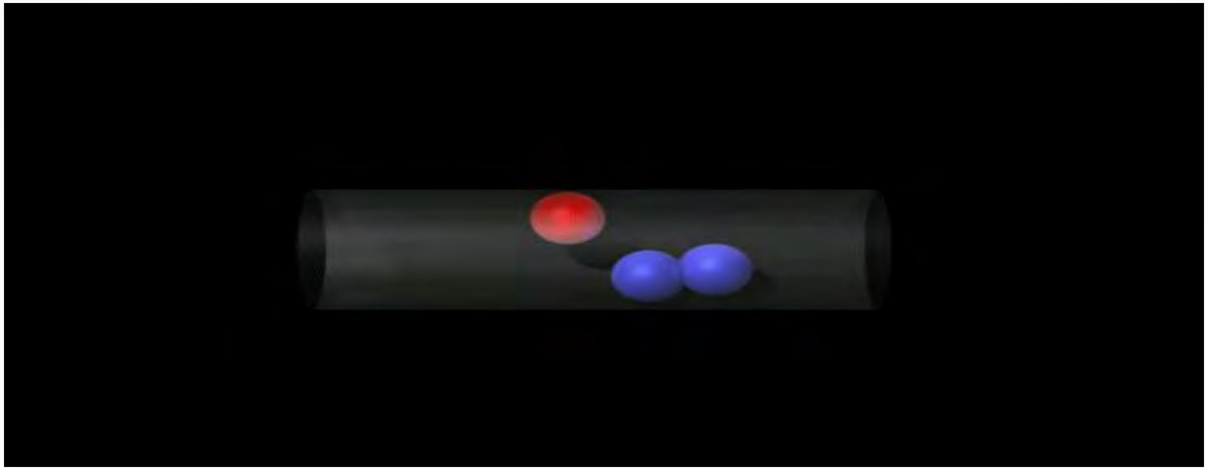
Langevin and Fokker-Planck Analyses of Inhibited Molecular Passing Processes in Nanoporous Materials

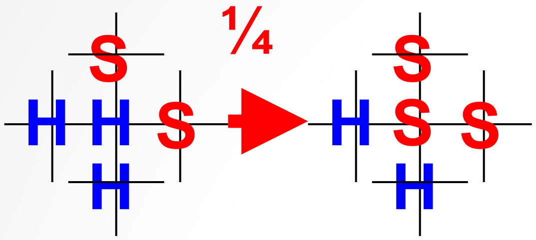


Chi-Jen Wang, **David M. Ackerman, Igor I. Slowing, Jim W. Evans**

Departments of Mathematics, Physics & Astronomy, Mechanical Engineering, Chemistry, and Ames Laboratory (USDOE), Iowa State University
School of Mathematics, Georgia Institute of Technology

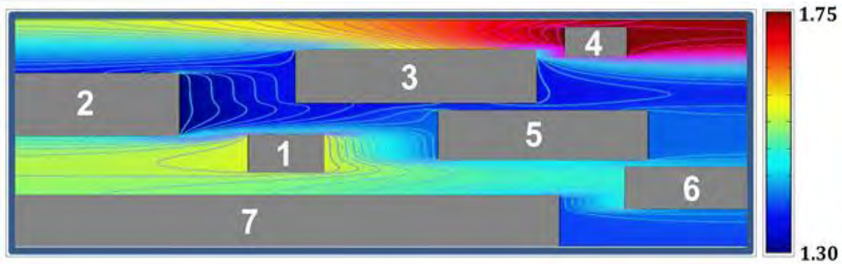
NTU, 31 Dec 2014

RESEARCH TOPICS



spatial epidemic models: lattice differential equation analysis of wave and droplet solutions

Wang, Liu, Evans, Phys. Rev. E 85 (2012) 041109



formalism for 1D decay of islands during coarsening on anisotropic surfaces

Wang, Han, Walen, Russell, Thiel, Evans, Phys. Rev. B 88 (2013) 155434

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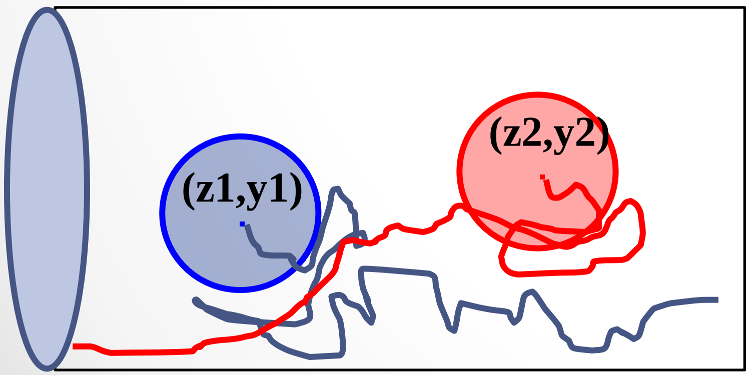


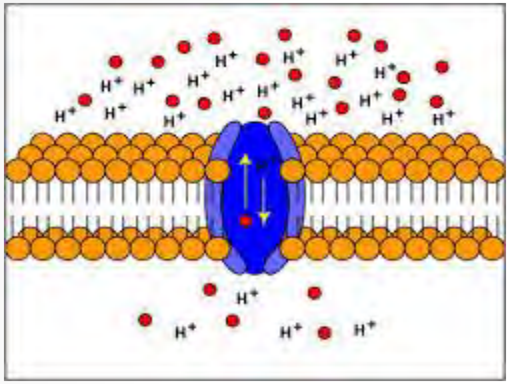
passing rate of particles in a narrow pore

Langevin and Fokker-Plank equation analysis

Wang, Ackerman, Slowing, Evans, Phys. Rev. Lett. 113, 038301 (2014)

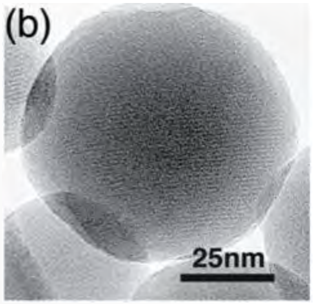
TRANSPORT IN POROUS MEDIA

- membrane



ion channel, gap junction: particles pass through the gated narrow channel in a high rate.

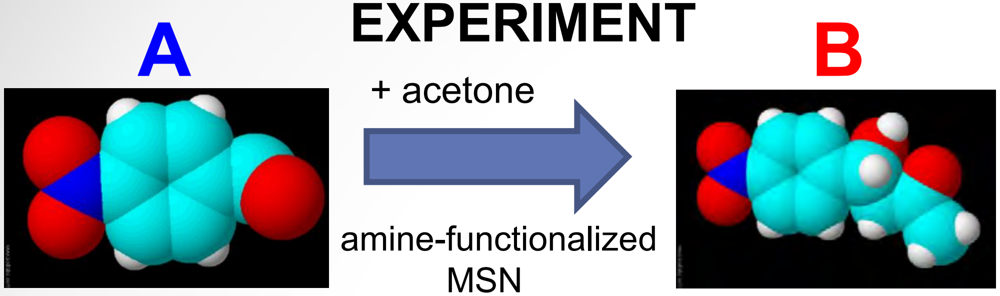
- porous materials



zeolites, capillary, activated carbon: particles pass through the ungated narrow channel

CATALYTIC CONVERSION REACTION A→B WITH INHIBITED TRANSPORT

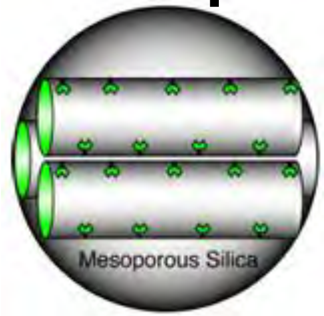
EXPERIMENT

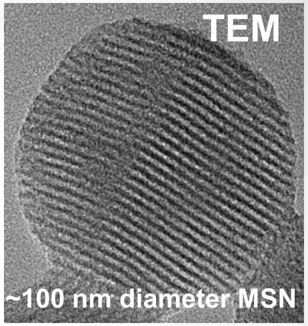


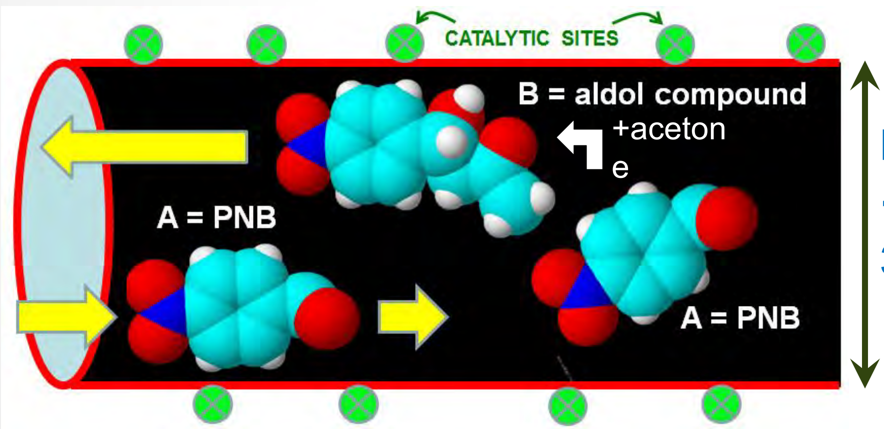
p-nitrobenzaldehyde (PNB , 對硝基苯甲醛)

4-(p-nitrophenyl)-4-hydroxy-2-butanone (4對硝基苯基-4羥基-2丁酮)

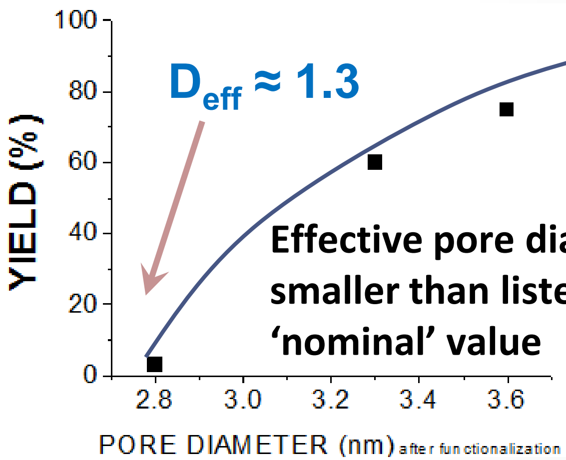
Mesoporous silica







$D_{eff} \approx$ 1.3 to 3+ nm

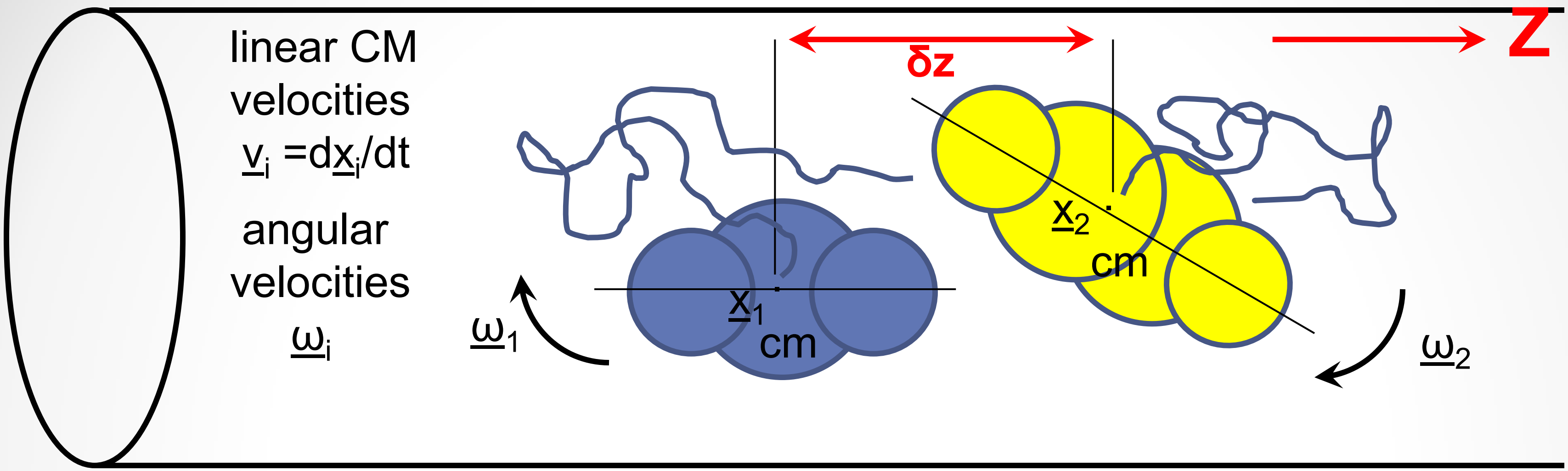


Liu, Chen, Lin, Evans, J. Chem. Phys. 132, 154102 (2010).

GOALS FOR MODELING:

Analyze influence of "anomalous transport" in narrow pores on reactivity (yield). Specifically, we analyze the difficulty for reactants & products to pass each other.

PROPOSED LANGEVIN ANALYSIS OF “RESTRICTED PASSING”



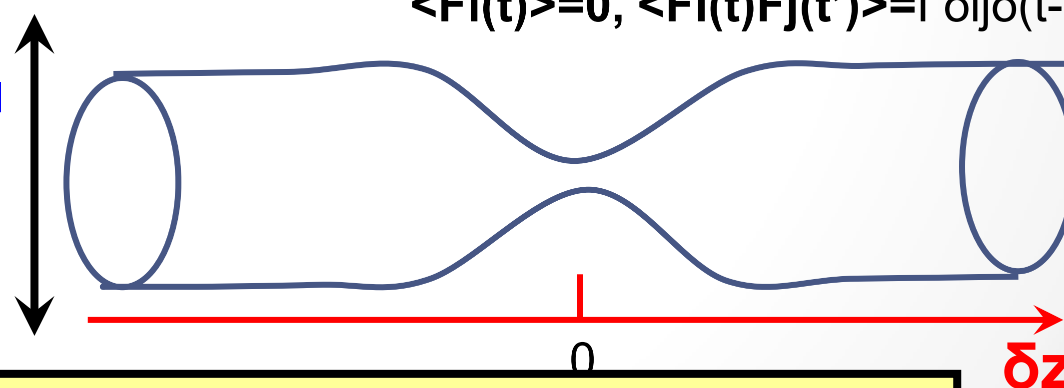
$m_i\, d/dt\, \underline{v}_i = -\,\underline{\gamma}\cdot\underline{v}_i$ + *random force*; $\underline{I}_i\, d/dt\, \underline{\omega}_i + \underline{\omega}_i \times \underline{I}_i\, \underline{\omega}_i = -\,\underline{\varsigma}\cdot\underline{\omega}_i$ + *random torque*

$\langle F_i(t)\rangle = 0,\ \langle F_i(t) F_j(t')\rangle = \Gamma\delta_{ij}\delta(t-t')$

$P_{TST} \sim V_{min}/V_{max}$

available 8-dimensional phase space

(4 angles given axial symmetry + 4 lateral translational degrees of freedom)



DETERMINE HOW THE “EXCHANGE” OR “PASSING” PROBABILITY DEPENDS ON:

(I) THE PORE DIAMETER (relative to the size of the reactant & product molecules)

(II) THE SHAPE OF THE MOLECULES (e.g., alignment mediated-passing)

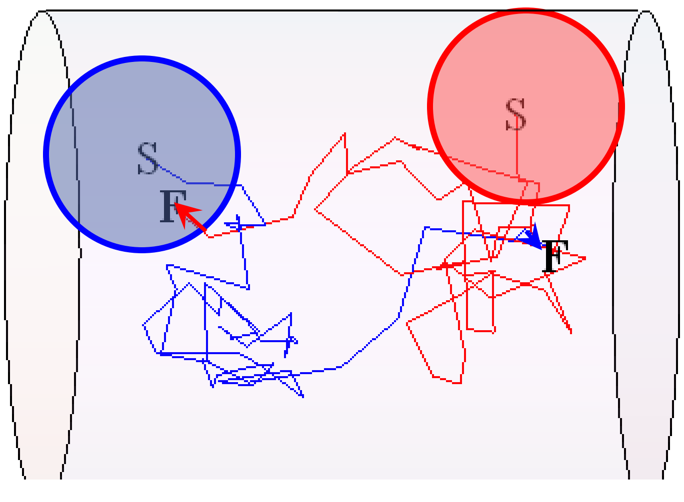
Coffey, Kalmykov, Waldron, The Langevin Equation, World Scientific, Singapore, (2004).

“RESTRICTED PASSING” of 2 SPHERES in a CYLINDRICAL PORE

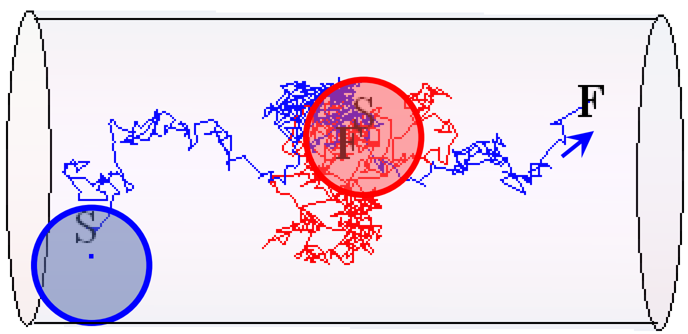
(David Ackerman)

Langevin dynamics analysis

overdamped



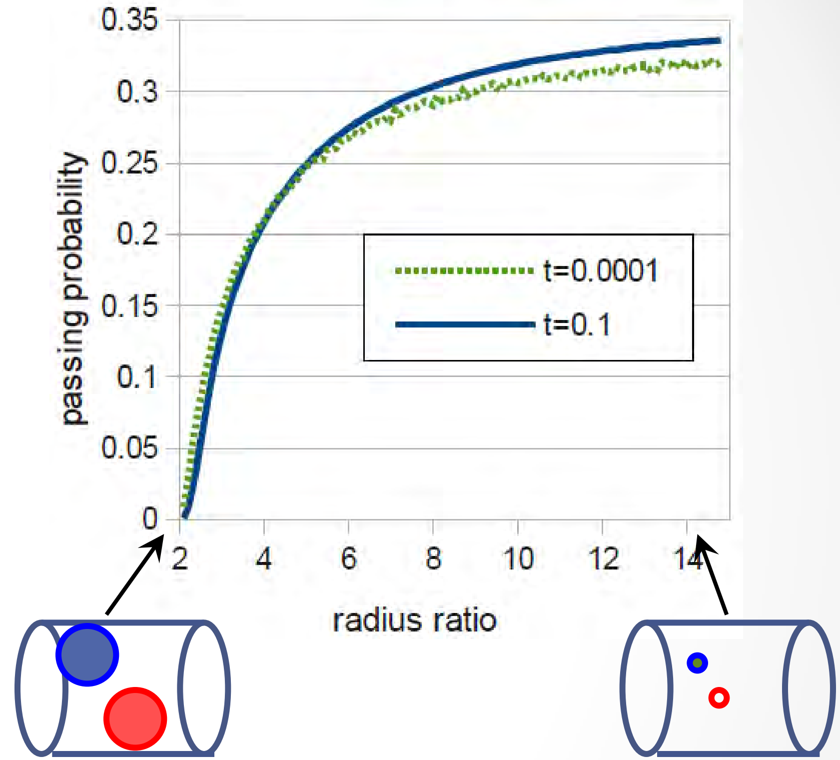
(Pore radius)/(Sphere radius) = Rp/r = 2.5



passing ~ (R-Rc)$^{\sigma}$

σ=2.5 in transition state theory (TST)

σ=1.7 in Langevin (LE) analysis



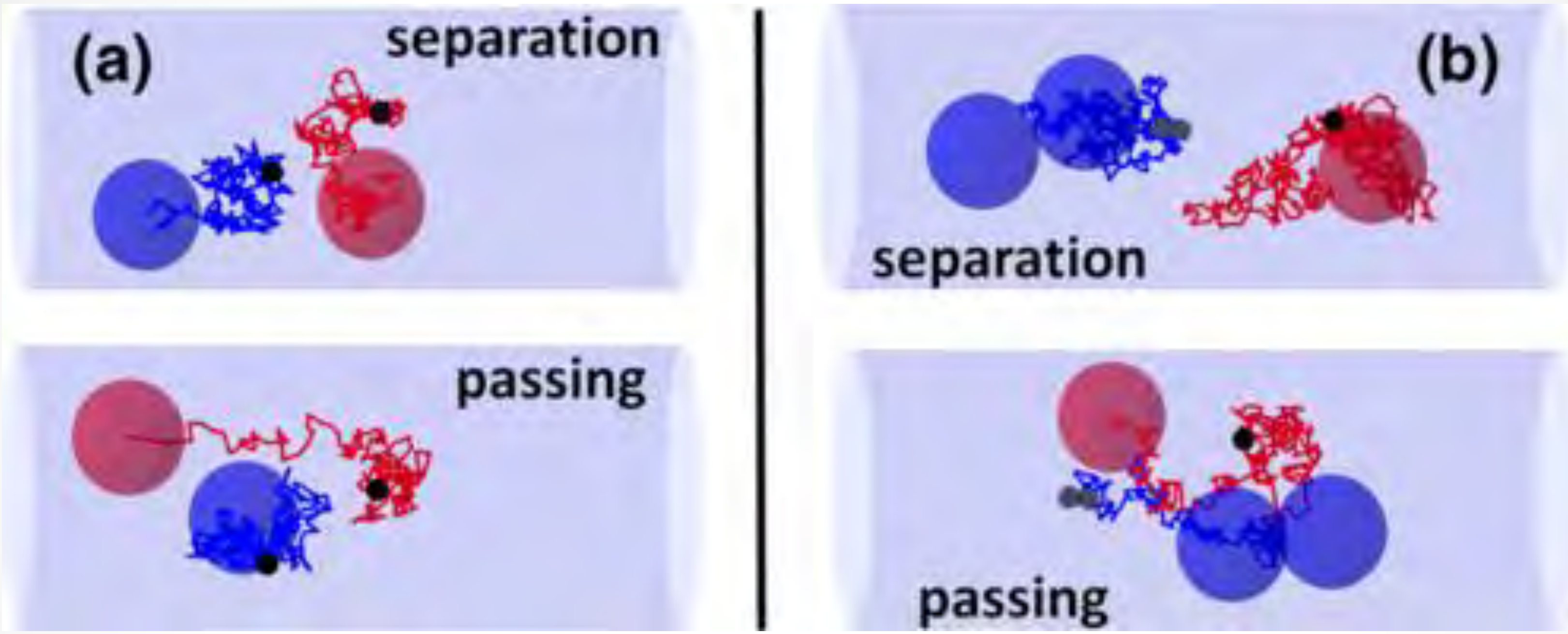
δz=z1-z2

δz=2r

δz= −2r

δz=4r

Examples of passing/separation



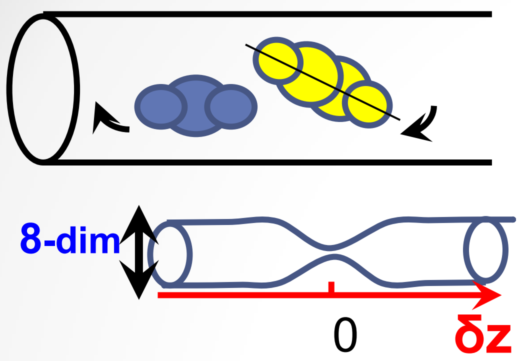
(a) two spheres, P=0.116;

(b) sphere and dumbbell, P=0.066.

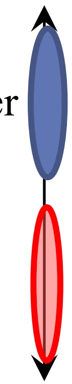
Langevin trajectories for separating and passing events in a cylindrical pore with g/r=1, small (large) circles indicate initial (final) configurations.

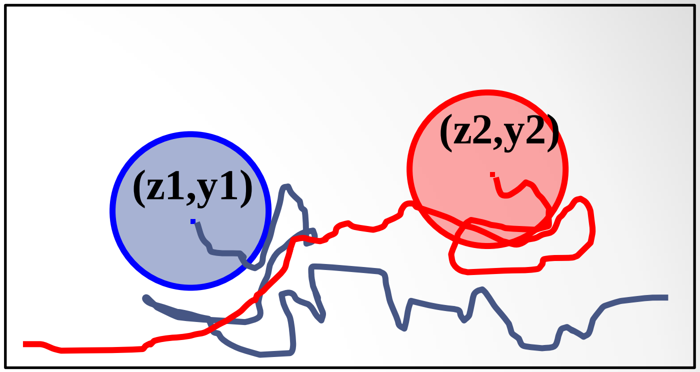
timestep = 0.0001

Fokker-Planck equation analysis (high dim. diffusion eqn.)

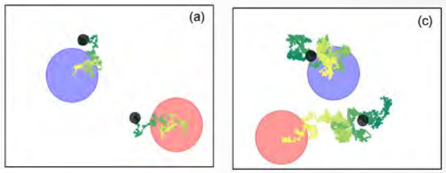


Pore diameter
$2Rp = 4r+g$
, g = gap





circle radius r



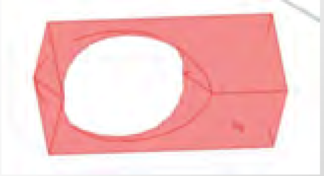
too complicated ⇨ **simplier circles**

Fokker-Planck equation for overdamped LE

$$\frac{d}{dt} P(\underline{x},t) = \frac{d}{d\underline{x}} \underline{D} \frac{d}{d\underline{x}} P(\underline{x}, t)$$
$$= D \left(d^2/dy_1^2\, P(y_1, y_2, \delta z, t) + d^2/dy_2^2\, P(y_1, y_2, \delta z, t) + \mathbf{2}\, d^2/d\Delta z^2\, P(y_1, y_2, \delta z, t) \right)$$

, where $P(\underline{x},t)$: probability density at $(\underline{x}, t)$, $\underline{x} = (y_1, y_2, \delta z)$, $D=\Gamma/2$.

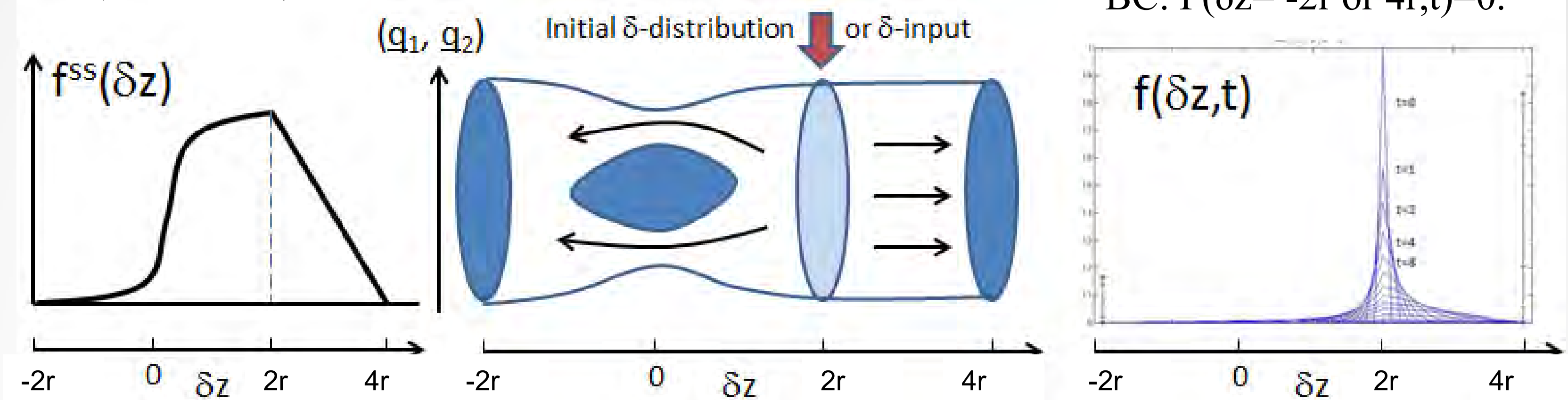
geometry: $\{-2r \leq \delta z \leq 4r,\ |y1|,|y2| \leq r + g/2,\ (y_1-y_2)^2+(\delta z)^2 \geq (2r)^2\}$



Examples of passing/separation

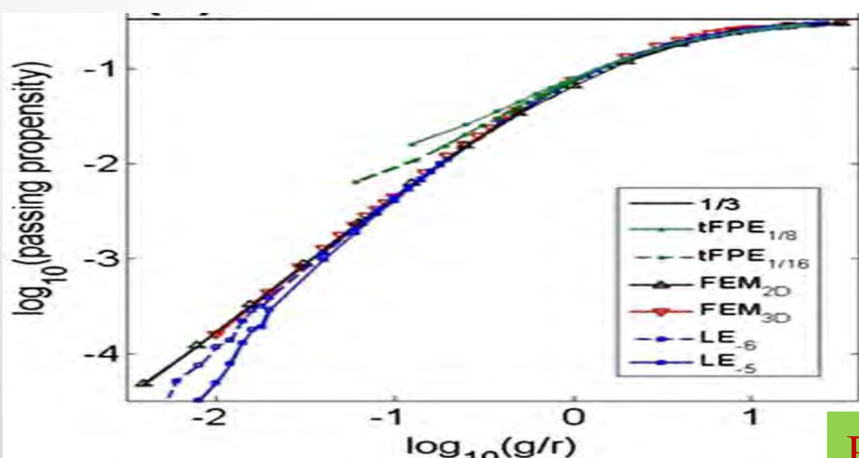
$f^{ss}(\delta z) = \iint dq_1 dq_2\, f^{ss}(q_1,q_2,\delta z)$.
BC: $P(\delta z = -2r \text{ or } 4r) = 0$

$f(\delta z,t) = \iint dq_1 dq_2\, f(q_1,q_2,\delta z; t)$.
IC: $P(\delta z=2r,0)=\delta(\delta z-2r)$;
BC: $P(\delta z= -2r \text{ or } 4r,t)=0$.



P(L)=flux of steady-state @δz= -2r
P(R)=flux of steady-state @δz= 4r
passing rate : P(L)/ [P(L)+ P(R)] .

$P_{trap}(L)=\int dt$ flux@δz= -2r
$P_{trap}(R)=\int dt$ flux@δz= 4r
passing rate : $P_{trap}(L)/ [P_{trap}(L)+ P_{trap}(R)]$

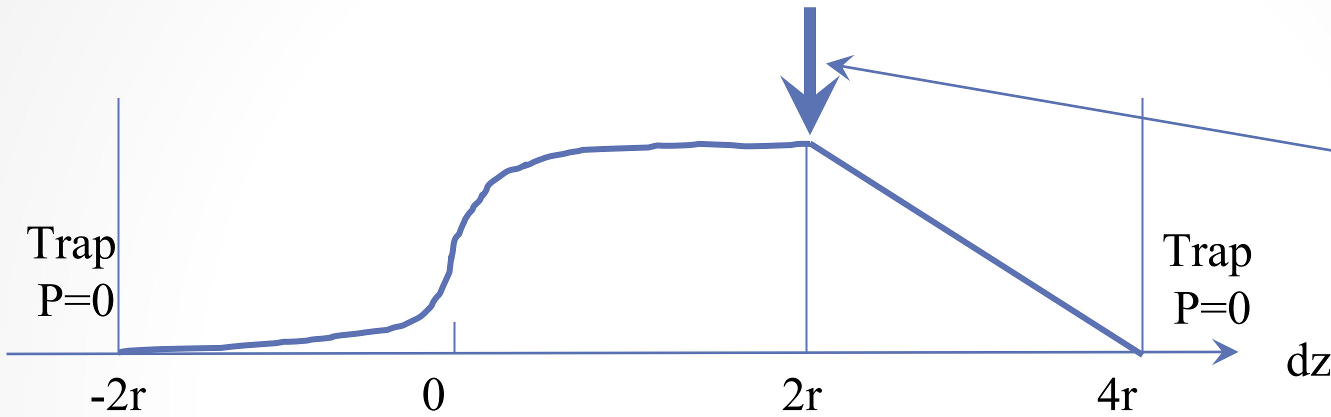


TIME-DEPENDENT FPE:
$\partial/\partial t\, f(q_1,q_2,\delta z; t) = L_{FPE}\, f(q_1,q_2,\delta z; t)$
with self-adjoint $L_{FPE} = \nabla \underline{D} \nabla$.

STEADY-STATE FPE:
$0 = L_{FPE}\, f^{ss}(q_1,q_2, \delta z) + V_d^{-1}\, \delta(\delta z - 2r)$.

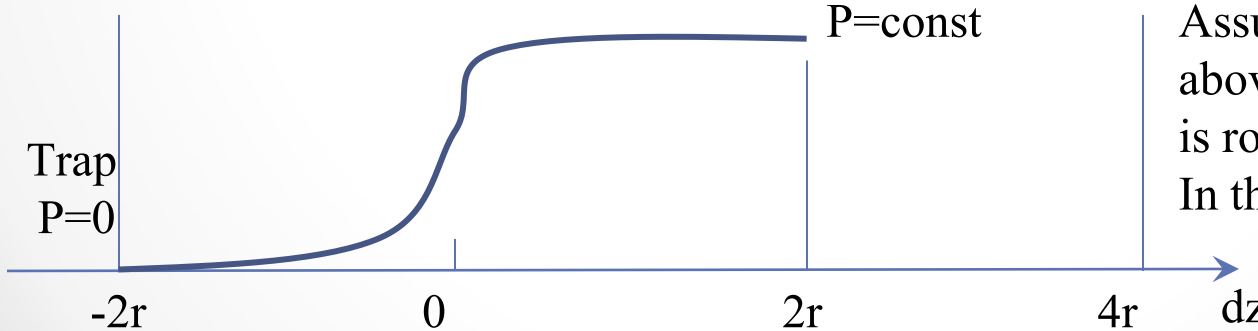
PASSING PROB.~ $(g/r)^{1.4}$

Equivalent time-independent diffusion equation problem



Delta function input

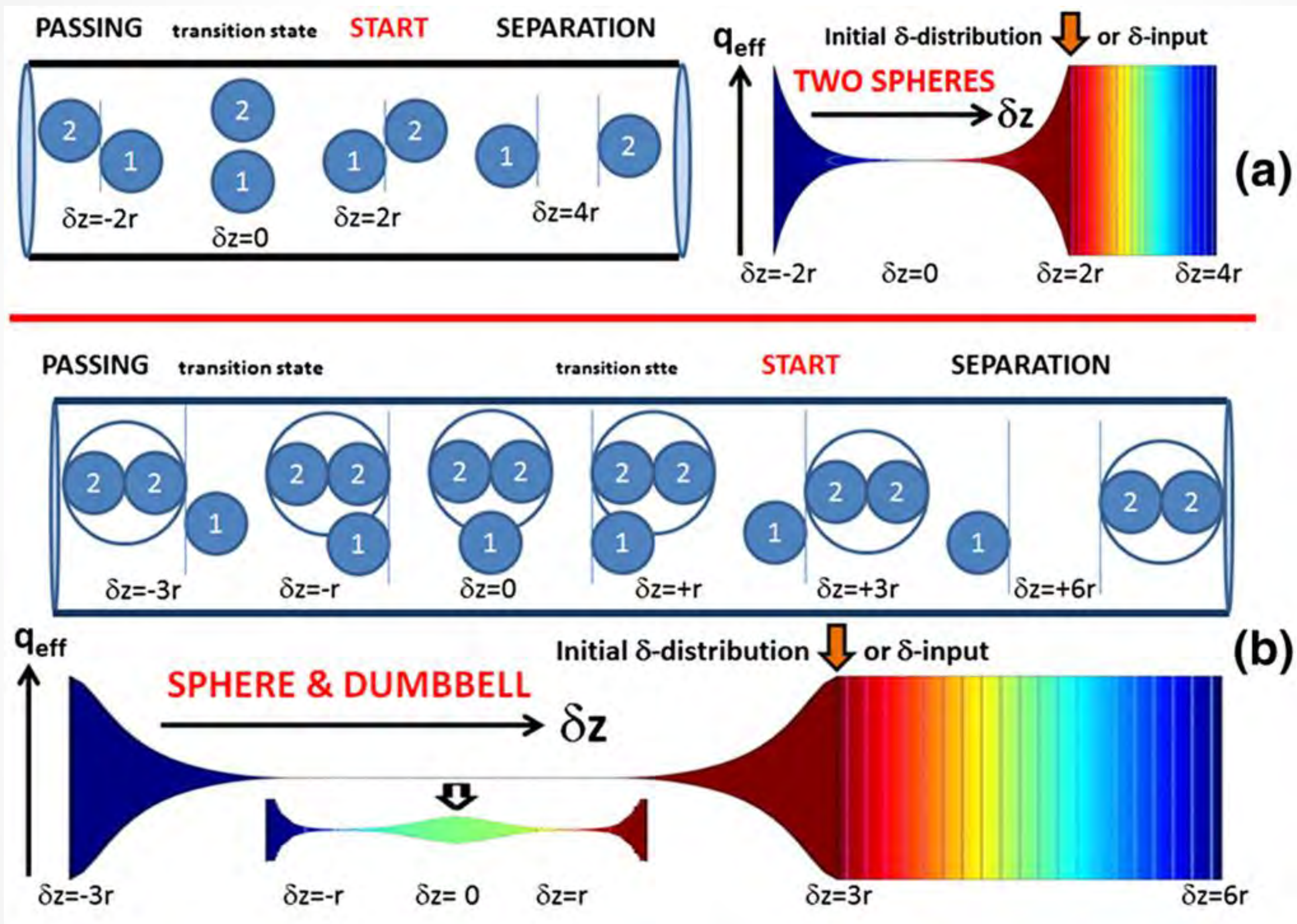
Determine steady-state fluxes at both ends which give passing + separation prob



Assumes solution of above steady-state problem is roughly uniform for dz=2r In the region of small gaps

Effective 2D FEM approximation

$q_{eff}(\delta z) = \int \ldots \int dq_1 \ldots dq_n\, f^{ss}(q_1, \ldots, q_n, \delta z).$

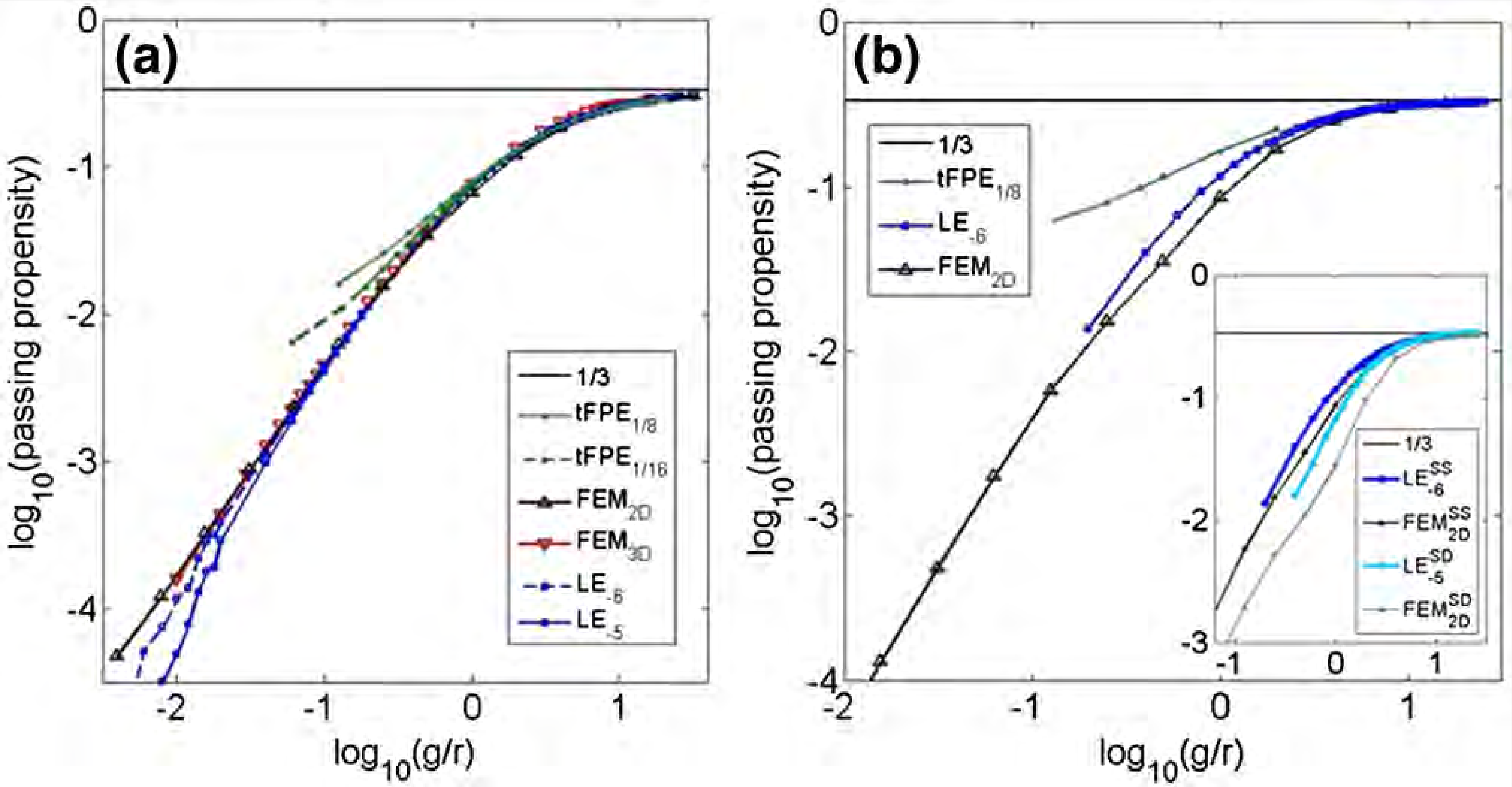


g/r= 1/8

g/r= 1/32

f^{ss}=0 at the ends is dark blue, and the maximum f^{ss} is dark maroon.

Langevin and Fokker-Planck results



(a) circle-circle in 2D: Langevin (LE) results; time-dependent Fokker-Planck equation (tFPE); 3D FEM; effective 2D FEM
(b) spheres in 3D: LE; tFPE; effective 2D FEM

Inset: two spheres (SS) versus sphere+dumbbell (SD); LE and 2D FEM

Wang, Ackerman, Slowing, Evans, Phys. Rev. Lett. 113, 038301 (2014)

Summary

table of passing propensity

	C+C	C+D	C+E	S+S	S+D	S+E
σ_{TST}	2	2	3	2.5	2.5	4.5
σ_{LE}	1.4	1.4	-	1.7	1.7	-

C: circle; S: sphere; D: dumbbell; E: ellipsoid

***molecular passing processes in narrow pores is not described by a simple TST, but rather depends on more global features of the confined geometry during the passing process.**

***we have provided a general picture for the behavior of molecular passing processes by Langevin dynamics and Fokker-Planck equation.**

ACKNOWLEDGMENTS

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*Department of Mathematics

*Ames Laboratory, U.S. Department of Energy (USDOE)

Thank You !

Liu, Chen, Lin, Evans, J. Chem. Phys. 132, 154102 (2010).
Ackerman, Wang, Evans, Phys. Rev. Lett. 108, 228301 (2012).
Wang, Ackerman, Slowing, Evans, Phys. Rev. Lett. 113, 038301 (2014)