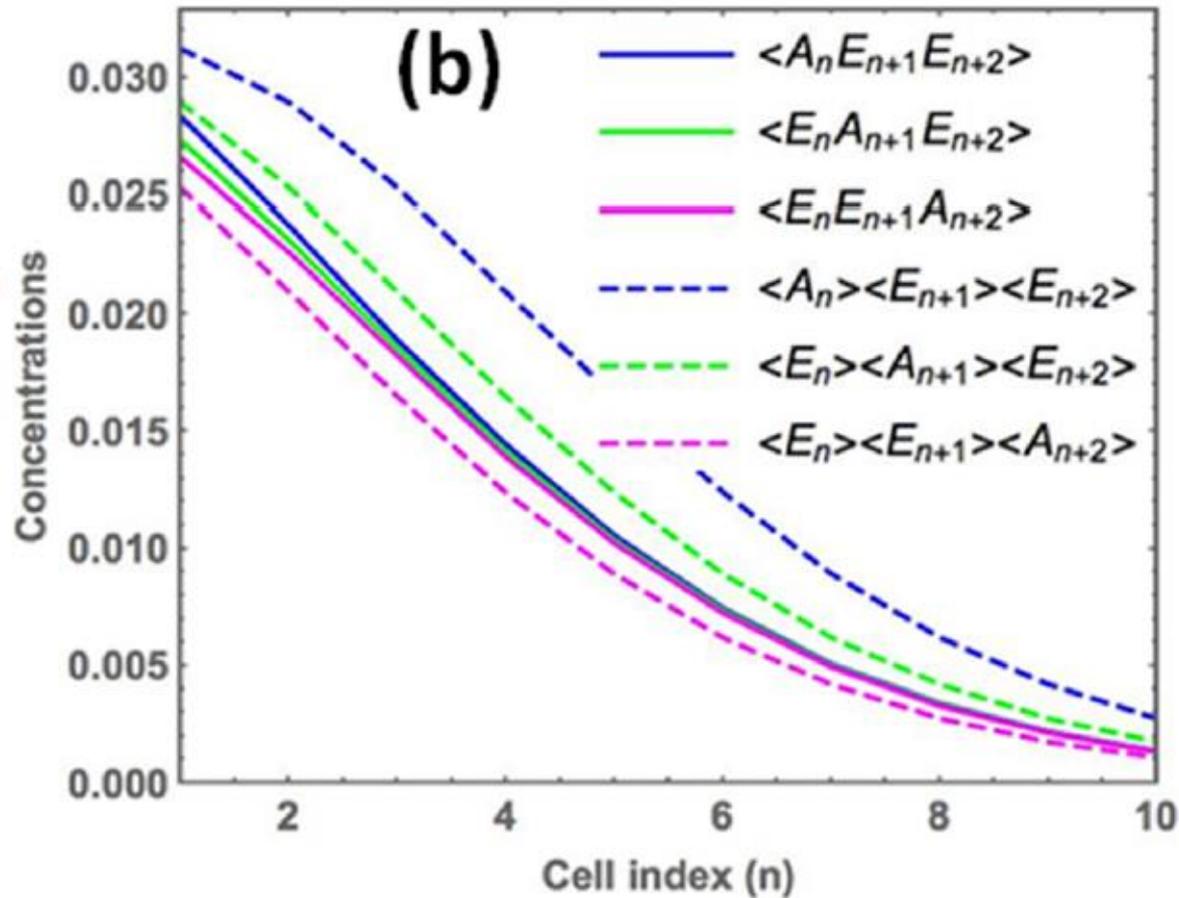
Recall that for SFD:

$$J_A(n \rightarrow n+1) = h([A_n E_{n+1}] - [E_n A_{n+1}]) \xrightarrow{\text{MF}} h([A_n][E_{n+1}] - [E_n][A_{n+1}]) = h[E]([A_n] - [A_{n+1}])$$



In fact, $[A_n E_{n+1}]$ & $[E_n A_{n+1}]$ are much closer than the MF prediction due to SFD constraint...

CATALYTIC CONVERSION REACTION $A \rightarrow B$: SPATIAL CORRELATIONS



Pair approximation enforces relations:

$$\langle A_n E_{n+1} E_{n+2} \rangle \approx \langle A_n E_{n+1} \rangle \langle E_{n+1} E_{n+2} \rangle / \langle E_{n+1} \rangle$$

$$\langle E_n A_{n+1} E_{n+2} \rangle \approx \langle E_n A_{n+1} \rangle \langle A_{n+1} E_{n+2} \rangle / \langle A_{n+1} \rangle, \text{ etc.}$$

which does not make these quantities similar

For conditional prob $P(\alpha | \beta) = P(\alpha + \beta) / P(\beta)$:

Pair approx says: $\langle A_n | E_{n+1} E_{n+2} \rangle \approx \langle A_n | E_{n+1} \rangle$

But $\langle A_n | E_{n+1} E_{n+2} \rangle$ does depend strongly on the feature that site $n+2$ is specified empty

IRREVERSIBLE REACTION $A \rightarrow B$ with SINGLE-FILE DIFFUSION (SFD):
Reaction-Diffusion Equations to describe evolution of concentration profiles

$\partial/\partial t A(x) = -k A(x) - \partial/\partial x J_A$, $\partial/\partial t B(x) = +k A(x) - \partial/\partial x J_B$. Set $X(x) = A(x) + B(x)$

Chem diff. fluxes $J_A = -D_{A,A} \partial/\partial x A(x) - D_{A,B} \partial/\partial x B(x)$, etc. **or** $\underline{J} = -\underline{D} \partial/\partial x \underline{C}$ (Onsager)

J. Quastel *Comm. Pure Appl. Math* 45 (1992): $J_A = -D(A/X)\partial X/\partial x - D_{tr}[(B/X)\partial A/\partial x - (A/X)\partial B/\partial x]$, etc.

where $D = a^2h$ = chem diff coefft for single component system and D_{tr} = tracer diffusion coefft

Consider steady-state where $A(x) + B(x) = X = \text{const.}$

so that $\partial B/\partial x \approx -\partial A/\partial x$ (counter diffusion mode)

$J_A = -D_{tr} \partial/\partial x A(x)$...where one can show that

$D_{tr} = D_{A,A} - D_{A,B}$ = "tagged particle" tracer diffusion coefft.

◆ **Mean-field theory:** $D_{tr} \propto [E] = 1 - [B] - [A]$

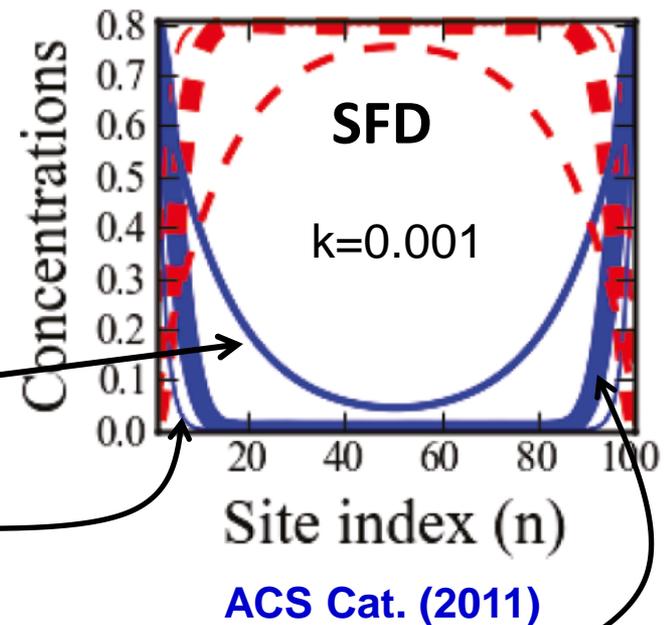
◆ **Standard "hydrodynamic" theory for SFD:**

$D_{tr} = 0$...or $D_{tr} \sim 1/(\text{pore length}) \sim \text{small}$

Harris, *J. Appl. Prob.* (1965)

◆ **Our "Generalized Hydrodynamic" theory:**

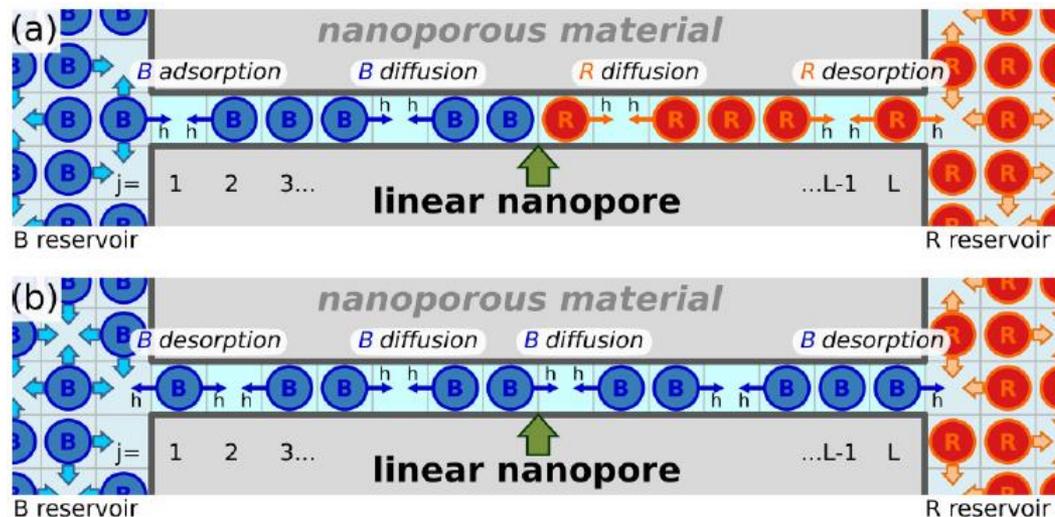
D_{tr} is enhanced near pore openings...



Exact KMC results

“TRACER COUNTER-PERMEATION” ANALYSIS OF GENERALIZED D_{tr}

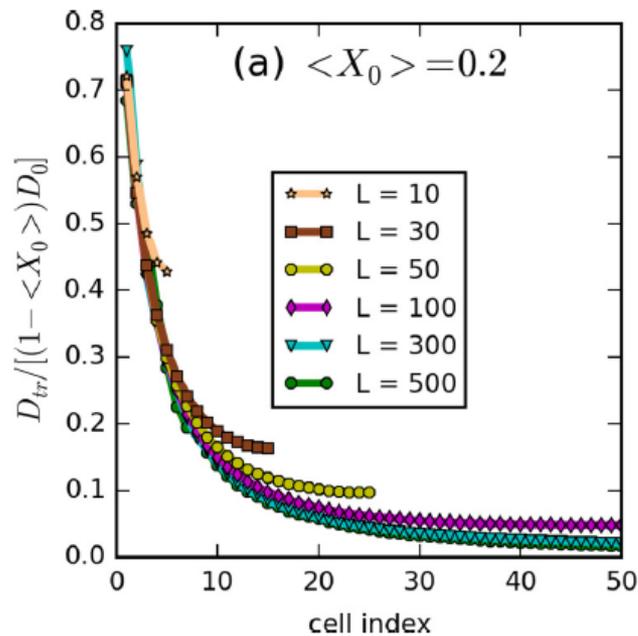
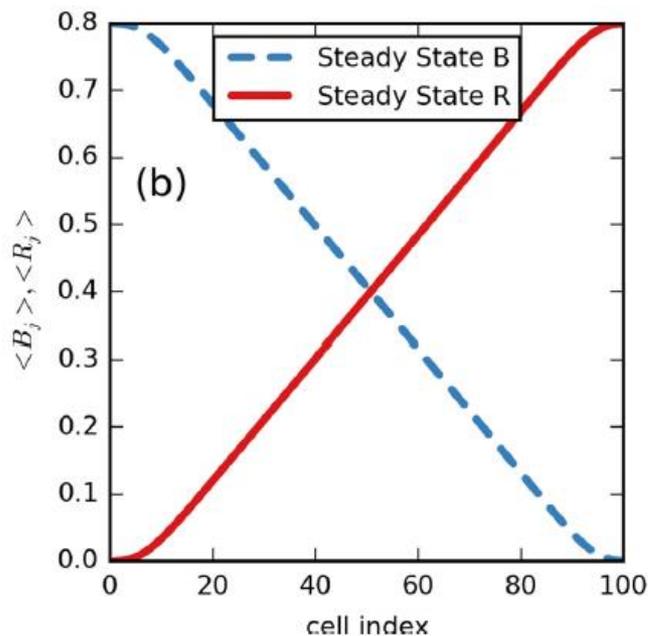
D.M. Ackerman, J.W. Evans, Phys. Rev. E 95 (2017) 012132. See also: Nelson, Auerbach, Chem. Eng. J. 74 (1999).



$$J_B = - D_{tr} \partial/\partial x [B] > 0$$

$$D_{tr}(x) \equiv -J_B / \partial/\partial x [B] = J_B / |\partial/\partial x [B]|$$

enhanced near pore openings where $|\partial/\partial x [B]|$ is smaller

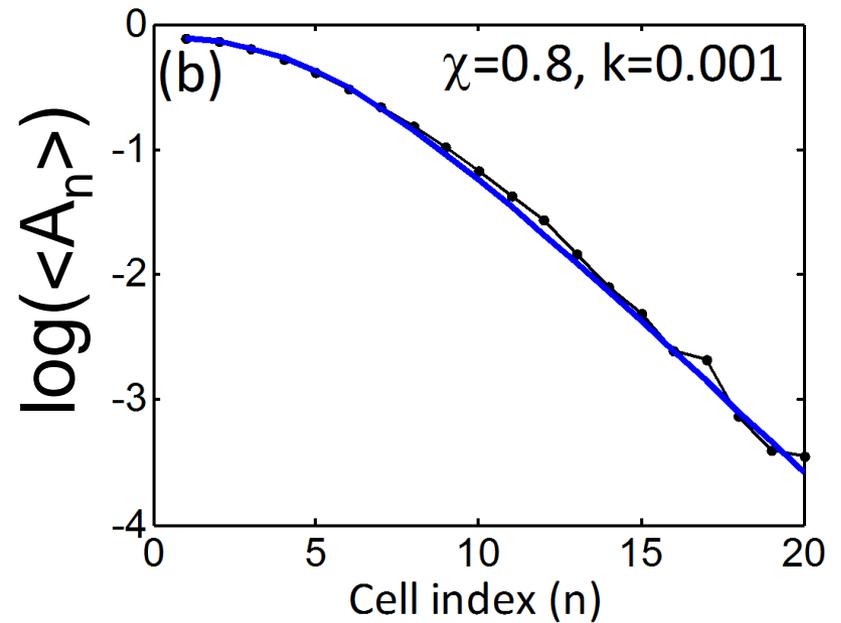
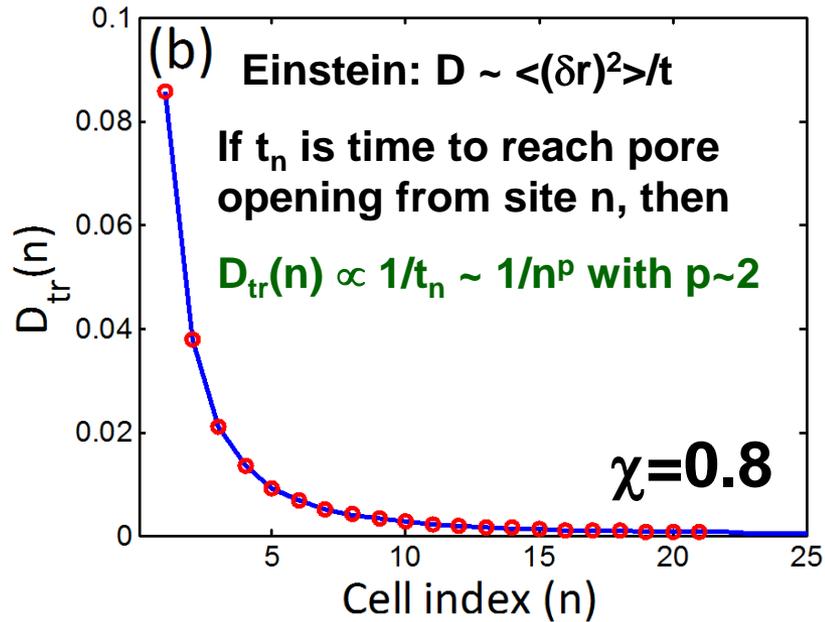


Alternative RW strategy:

...assess time of tagged particle to escape the pore starting at various locations, x , inside the pore.

[PRL 108 \(2012\) 228301](#)

IRREVERSIBLE REACTION $A \rightarrow B$ with SINGLE-FILE DIFFUSION (SFD):
Success of “generalized hydrodynamic theory” for concentration profiles



PREDICTIONS OF “GENERALIZED HYDRODYNAMIC” THEORY:

$D_{tr}(n) \sim 1/n^p$ with $p \sim 2 \Rightarrow L_p \sim (k/h)^{-n}$ with $n = 1/(2+p)$ so $n \sim 1/4$ (vs MF $n = 1/2$)

$\langle A(x) \rangle \sim \exp[-(x/L_p)^q]$ with $q = (2+p)/2$ (so $q = 2$ is Gaussian not exponential decay)

David Ackerman, Jing Wang, JWE,
Phys. Rev. Lett. 108 (2012) 228301

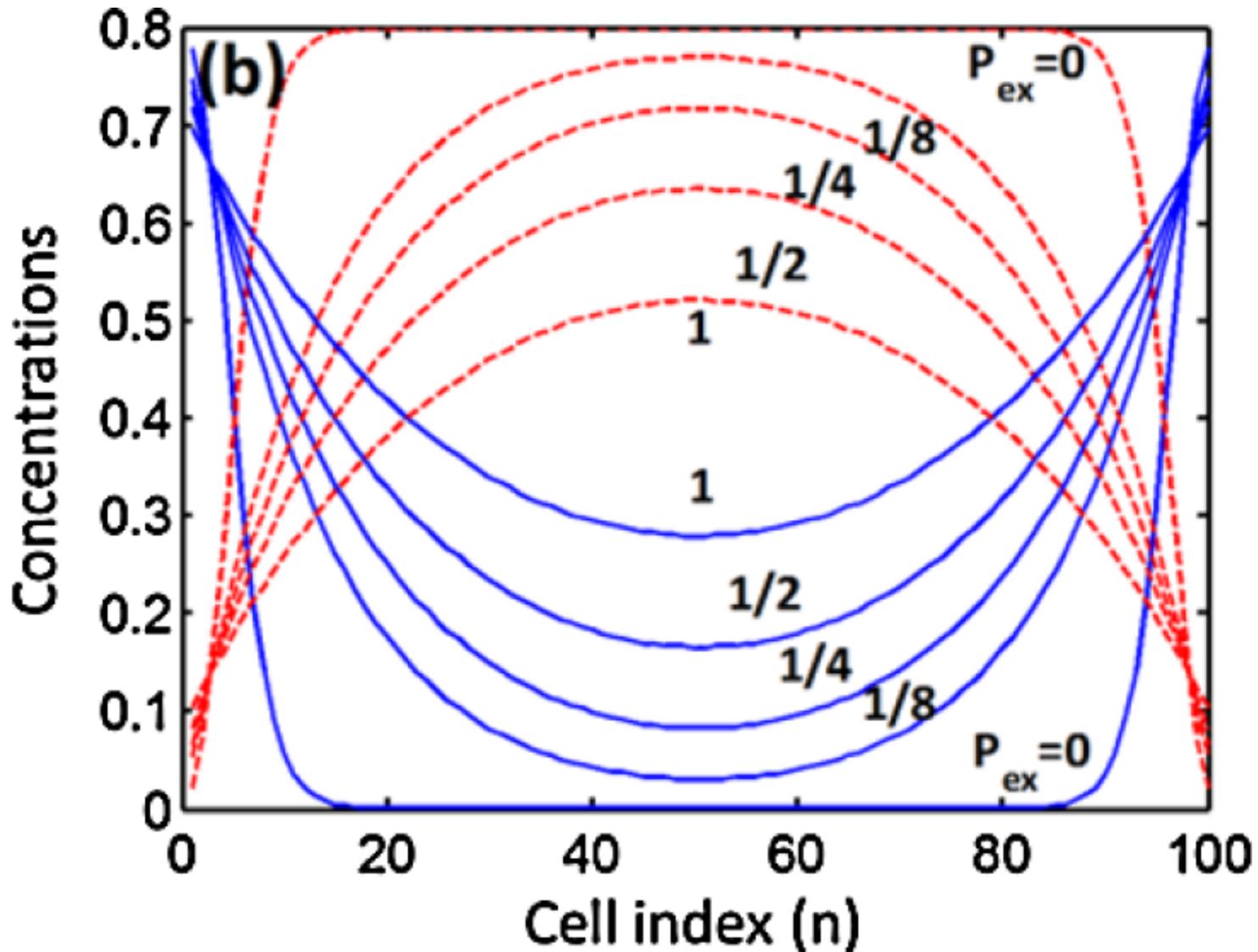


David
 Ackerman
 (Chemistry)



Jing
 Wang
 (AMath)

CATALYTIC CONVERSION REACTION $A \rightarrow B$ WITH INHIBITED TRANSPORT:
RELAXING SFD CONSTRAINT TO ALLOW PASSING WITH PROBABILITY P_{ex}



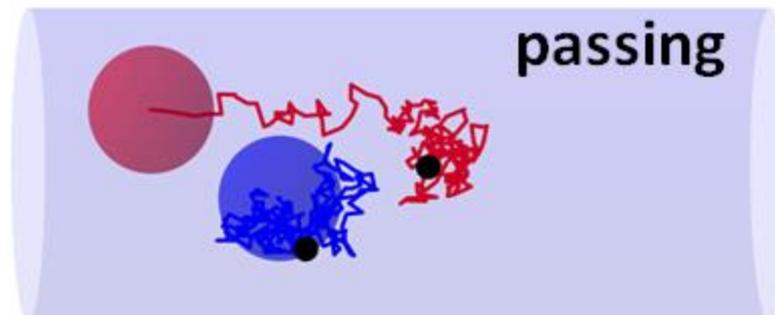
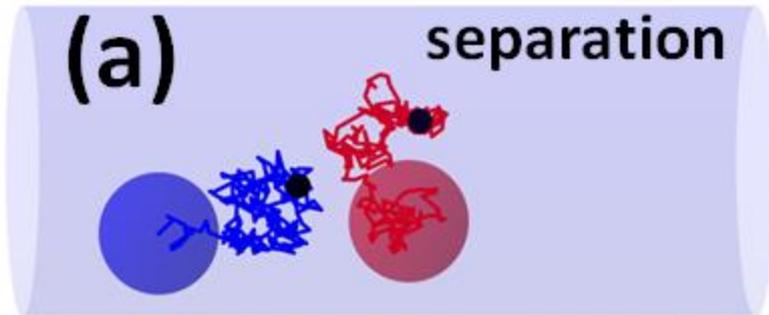


Chi-Jen Wang

Langevin and Fokker-Planck Analyses of Inhibited Molecular Passing Processes Controlling Transport and Reactivity in Nanoporous Materials

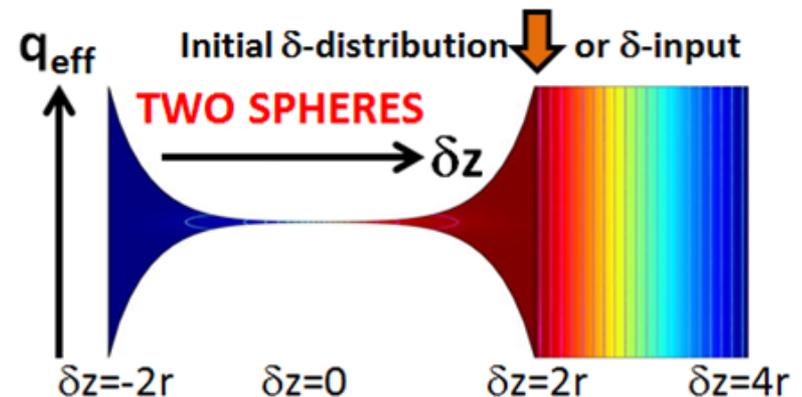
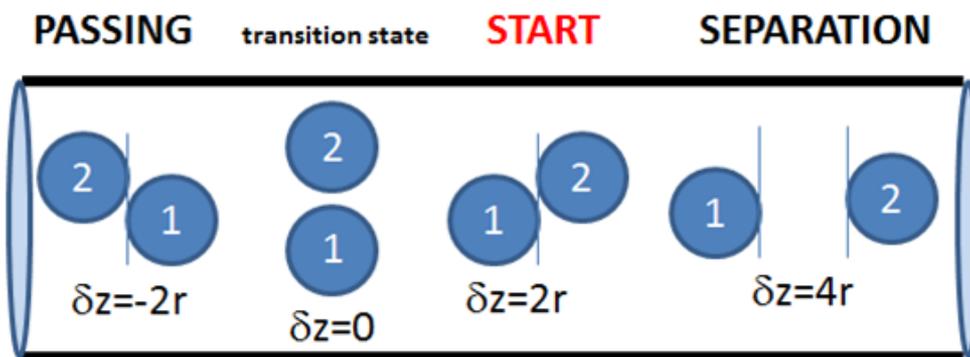
Chi-Jen Wang,^{1,2} David M. Ackerman,¹ Igor I. Slowing,^{1,3} and James W. Evans^{1,4}

Strongly-damped Langevin dynamics: $\zeta_i dx_i/dt = F_i^{rnd}(t)$ where $\langle F_i^{rnd} \rangle = 0$, $\langle F_i^{rnd}(t) F_j^{rnd}(t') \rangle = 2k_B T \zeta_i \delta_{i,j} \delta(t-t')$
with additional equations for any rotational degrees of freedom

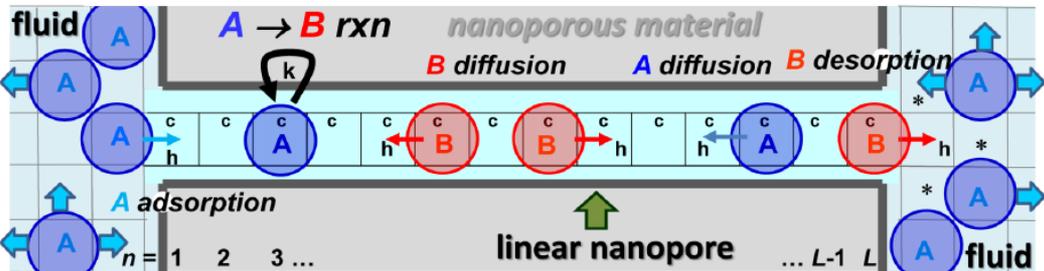


Passing
Probability
= 0.116

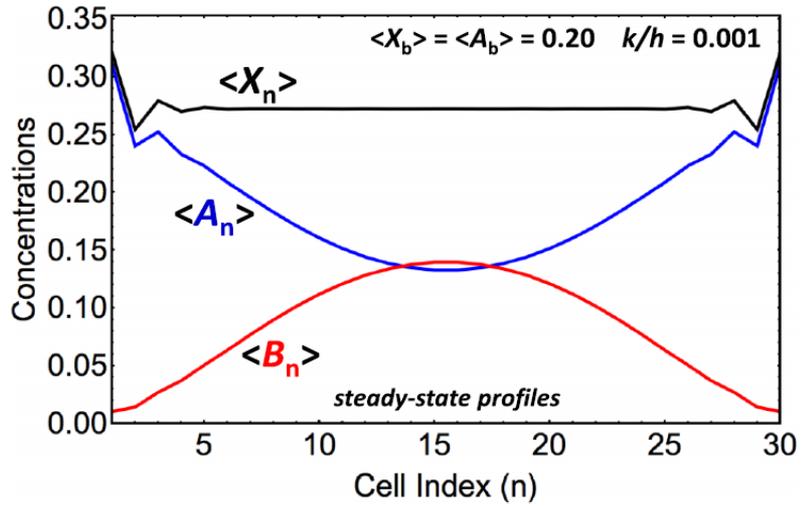
Fokker-Planck equation = diffusion equation in 5D, i.e., $(x_1, y_1, x_2, y_2, \delta z)$, in a “restricted-channel geometry”



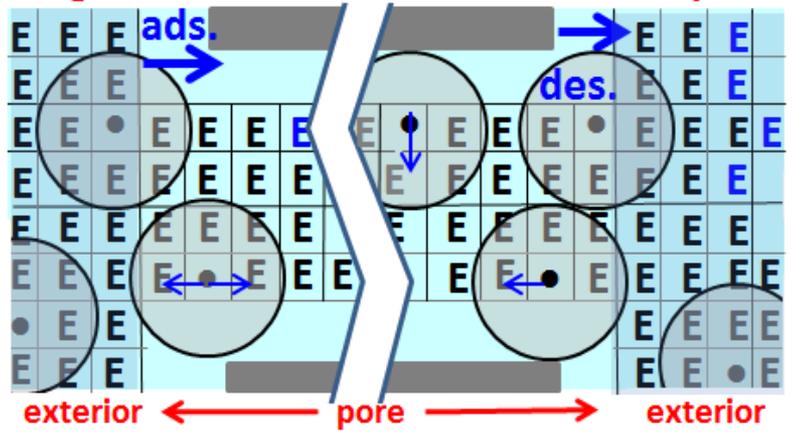
FINER-GRAINED MODELS (APPROACHING CONTINUUM LANGEVIN PICTURE)



A. Garcia & JWE, J. Chem. Phys. 145 (2016) 174705



Single-file diffusion in a linear nanopore



A. Garcia & JWE, J. Phys. Chem. C, submitted (2017)

Complications:

- ◆ Desorption depends on multiple cells just outside the pore being empty
- ◆ Adsorption reflects external fluid concentration just outside pore (which differs from bulk concentration)
- ◆ Can show behavior is determined by a finite number of non-trivial BC's
- ◆ Exploit spatial Markov property for the equilibrated external fluid

CO-OXIDATION ON SURFACES AT HIGH PRESSURE & TEMPERATURE



Liu & Evans, J. Chem. Phys. 142 (2015) 134703; see also Chem. Rev. 115 (2015)

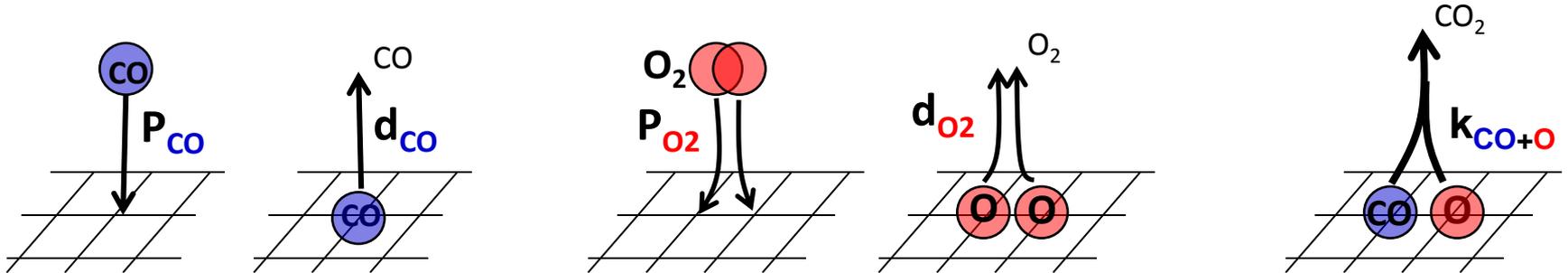
Da-Jiang Liu
Scientist Ames Lab DCBS

★ = E = available (empty) surface site

$\text{CO}(\text{gas}) + \star \leftrightarrow \text{CO}(\text{ads})$...reversible adsorption & desorption at single surface sites

$\text{O}_2(\text{gas}) + 2 \star \leftrightarrow 2\text{O}(\text{ads})$...reversible dissociative adsorption & recombinative desorption at adjacent (nearest-neighbor = NN) pairs of sites

$\text{CO}(\text{ads}) + \text{O}(\text{ads}) \rightarrow \text{CO}_2(\text{gas})$...irreversible reaction between CO & O on NN surface sites



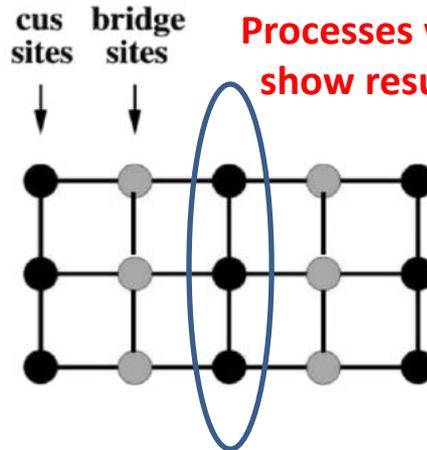
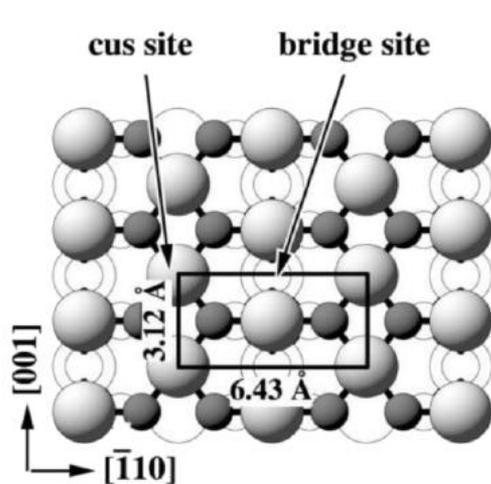
CO-OXIDATION on surfaces: TRADITIONAL MEAN-FIELD TREATMENT

$$d/dt [\text{CO}] = P_{\text{CO}}[\text{E}] - d_{\text{CO}}[\text{CO}] - R_{\text{CO}+\text{O}}, \quad d/dt [\text{O}] = P_{\text{O}_2}[\text{E}\cdot\text{E}] - d_{\text{O}_2}[\text{O}\cdot\text{O}] - R_{\text{CO}+\text{O}}$$

$$\text{where } [\text{E}] = 1 - [\text{CO}] - [\text{O}], \quad [\text{E}\cdot\text{E}] \approx [\text{E}]^2 ? \quad R_{\text{CO}+\text{O}} = k_{\text{CO}+\text{O}}[\text{CO}\cdot\text{O}] \approx k_{\text{CO}+\text{O}}[\text{CO}][\text{O}] ?$$

EXAMPLE: CO-OXIDATION ON $\text{RuO}_2(110)$ AT HIGH P & T

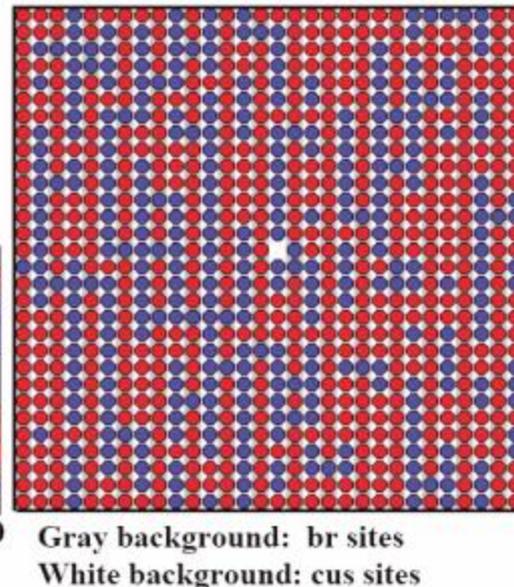
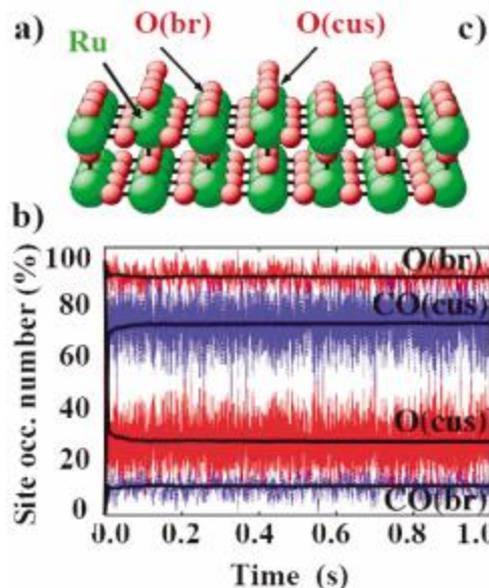
Reuter, Frenkel & Scheffler, PRL 93 (2004) 116105; Reuter & Scheffler PRB 73 (2006) 045433



Processes within cus column dominate – henceforth just show results for this 1D model (but 2D model is similar)

At “high” total pressures...
 $P_{\text{CO}} + P_{\text{O}_2} \approx 1 \text{ atm} = 10^8/\text{sec}$
(vs. most studies at $\sim 10^{-7} \text{ atm}$)
...adsorption rates dominate
desorption and reaction rates.

So surface is very crowded,
and surface mobility (stirring)
is strongly inhibited.

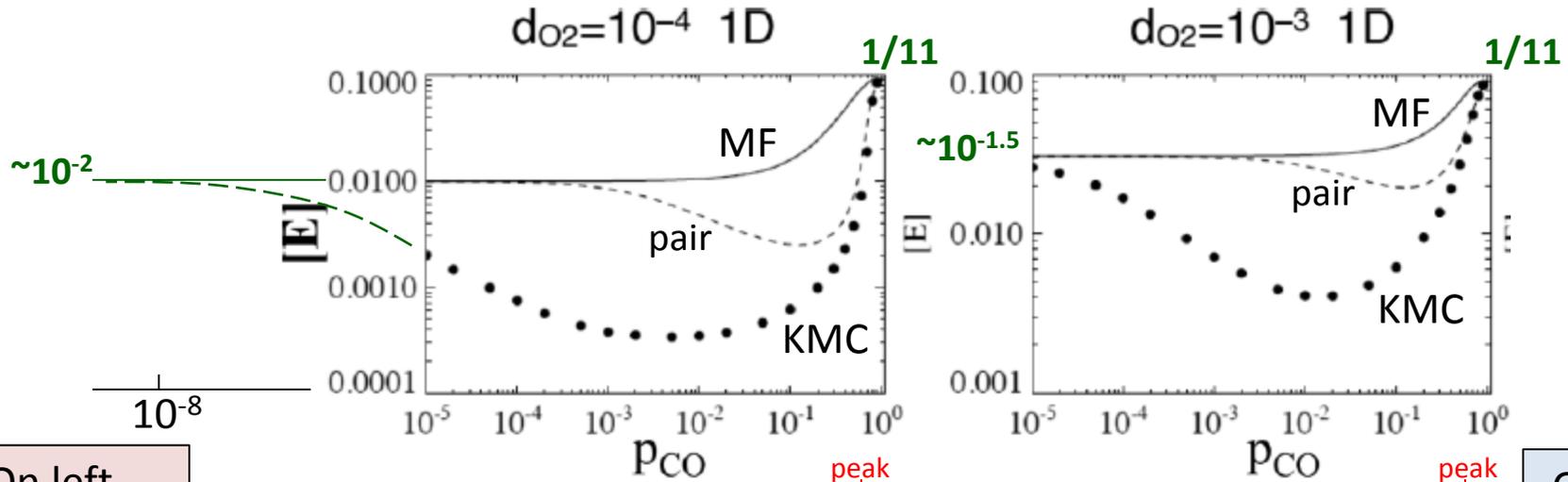


KMC simulation under
optimal reaction conditions
@ 600K with $P_{\text{CO}} : P_{\text{O}_2} = 20 : 1$

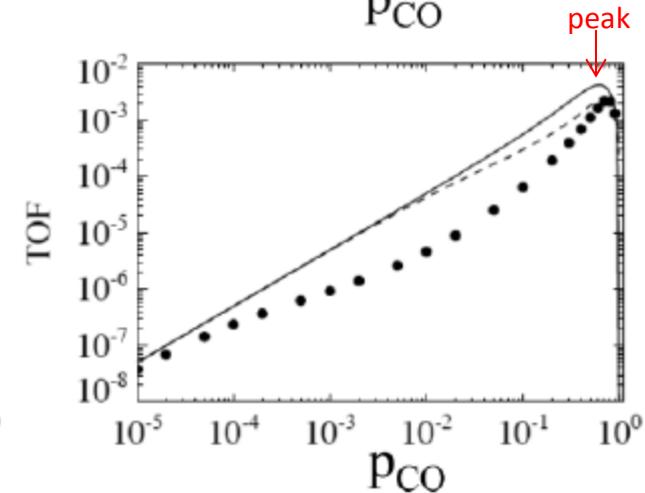
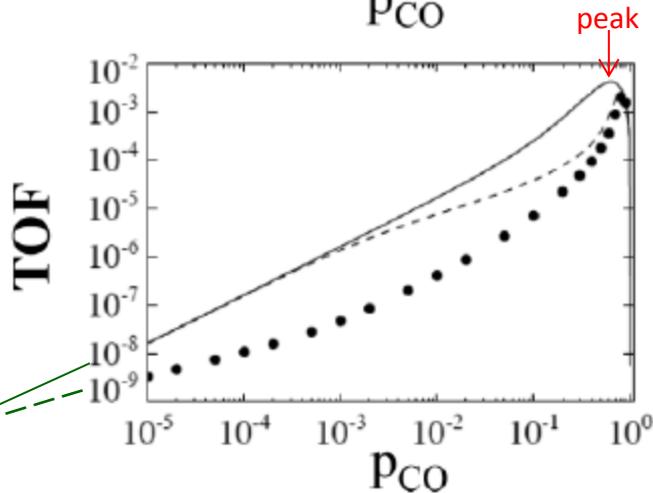
CO-OXIDATION ON SURFACES AT HIGH PRESSURE & TEMPERATURE

Liu & Evans, J. Chem. Phys. 142 (2015) 134703

$P_{CO} + P_{O_2} = 1$ and vary $0 \leq P_{CO} \leq 1$; fix $d_{CO} = 0.1$, $d_{O_2} = 10^{-4}$ (or 10^{-3} or...), and $k_{CO+O} = 0.01$



On left...
 $p_{CO} \approx 0$
 $p_{O_2} \approx 1$
 ...pure O_2
 adsorption
 -desorption
 ...no reaction

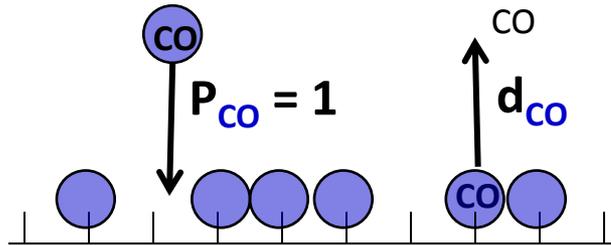


On right...
 $p_{CO} \approx 1$
 $p_{O_2} \approx 0$
 ...pure CO
 adsorption
 -desorption
 ...no reaction

TOF = "turn over frequency" = rate of production of CO_2

(NO) CO-OXIDATION – LIMITING CASES JUST CO or JUST O₂ ADSORPTION

Pure CO
adsorption
-desorption



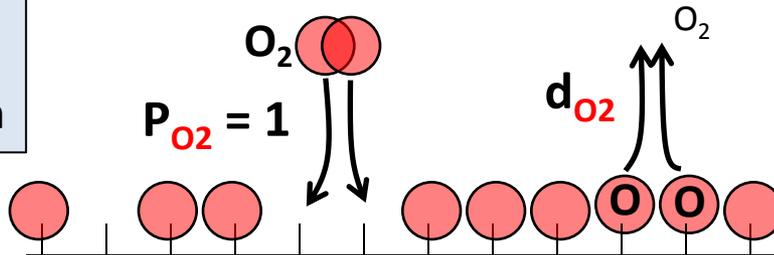
$$[\text{CO}] + [\text{E}] = 1$$

$$0 = d/dt [\text{CO}] = P_{\text{CO}}[\text{E}] - d_{\text{CO}}[\text{CO}]$$

$$\Rightarrow [\text{CO}] = P_{\text{CO}} / (P_{\text{CO}} + d_{\text{CO}}) = 1 / (1 + d_{\text{CO}})$$

$$[\text{E}] = 1 - [\text{CO}] = d_{\text{CO}} / (1 + d_{\text{CO}}) \approx d_{\text{CO}}$$

Pure O₂
adsorption
-desorption



$$[\text{O}] + [\text{E}] = 1$$

$$0 = d/dt [\text{O}] = P_{\text{O}_2}[\text{E}\text{E}] - d_{\text{O}_2}[\text{O}\cdot\text{O}]$$

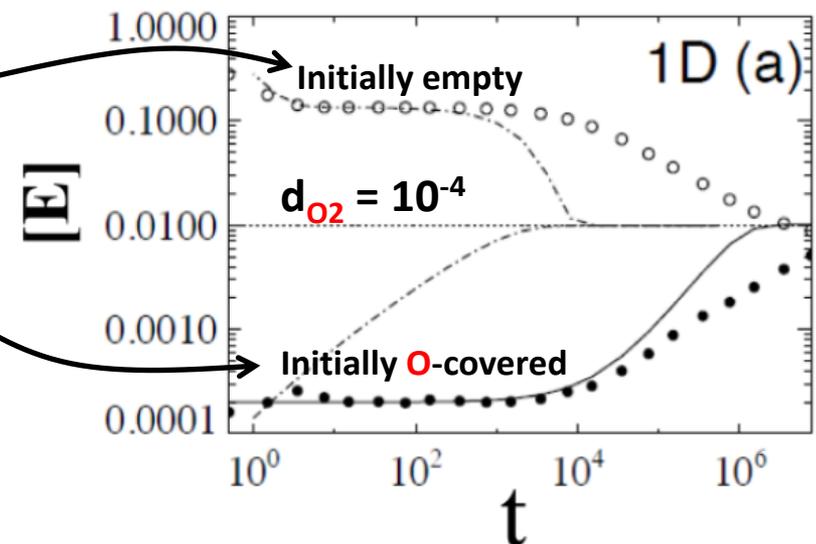
$$\text{MF factorization: } [\text{E}\text{E}] = [\text{E}]^2, [\text{O}\cdot\text{O}] = [\text{O}]^2 \Rightarrow$$

$$[\text{E}] = (d_{\text{O}_2}/P_{\text{O}_2})^{1/2} / [1 + (d_{\text{O}_2}/P_{\text{O}_2})^{1/2}] \approx (d_{\text{O}_2})^{1/2}$$

Initially empty, $d_{\text{O}_2} = 0 \Rightarrow [\text{E}] \rightarrow e^{-2} \approx 0.1353$

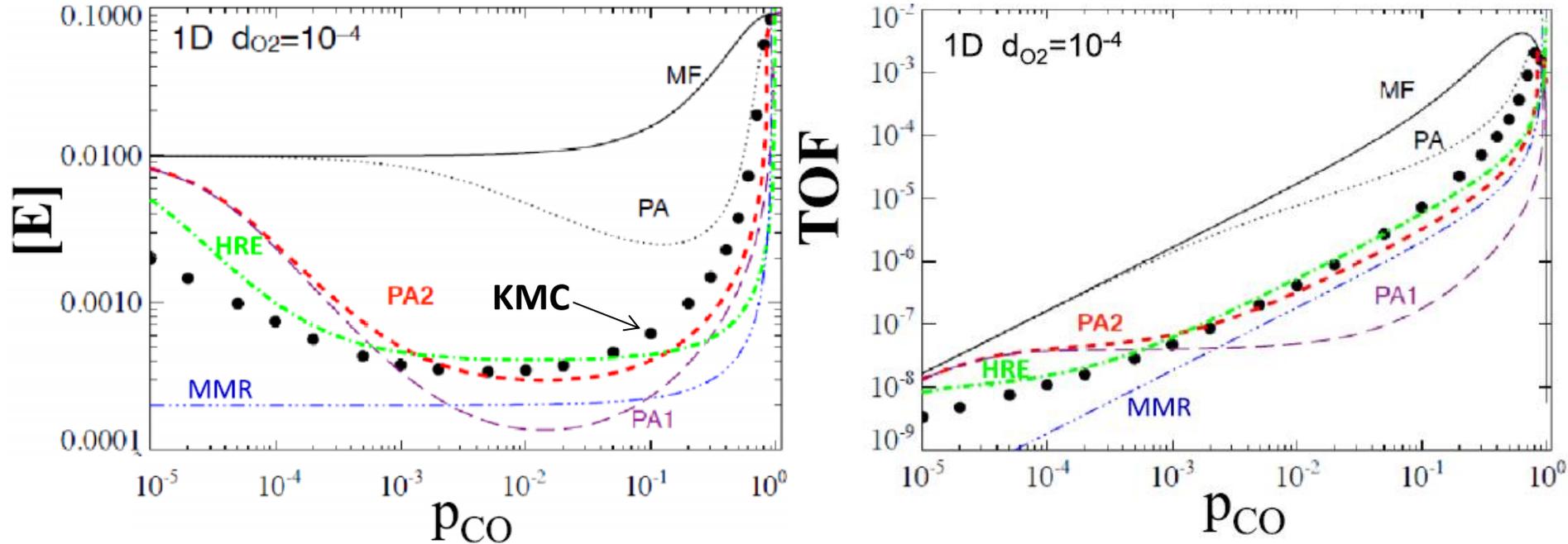
Initially O-covered: assume all empty sites occur in isolated NN pairs $\Rightarrow [\text{E}\cdot\text{E}] = \frac{1}{2}[\text{E}]$ which implies that $[\text{O}\cdot\text{O}] = 3[\text{E}]/2$ and that

$$[\text{E}] \approx 2(d_{\text{O}_2}/P_{\text{O}_2}) = 2d_{\text{O}_2}$$



CO-OXIDATION ON SURFACES AT HIGH PRESSURE & TEMPERATURE

Liu & Evans, *J. Chem. Phys.* 142 (2015) 134703



MMR = Matera, Meskine, Reuter *J. Chem. Phys.* 134 (2011) 064713

For small p_{CO} and “high” p_{O_2} with a near O -covered surface, most empty sites occur in isolated NN pairs noting that they are created by O_2 desorption and also by reaction and removal of adjacent $CO+O$. Thus $[E \cdot E] = \frac{1}{2} [E]$ as above, and also $[CO \cdot O] = \frac{1}{2} [CO]$ since most CO adsorbs in isolated vacancy pairs

PAx = modified pair approximations (PA): PA sets $[EEE] = [EE][EE]/[E]$, a gross overestimate.
PA1 just sets $[EEE] = [EE][E]$; **PA2** is more sophisticated... $[EEE] = [EE] \{ [E] + \text{corrections} \}$

HRE = Heuristic Rate Equations: consider ways to create/destroy isolated empty sites & pairs

SUMMARY

Kinetic Monte Carlo (KMC) simulation analysis can provide precise assessment of behavior of **stochastic reaction-diffusion models**

Behavior is described exactly by (**heterogeneous**) **master equations**. However, reliable assessment of behavior via approximate truncation techniques is difficult, especially for the treatment of chemical diffusion ...controlled by subtle spatial correlations.

For **catalysis in 1D nanoporous systems**, appropriate treatment of **chemical diffusion** requires a “**generalized hydrodynamic**” **formulation** to account for the feature significant fluctuations in adsorption-desorption at the pore openings control reactivity.

For **catalysis on 2D surfaces at higher pressure**, assessment of non-equilibrium correlations is key, e.g., $[EE] \approx \frac{1}{2} [E]$ vs MF $[EE] = [E]^2$
But effective analytic approx. is tailored to details of model.