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

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Liu, Garcia, J Wang, Ackerman, CJ Wang, and Evans, Chemical Reviews 115 (2015) 5979-6050
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 equn
“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

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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...**

Reactants in...

**Products out...**

Products out...

"stirring" via hopping at rate $h$ to adjacent empty sites

2D lattice-gas model

Inhibited stirring $\Rightarrow$ spatial correlations $\Rightarrow$ [●●] $\neq$ [●][●]

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

$\Rightarrow$ catalytic system **equilibrated**

$\Rightarrow$ species randomized if no interactions between them

$\Rightarrow$ rxn rate $= k[●●] = k[●][●]$

Inhibited stirring $\Rightarrow$ spatial correlations $\Rightarrow$ [●●] $\neq$ [●][●]
CATALYTIC CONVERSION $A \rightarrow B$ IN ZEOLITES WITH INHIBITED TRANSPORT

neopentane ($A$) $\rightarrow$ isobutane ($B$) $\rightarrow$ methane

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

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

+ appropriate adsorption-desorption boundary conditions @ pore openings
CATALYTIC CONVERSION REACTION $A \rightarrow B$ WITH INHIBITED TRANSPORT

**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**


IRREVERSIBLE REACTION A → 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 $<A(x)> \sim \exp(-x/L_p)$?
where $x = na$ ($<< L/2$) distance into pore

$k/h = 1, 0.1, 0.01, 0.001, 0.0001$ 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 $[X_n] = [A_n] + [B_n] =$ tot. conc., then $[E_n] = 1 - [X_n] =$ prob. cell $n$ is empty.

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

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

\begin{figure}
\centering
\includegraphics[width=\textwidth]{sfd.pdf}
\caption{(a) Concentration profiles for different reaction configurations: Quartet, Triplet, Pair, Site (MF), KMC, and B.}
\end{figure}

- $k=0.001$
- SFD
- Concentrations vs. Cell index ($n$)
Recall that for SFD:
\[ J_A(n \rightarrow n+1) = h( [A_n E_{n+1}] - [E_n A_{n+1}] ) \quad \text{MF} \rightarrow \quad h( [A_n][E_{n+1}] - [E_n][A_{n+1}] ) = h[E] ([A_n] - [A_{n+1}]) \]

In fact, \([A_n E_{n+1}] \) & \([E_n A_{n+1}] \) are much closer than the MF prediction due to SFD constraint...
Pair approximation enforces relations:

\[ <A_n E_{n+1} E_{n+2}> \approx \frac{<A_n E_{n+1} E_{n+2}>}{<E_{n+1}>} \]
\[ <E_n A_{n+1} E_{n+2}> \approx \frac{<E_n A_{n+1} E_{n+2}>}{<A_{n+1}>} \]
\[ <A_n E_{n+1} E_{n+2}> \approx \frac{<A_n E_{n+1} E_{n+2}>}{<E_{n+1}>} \]
\[ <E_n A_{n+1} E_{n+2}> \approx \frac{<E_n A_{n+1} E_{n+2}>}{<A_{n+1}>} \]

which does not make these quantities similar.

For conditional prob \( P(\alpha | \beta) = \frac{P(\alpha + \beta)}{P(\beta)} \):

Pair approx says: \( <A_n | E_{n+1} E_{n+2}> \approx \frac{<A_n | E_{n+1}>}{<E_{n+1}>} \)

But \( <A_n | E_{n+1} E_{n+2}> \) does depend strongly on the feature that site \( n+2 \) is specified empty.
**IRREVERSIBLE REACTION** $\text{A} \rightarrow \text{B}$ with **SINGLE-FILE DIFFUSION (SFD):**

Reaction-Diffusion Equations to describe evolution of concentration profiles

\[
\frac{\partial}{\partial t} A(x) = -k A(x) - \frac{\partial}{\partial x} J_A, \quad \frac{\partial}{\partial t} B(x) = +k A(x) - \frac{\partial}{\partial x} J_B. \quad \text{Set } X(x) = A(x) + B(x)
\]

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

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

so that $\frac{\partial B}{\partial x} \approx -\frac{\partial A}{\partial x}$ (counter diffusion mode)

\[
J_A = -D_{\text{tr}} \frac{\partial}{\partial x} A(x)
\]

...where one can show that

$D_{\text{tr}} = D_{A,A} - D_{A,B}$ = “tagged particle” tracer diffusion coefft.

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

**Standard “hydrodynamic” theory for SFD:**

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

Harris, J. Appl. Prob. (1965)

**Our “Generalized Hydrodynamic” theory:**

$D_{\text{tr}}$ is enhanced near pore openings...

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**ACS Cat. (2011)**

$k = 0.001$
**“TRACER COUNTER-PERMEATION” ANALYSIS OF GENERALIZED D\text{tr}**


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

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

enhanced near pore openings where \( |\frac{\partial}{\partial x} [B]| \) 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

Einstein: $D \sim \langle (\delta r)^2 \rangle / t$

If $t_n$ is time to reach pore opening from site $n$, then

$D_{tr}(n) \propto 1/t_n \sim 1/n^p$ with $p \sim 2$

$\chi = 0.8$

**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 $n \sim \frac{1}{4}$ (vs MF $n = \frac{1}{2}$)

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

David Ackerman, Jing Wang, JWE, Phys. Rev. Lett. 108 (2012) 228301
CATALYTIC CONVERSION REACTION $A \rightarrow B$ WITH INHIBITED TRANSPORT: RELAXING SFD CONSTRAINT TO ALLOW PASSING WITH PROBABILITY $P_{ex}$
Strongly-damped Langevin dynamics: \( \zeta_i \frac{dx_i}{dt} = F_i^{\text{rnd}}(t) \) where \( \langle F_i^{\text{rnd}} \rangle = 0 \), \( \langle F_i^{\text{rnd}}(t) F_j^{\text{rnd}}(t') \rangle = 2k_B T \zeta_i \delta_{ij} \delta(t-t') \) with additional equations for any rotational degrees of freedom.

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

Passing Probability = 0.116
FINER-GRAINED MODELS (APPROACHING CONTINUUM LANGEVIN PICTURE)

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


★ = E = available (empty) surface site

**CO(gas) + ★ ↔ CO(ads) ...reversible adsorption & desorption at single surface sites**

**O₂(gas) + 2 ★ ↔ 2O(ads) ...reversible dissociative adsorption & recombinative desorption at adjacent (nearest-neighbor = NN) pairs of sites**

**CO(ads) + O(ads) → CO₂(gas) ...irreversible reaction between CO & O on NN surface sites**

**CO-OXIDATION on surfaces: TRADITIONAL MEAN-FIELD TREATMENT**

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

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

where \([E] = 1-[\text{CO}]-[O], [E\cdot E] \approx [E]^2\) ? \(R_{\text{CO}+\text{O}} = k_{\text{CO}+\text{O}}[\text{CO}cdot \text{O}] \approx k_{\text{CO}+\text{O}}[\text{CO}][O] \) ?
EXAMPLE: CO-OXIDATION ON RuO$_2$(110) AT HIGH P & T


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 \(~10^{-7}\text{ atm}\))

...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 \( P_{\text{CO}} : P_{\text{O}_2} = 20 : 1 \)
$P_{\text{CO}} + P_{\text{O}_2} = 1$ and vary $0 \leq P_{\text{CO}} \leq 1$; fix $d_{\text{CO}} = 0.1$, $d_{\text{O}_2} = 10^{-4}$ (or $10^{-3}$ or...), and $k_{\text{CO}+\text{O}} = 0.01$.

On left...
$p_{\text{CO}} \approx 0$
$p_{\text{O}_2} \approx 1$
...pure $\text{O}_2$
adsorption-desorption
...no reaction

On right...
$p_{\text{CO}} \approx 1$
$p_{\text{O}_2} \approx 0$
...pure $\text{CO}$
adsorption-desorption
...no reaction

TOF = “turn over frequency” = rate of production of $\text{CO}_2$
(NO) CO-OXIDATION – LIMITING CASES JUST CO or JUST O₂ ADSORPTION

**Pure CO adsorption-desorption**

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

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

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

\[
[\text{E}] = 1 - [\text{CO}] = \frac{d_{\text{CO}}}{1+d_{\text{CO}}} = \frac{1}{11} \approx d_{\text{CO}}
\]

**Pure O₂ adsorption-desorption**

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

\[
0 = \frac{d}{dt} [\text{O}] = P_{\text{O}_2}[\text{EE}] - d_{\text{O}_2}[\text{O} \cdot \text{O}]
\]

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

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

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 \( [\text{E} \cdot \text{E}] = \frac{1}{2}[\text{E}] \) which implies that \( [\text{O} \cdot \text{O}] = 3[\text{E}]/2 \) and that \( [\text{E}] \approx 2(d_{\text{O}_2}/P_{\text{O}_2}) = 2d_{\text{O}_2} \)

See also: Barma, Grynberg, Stinchcombe, PRL 70 (1993) 1033
MATERIALS OF CO-OXIDATION ON SURFACES AT HIGH PRESSURE & TEMPERATURE


For small $P_{CO}$ and “high” $P_{O2}$ 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 $[E-E] = \frac{1}{2} [E]$ as above, and also $[CO-O] = \frac{1}{2} [CO]$ 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... $[EEE] = [EE] \{ [E] + corrections \}$

**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.