Molecular Modeling as an Enabling Tool in Advanced Material Research

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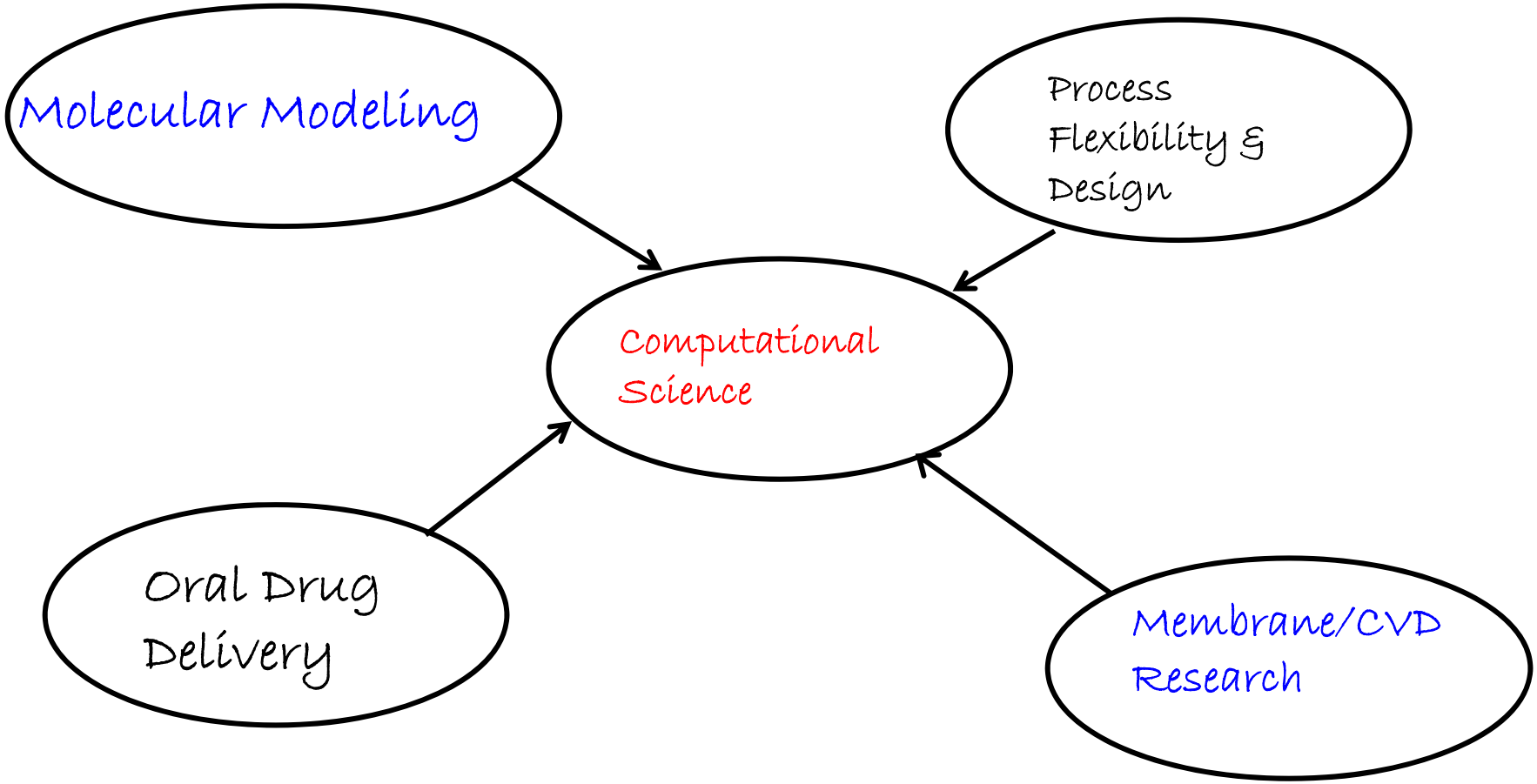
NSF (US/China) Workshop – March 2014

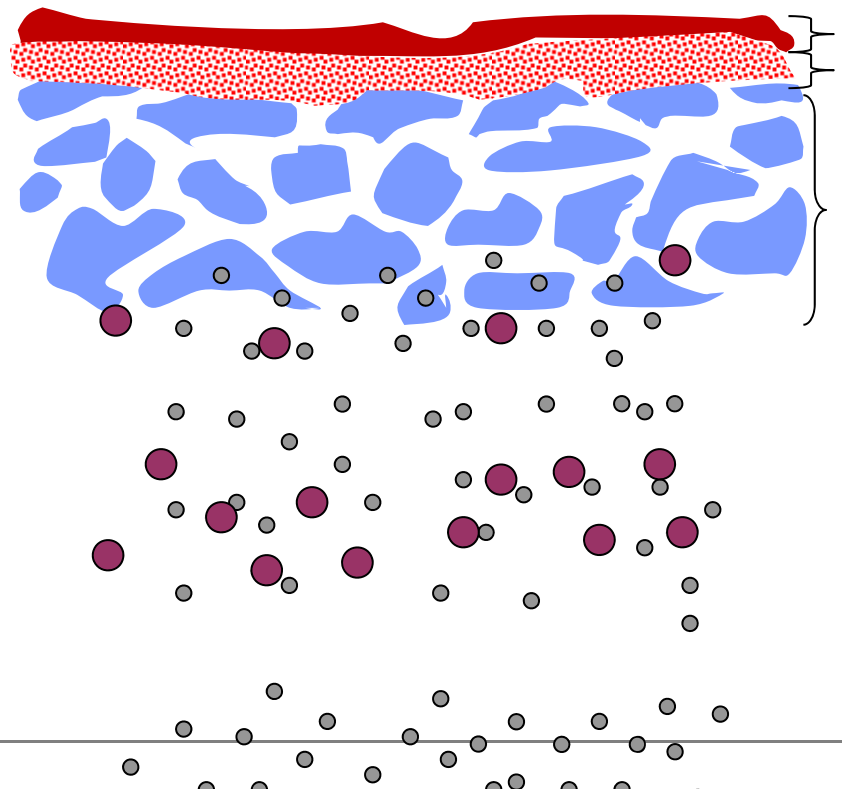
Outline


Molecular Modeling
Process Flexibility & Design
Computational Science
Oral Drug Delivery
Membrane/CVD Research

With Oyama Group – Molecular Dynamics Study (Hybrid Inorganic / Organic membranes)

Membrane separation -- wide use in natural gas processing

inorganic membrane



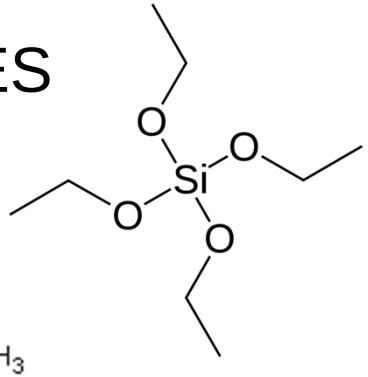
Selective layer (silica, palladium)

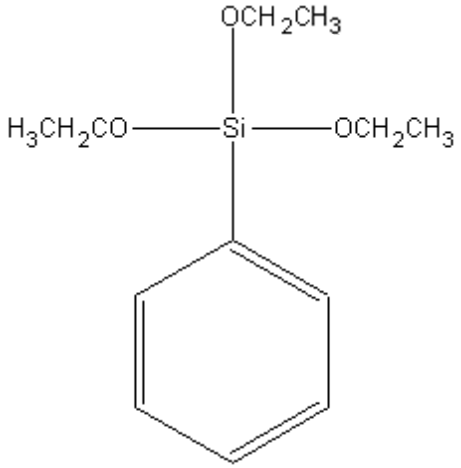
Intermediate layer (alumina)

Support (alumina, stainless steel)

Hybrid Inorganic-Organic Membrane (exploit the reactivity of the Si-OR bonds)

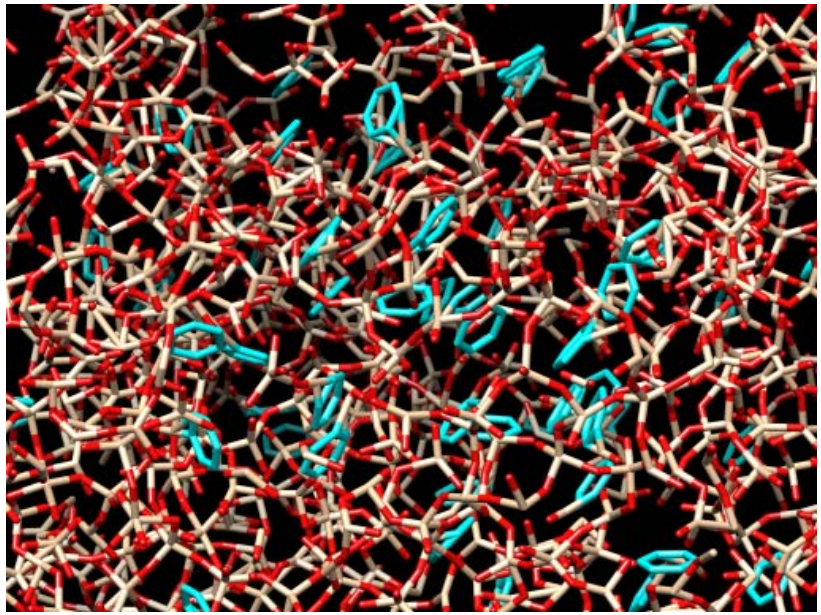
PTES





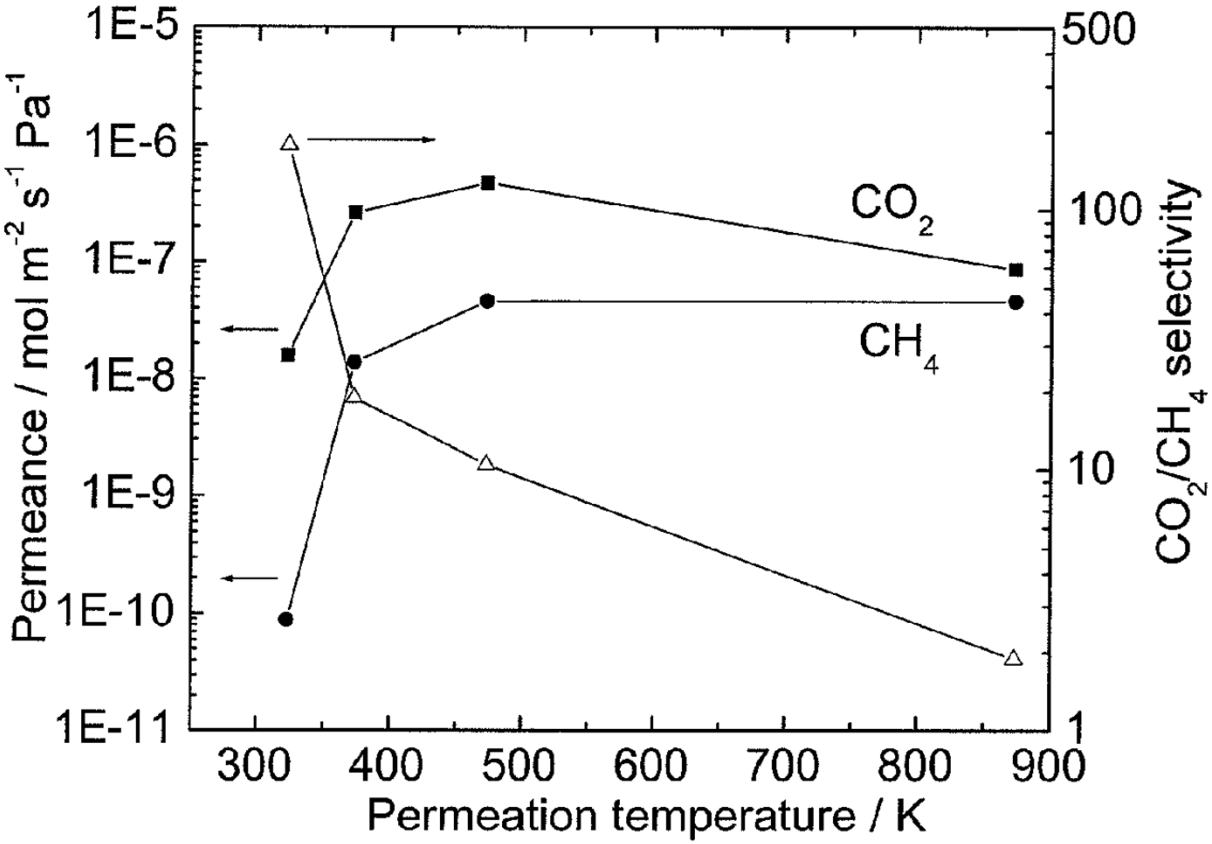
Prepared by high-temperature thermal decomposition of organic precursors

Polymer



- Phenyltriethoxysilane
- Other derivatives:Tetraethyl orthosilicate (TEOS)

Experimental data (need high P & S)



STL-873-II

At 373 K

Selectivity: 19

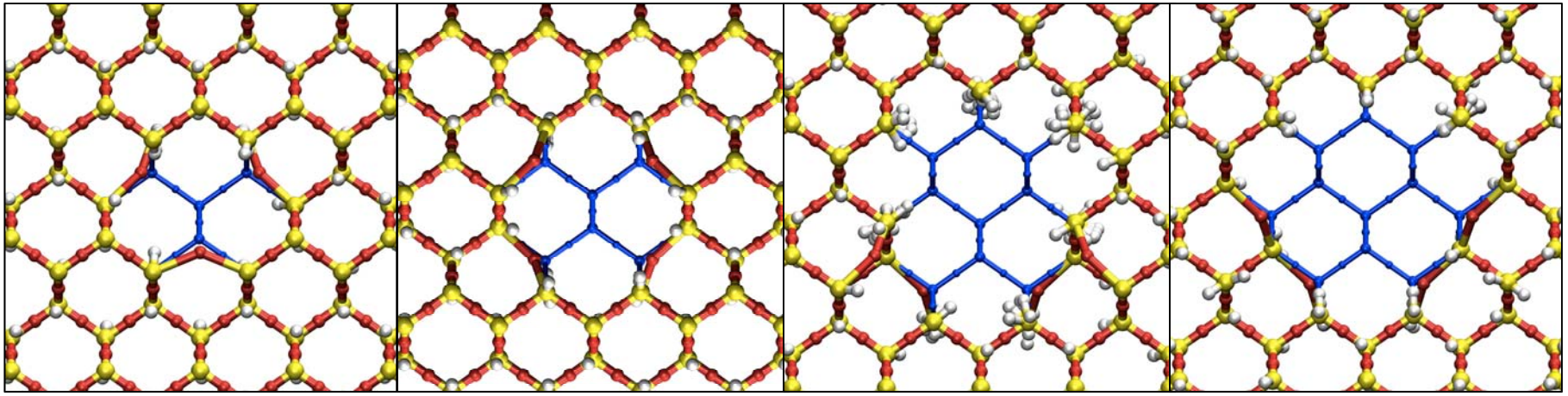
S. Ted Oyama et al., Hybrid organic-inorganic gas separation membranes, US patent 7,938,894.,2011 May 10

Two Specific Aims

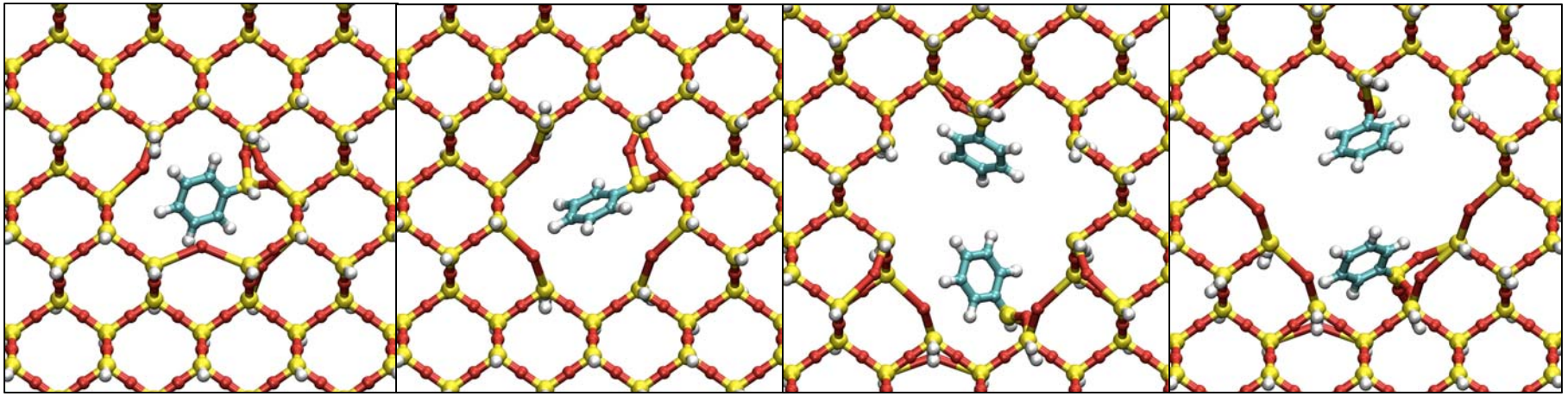
1. Construct Inorganic/Organic Membrane by MD
2. Simulate Separation of CO_2/CH_4 by MD

AIM1-- Membrane Structure: Pore Creation and Insertion of Phenyl Groups

- Zhenxing Wang, Luke E.K. Achenie, Sheima Jativ Khativa and S. Ted Oyama, “Simulation study of carbon dioxide and



#1 4.60 Å #2 5.22 Å #3 11.23 Å #4 11.93 Å



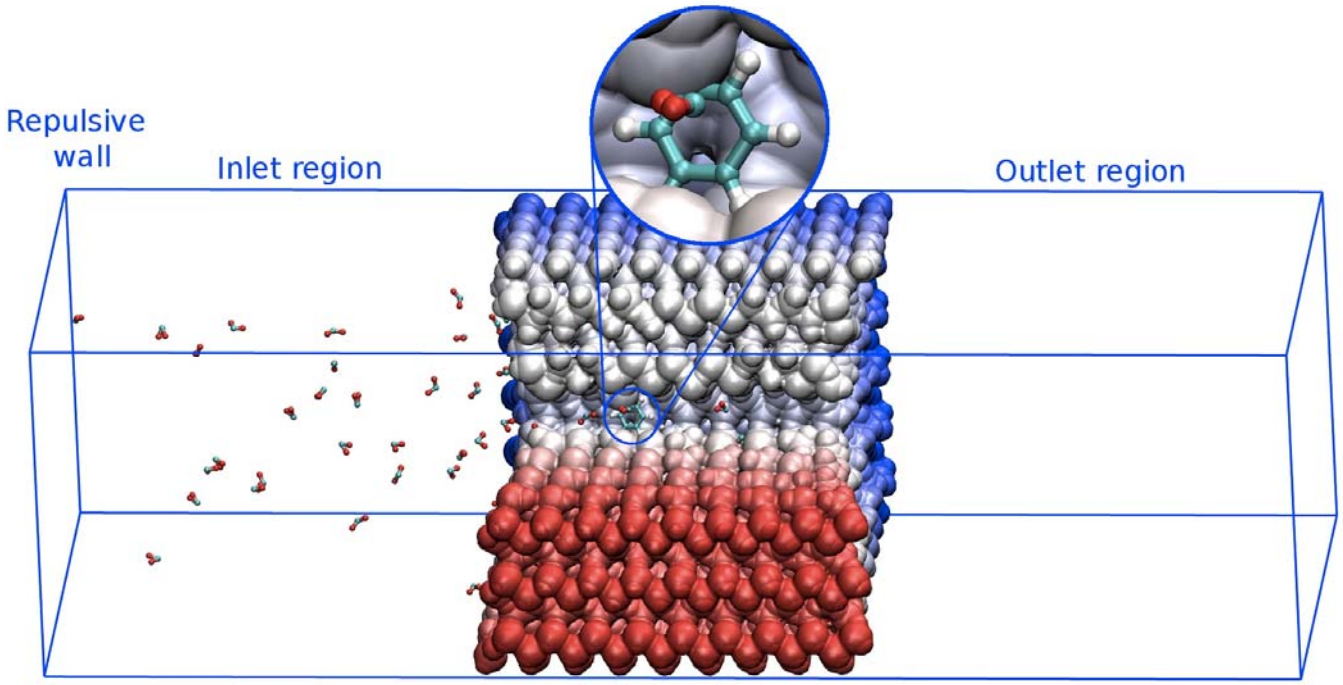
#1-1 #2-1 #3-2 #4-2

AIM 1 –
Phenyl Group & Partial Charge Effects – Initial MD

	CO_2 (mol m^{-2} s^{-1} Pa^{-1})	CH_4 (mol m^{-2} s^{-1} Pa^{-1})	Selectivity
No Phenyl Groups No Charge	1.97×10^{-4}	6.66×10^{-4}	0.30
7Phenyl Groups No Charge	6.62×10^{-5}	2.52×10^{-5}	2.63
7 Phenyl Groups Partial Charge	1.18×10^{-4}	1.64×10^{-6}	71.95

AIM 2: Gas Permeation

- P=2 MPa T=373 K
- NVT & NPT
- Dreiding force field



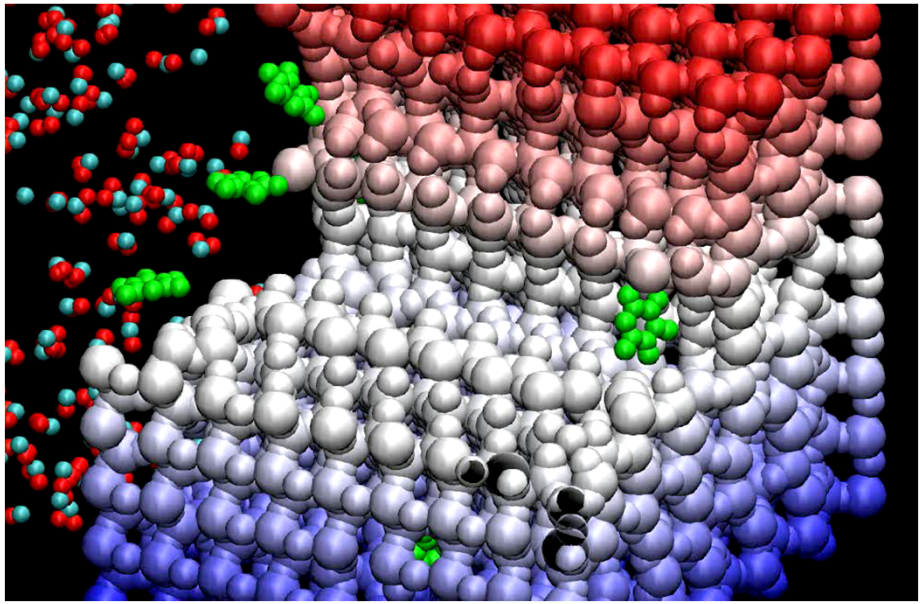
Gas region
54 Å

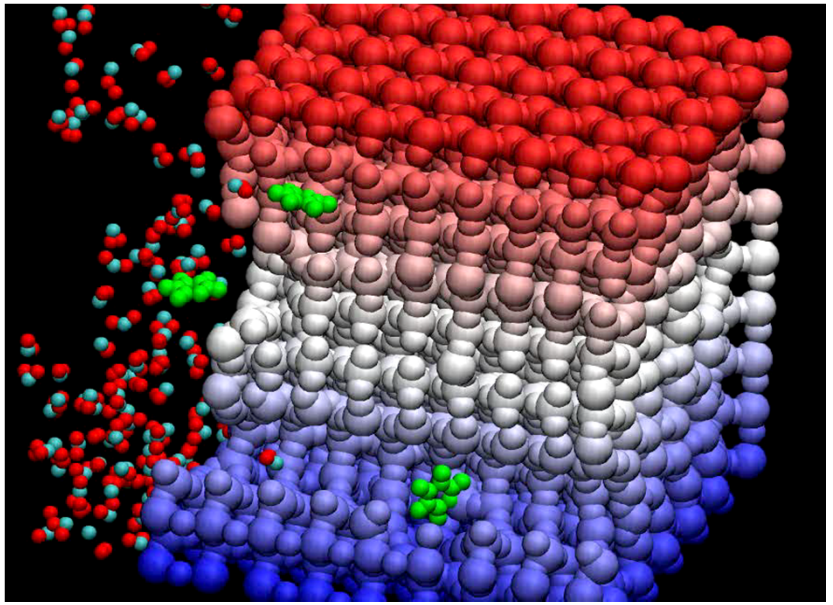
- Zhenxing Wang, Luke E.K. Achenie, Sheima Jativ Khativa and S. Ted Oyama, “Simulation study of carbon dioxide and methane gas permeation in hybrid organic-inorganic membrane,” Journal of Membrane Science., **387/388,** 30–39, 2012.

MD Simulation

-- Gu, Yunfeng, Vaezian, Bita, Jatib Khatib, Sheima, Oyama, S. Ted, Wang, Zhenxing and Achenie, Luke, “Hybrid H2-Selective Membranes Prepared by Chemical Vapor Deposition,” *Separation Science and Technology.* **47(12),** 1698-1708, 2012.

-- Zhenxing Wang, Luke E.K. Achenie, Sheima Jativ Khativa and S. Ted Oyama, “Simulation study of carbon dioxide and methane gas permeation in hybrid organic-inorganic membrane,” Journal of Membrane Science., **387/388,** 30–39, 2012.





Results of models *without* phenyl group

	CO_2 permeance (mol m^{-2} s^{-1} Pa^{-1})	CH_4 permeance (mol m^{-2} s^{-1} Pa^{-1})	selectivity
1	5.12×10^{-4}	6.47×10^{-4}	0.79
2	6.35×10^{-4}	8.92×10^{-4}	0.71
3	1.45×10^{-3}	1.73×10^{-3}	0.84
4	1.24×10^{-3}	2.04×10^{-3}	0.61

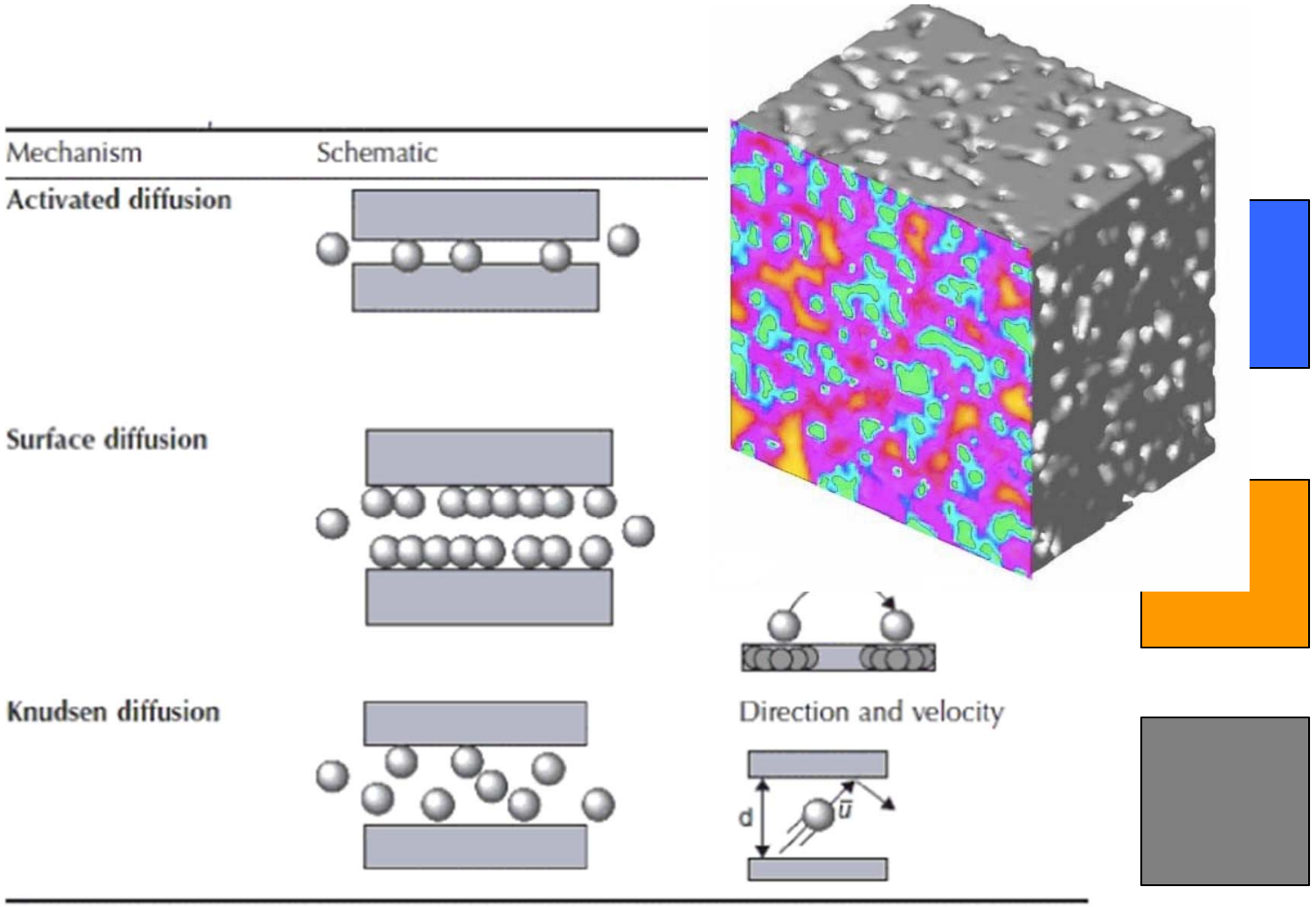
Molecular dynamics study

Permeance of models with phenyl group

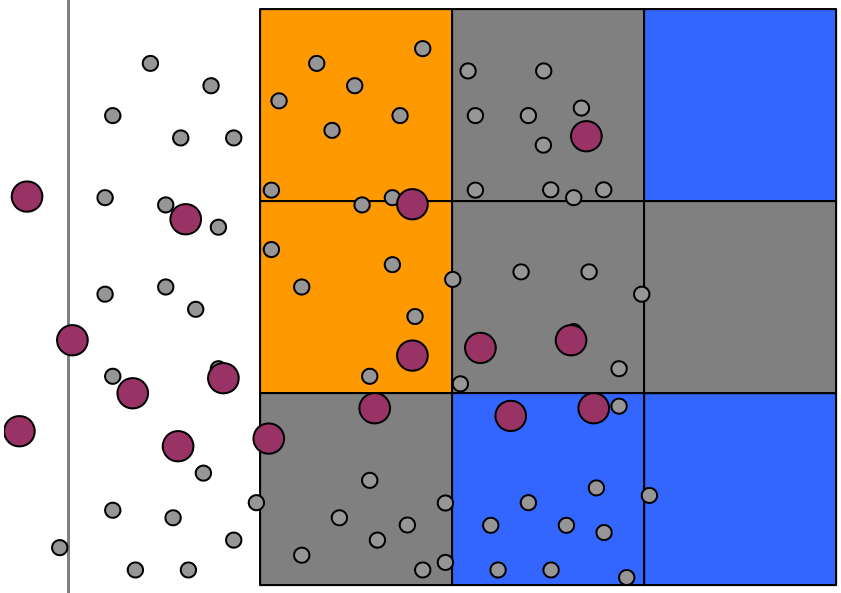
	# Ph Grps	CO_2 permeance (mol m^{-2} s^{-1} Pa^{-1})	CH_4 permeance (mol m^{-2} s^{-1} Pa^{-1})	selectivity
O4.0-1	1	2.87×10^{-4}	1.66×10^{-5}	17.3
O4.0-2	2	1.20×10^{-4}	3.88×10^{-6}	-
S 5.0-2	2	1.14×10^{-3}	8.53×10^{-4}	1.34
S 5.0-4	4	1.10×10^{-3}	5.33×10^{-4}	2.06
S 5.3-2	2	1.12×10^{-3}	1.06×10^{-3}	1.06
S 5.3-4	4	1.16×10^{-3}	1.27×10^{-3}	0.91

Compare with Selectivity of 19 from Expts.

2nd Modeling Approach – Mixed Mechanisms

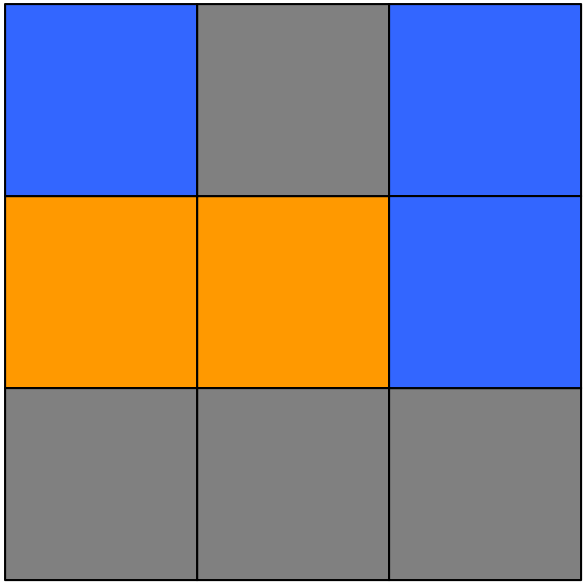


Mixed Mechanism Diffusion Model



Micro-structure # 1

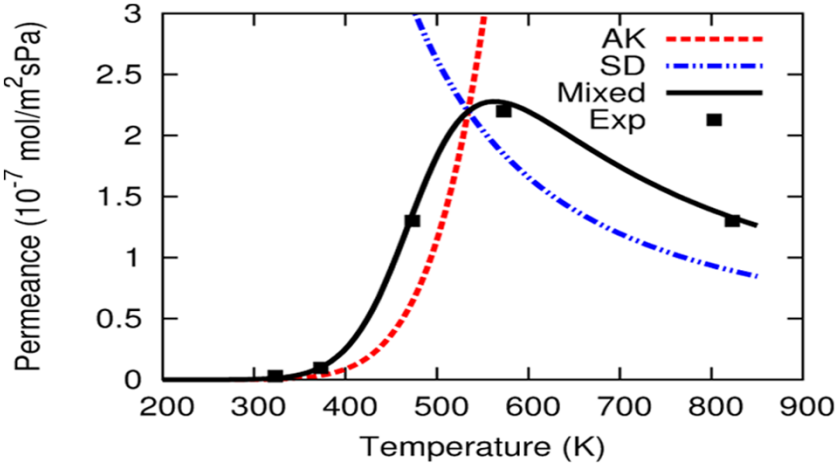
Micro-structure # 2



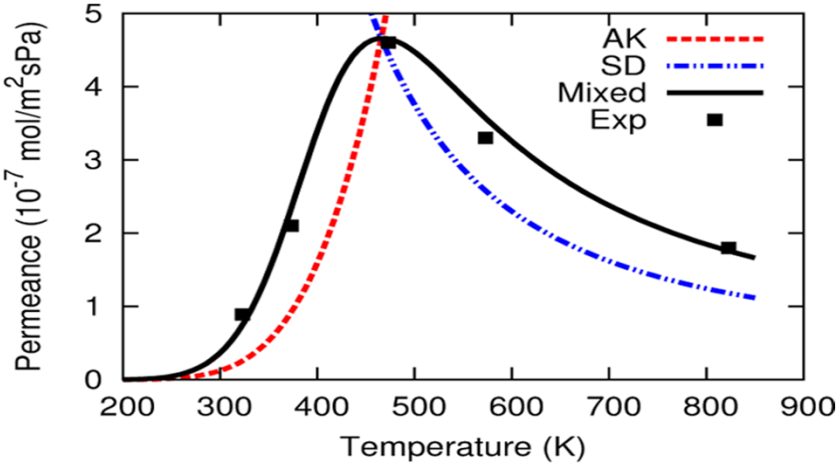
-- Zhenxing Wang, Luke E.K. Achenie, Sheima J. Khatib, and S. Ted Oyama (2013), "Mixed mechanism model for permeation of gases in hybrid inorganic-organic membranes," *Ind. Eng. Chem. Res.,* **52,** 3258–3265, 2013.

Some Results

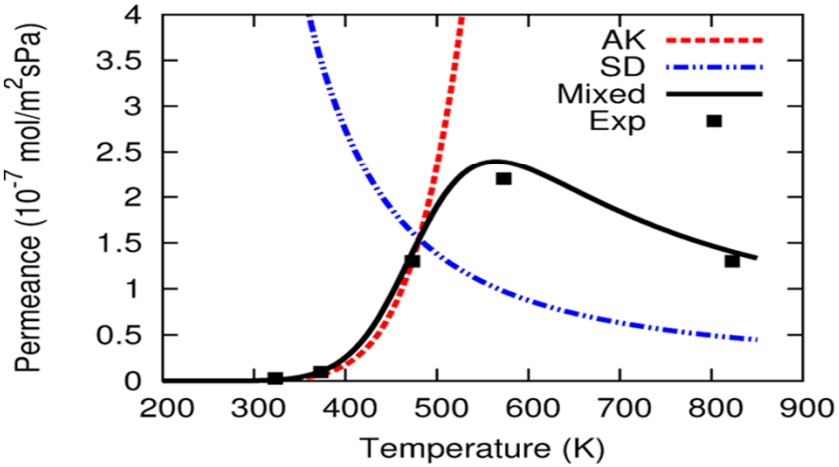
-- Zhenxing Wang, Luke E.K. Achenie, Sheima J. Khatib, and S. Ted Oyama (2013), "Mixed mechanism model for permeation of gases in hybrid inorganic-organic membranes," *Ind. Eng. Chem. Res.*, **52,** 3258–3265, 2013.



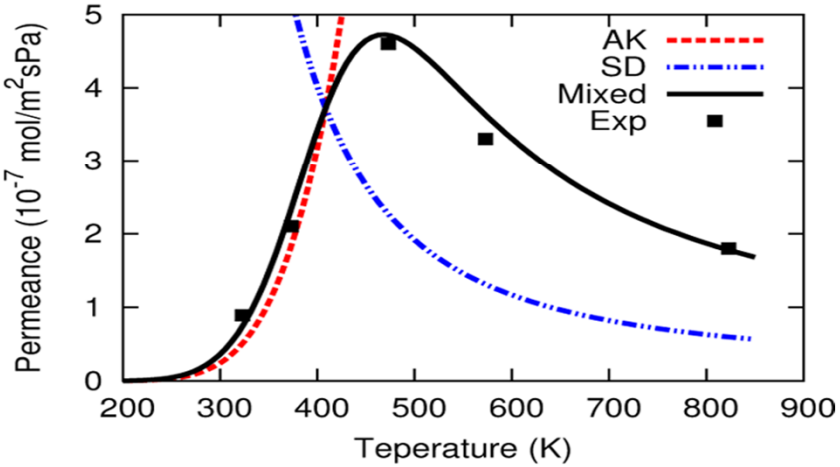
(a) Methane in M1-1



(b) Carbon dioxide in M1-1

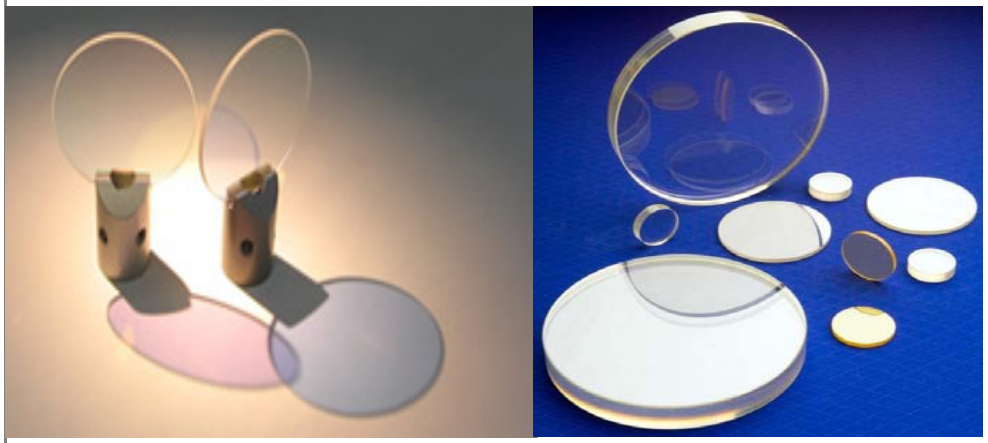


(c) Methane in M1-2



(d) Carbon dioxide in M1-2

Multi-Scale modeling of chemical vapor deposition processes



Application:

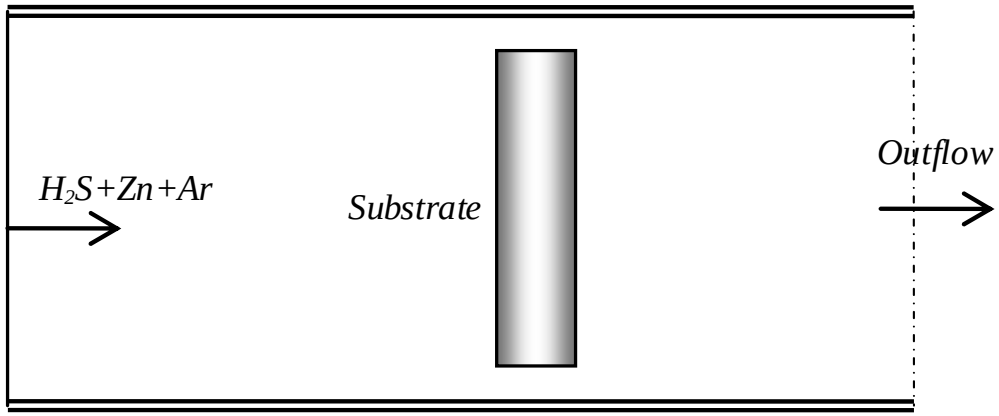
- Used in the semiconductor industry to produce thin films on wafer substrate
- Reflective window
- Laser dooms
- Nano sensors
- Blue light diodes
- Luminescent displays
- Infra-red devices(anti reflection coating)

1. T, Matsuoka, A. Ohki, T. Ohno, and Y.Kawaguchi, J. Cryst. Growth 138, 727, 1994.

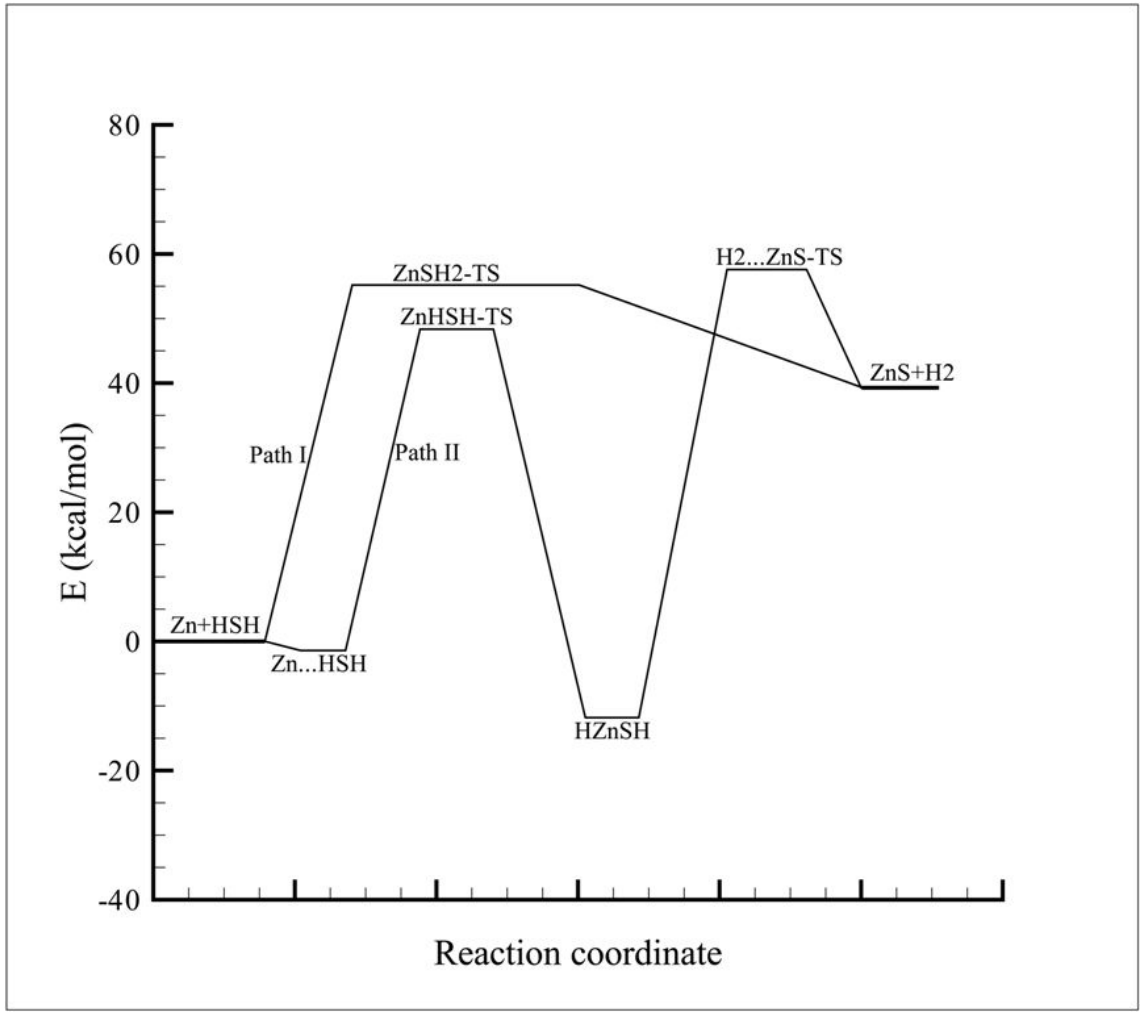
CVD of Zinc Sulfide

Gas phase reaction $Zn(g) + H_2S \rightarrow ZnS(g) + H_2(g)$

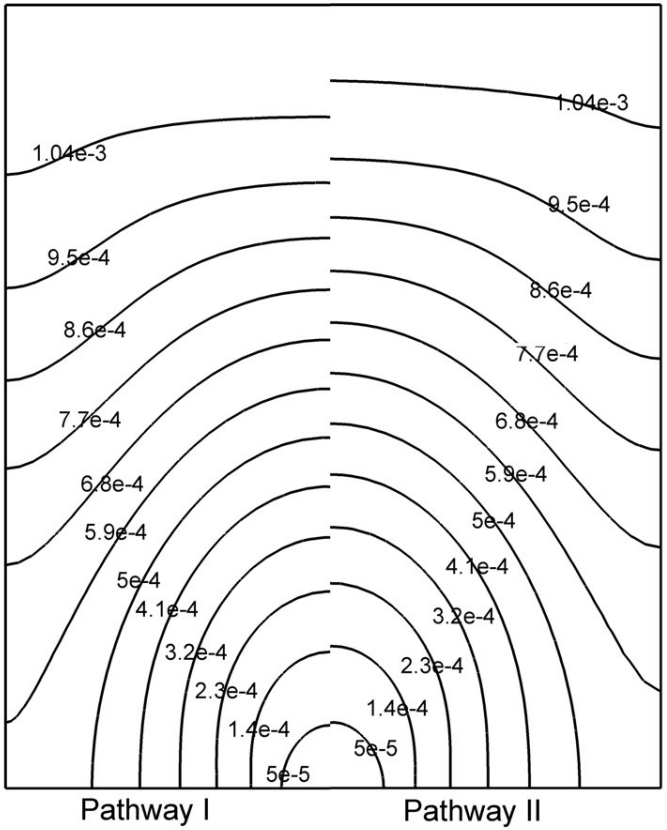
Surface reactions $ZnS(g) \rightarrow ZnS(s)$



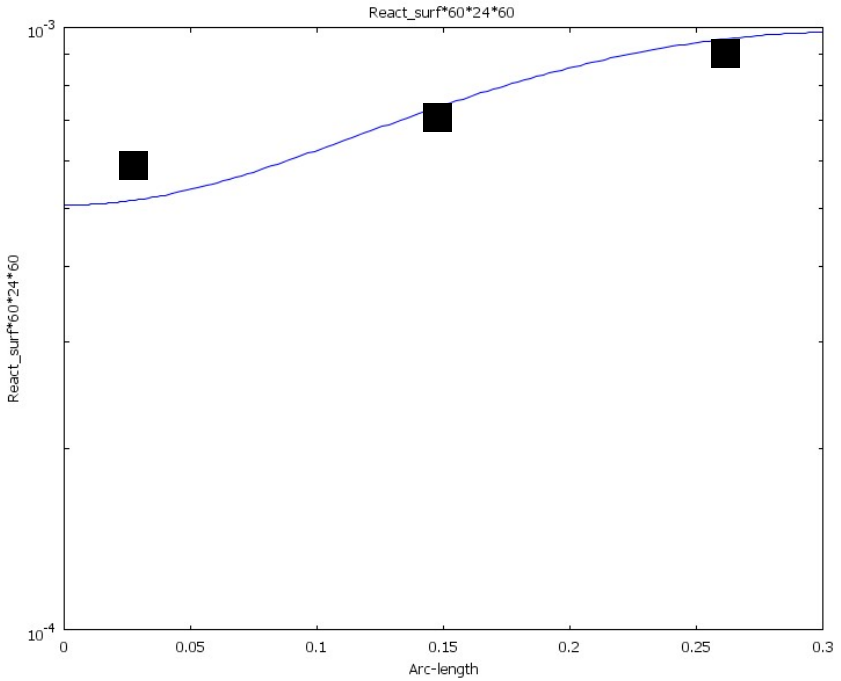
Gas Phase reaction mechanism (ZnS) via DFT Molecular Modeling



Pathway selection and Deposition rate



Zinc Sulfide concentration mol/m3



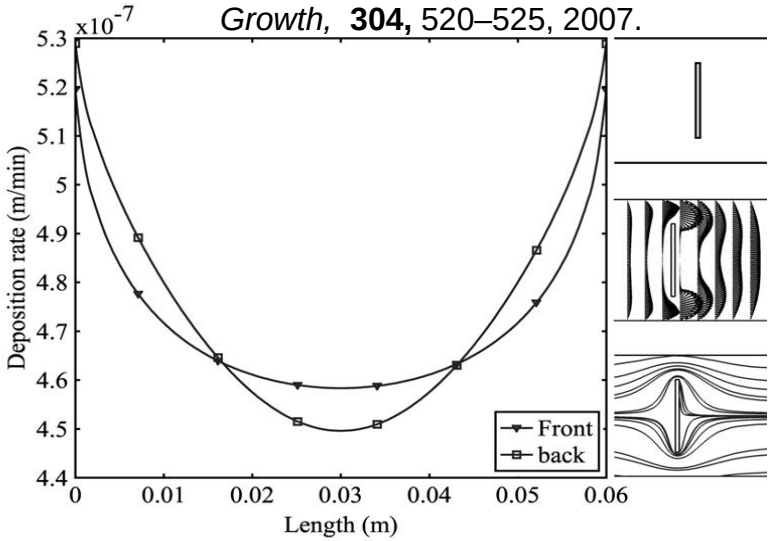
Deposition rate (0.5-.9 mm/day)[1]

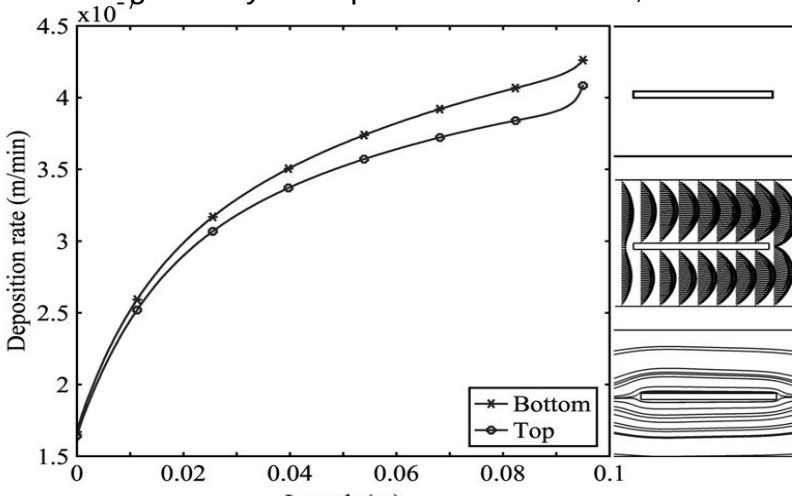
Sharifi, Y. and Achenie, L.E.K., "Using Density Functional Theory to Postulate a Mechanism for Zinc Sulfide Formation in a CVD Reactor," *Journal of Crystal Growth,* **307,** 440–447, 2007.

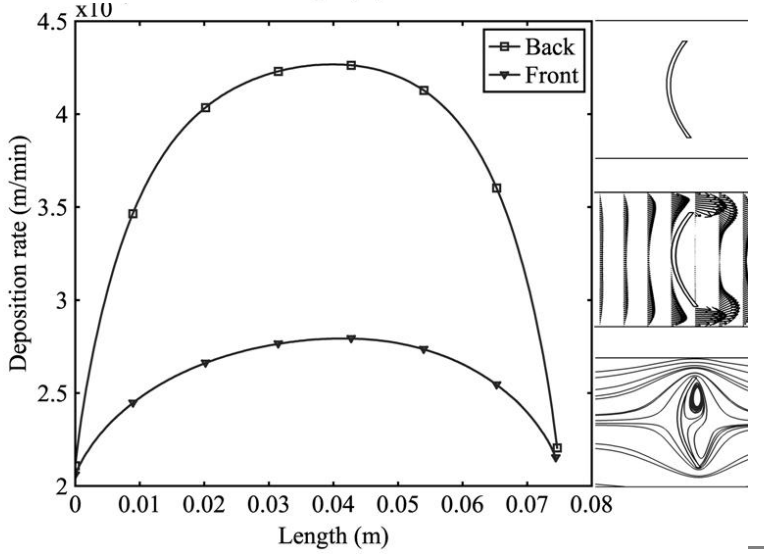
Fang Z. et al, J of Crystal Growth, 237–239 (2002) 1707–1710

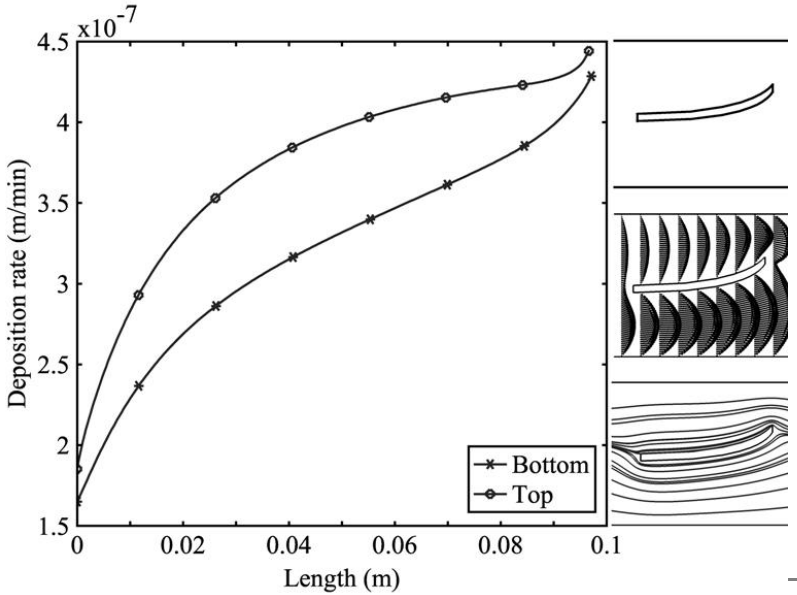
Effect of substrate geometry on deposition rate

Sharifi, Y. and Achenie, L.E.K. "Effect of substrate geometry on deposition rate in CVD," *Journal of Crystal Growth,* **304,** 520–525, 2007.



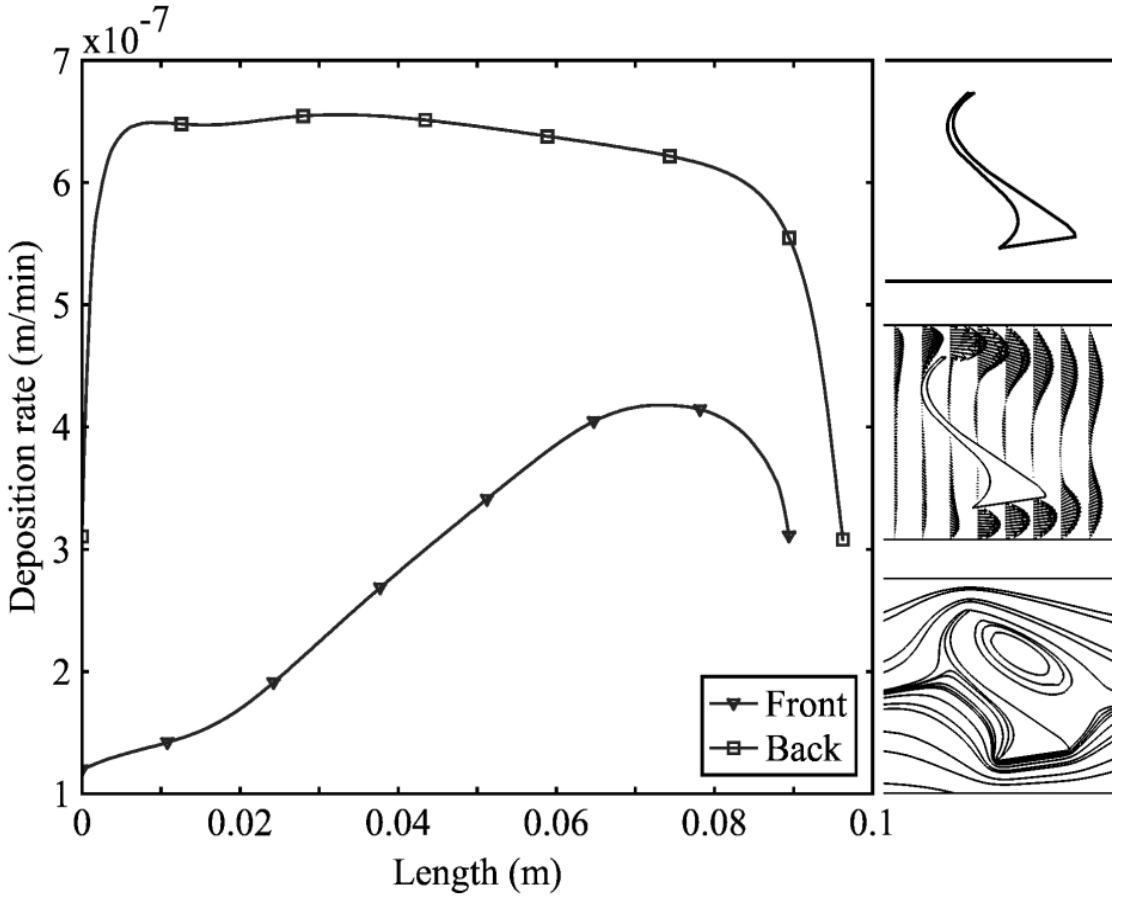






Uniform Deposition – Shape Optimization

Sharifi, Y. and Achenie, L.E.K. “Effect of substrate geometry on deposition rate in CVD,” *Journal of Crystal Growth,* **304,** 520–525, 2007.



Cluster formation in Zinc Sulfide CVD

Cause:

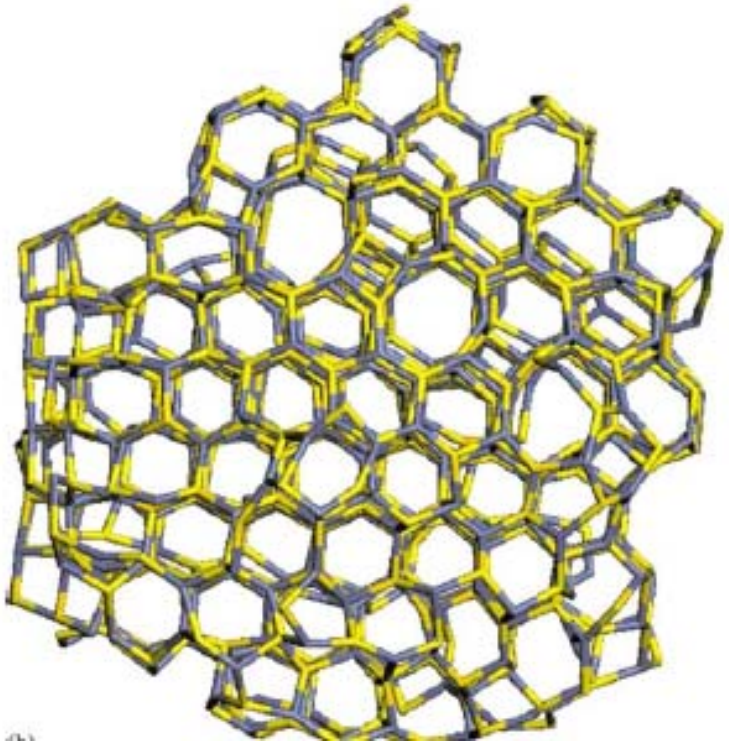
1. High temperature (973K)
2. Highly reactive precursors

Disadvantages:

1. Particle settlement(gravity)
2. Outflow of particles
3. Impurity and defects [1].
4. Inefficient Use of precursors

Control the cluster formation [2]:

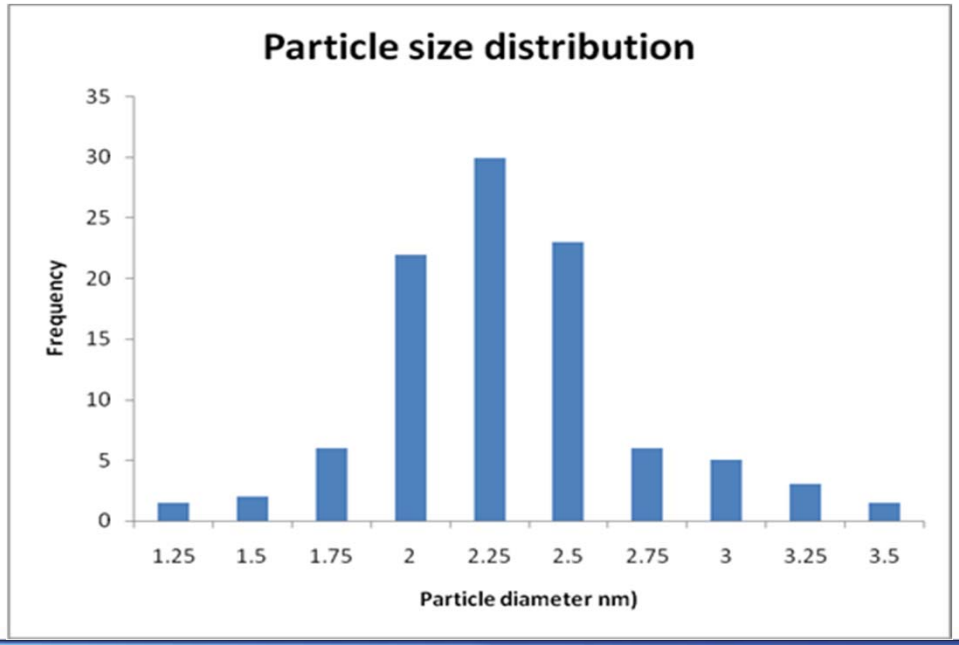
1. Mechanism
2. Dynamics

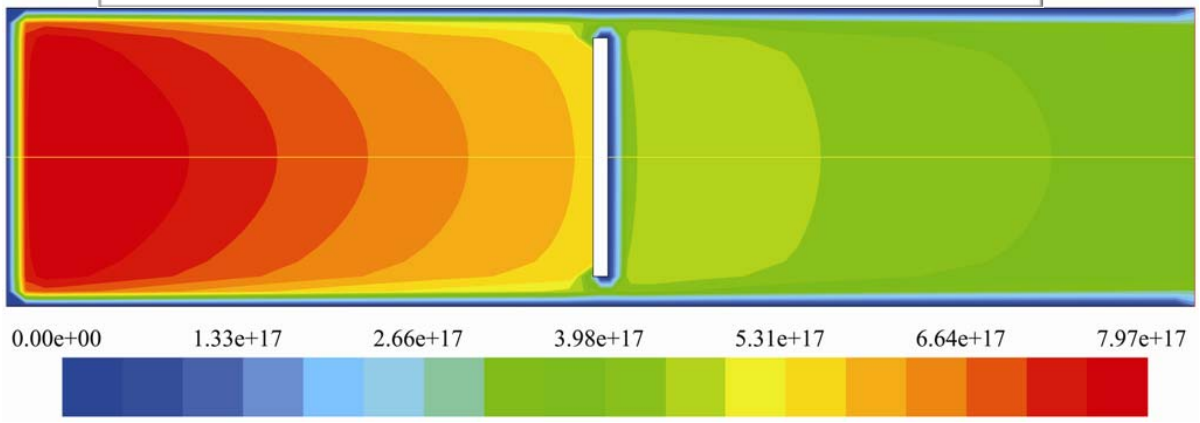


What is the morphology of these particles?

[1] Wear 255 (2003) 115–120 [2] Journal of Crystal Growth 208 (2000) 259-263.

Particle size and distribution





-- Sharifi, Y. and Achenie, L.E.K., "Particle Dynamics in a CVD Reactor: A Multiscale Approach," *Ind. Eng. Chem. Res.*, **48(13)**, 5969-5974, 2009.

Summary

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Acknowledgements:

- Funding from NSF, DOE
- Graduate Students

Thank You !!