Modeling of Gas Adsorption on Coalbeds

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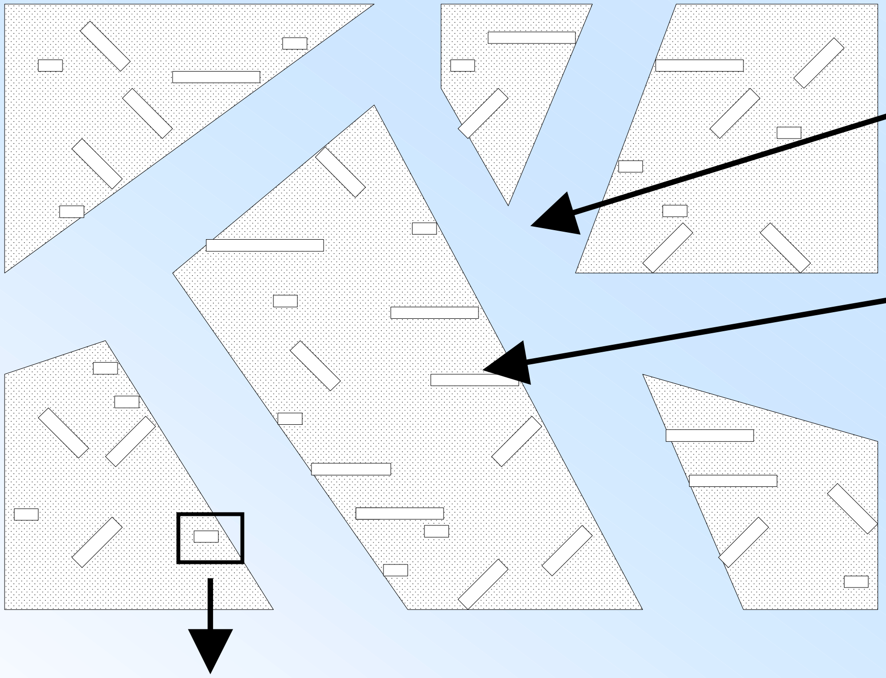
RATIONALE

- Modeling of the adsorption behavior of coalbed gases (methane, CO_2, nitrogen) is essential in CBM production and in CO_2 sequestration.
- Further, knowledge of the competitive adsorption of CBM gases is required to elucidate mechanisms for enhanced recovery of CBM and CO_2 sequestration processes.
- Reliable adsorption predictions cannot be generated using simple, empirical models. Accurate models require sound theory, judicious approximations, and accurate experimental information.

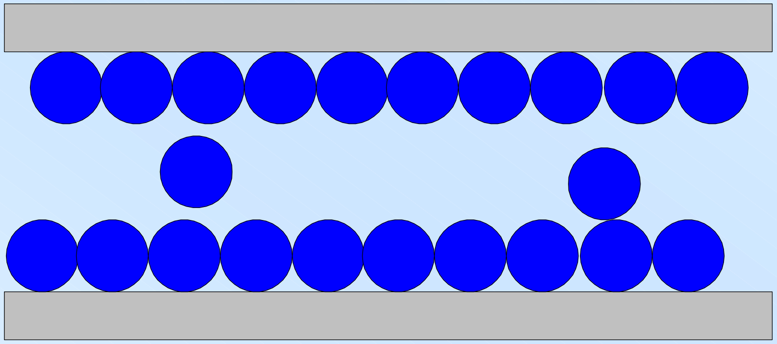
Coalbed Adsorption Phenomenon



Cleat system where free gas resides

Micropores where Adsorbed gas resides

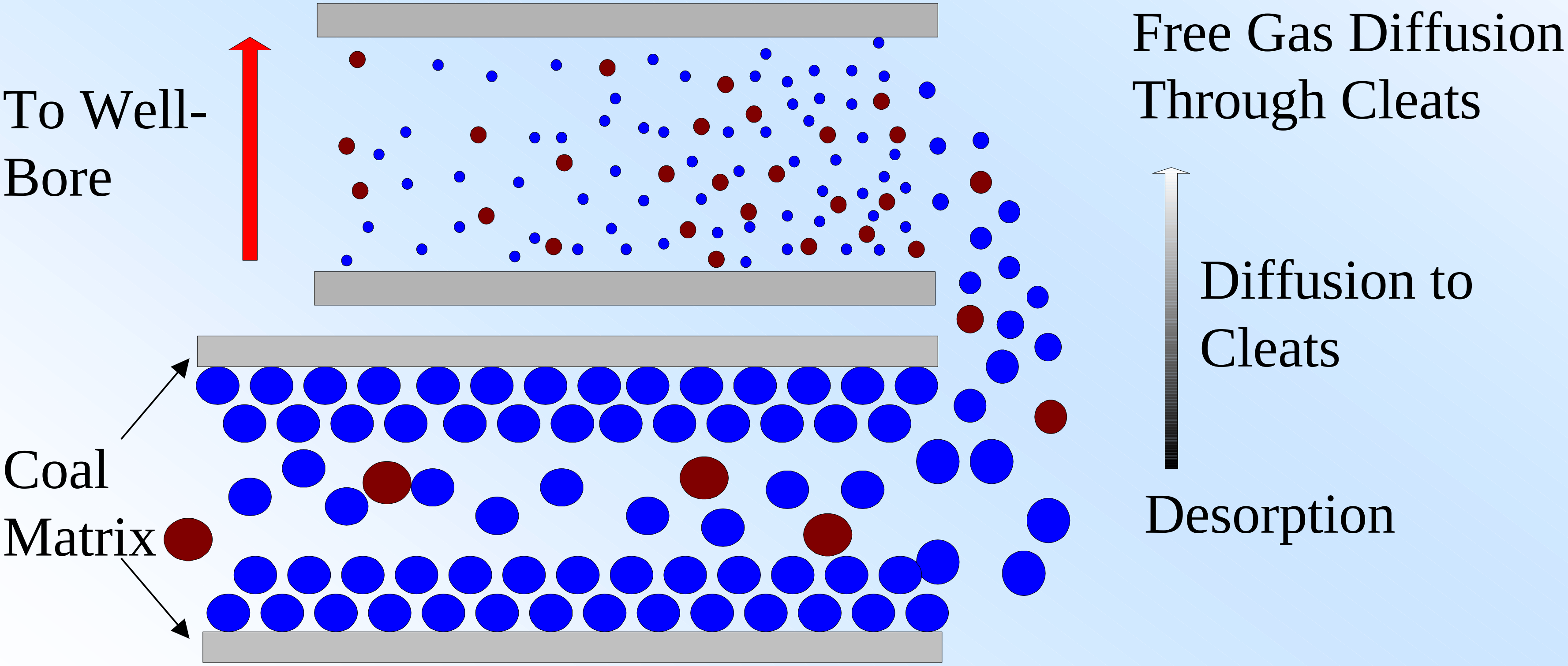
Zoom-in view of model micropore



Primary Recovery

- Reduce cleat pressure by producing water
- Methane desorbs from matrix to cleats
- Methane and water flow to well bore

● Water
● Methane



To Well-Bore

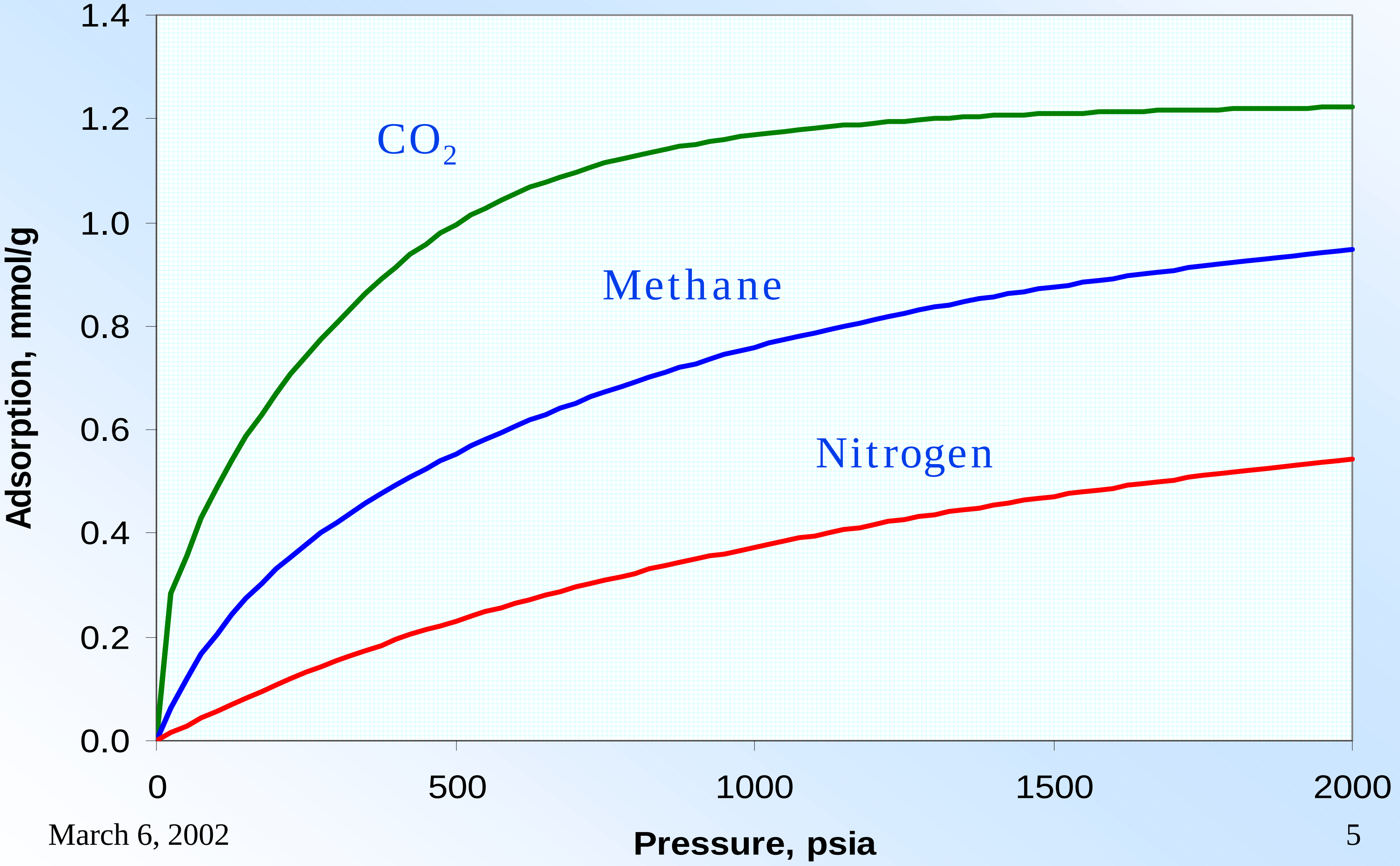
Coal Matrix

Free Gas Diffusion Through Cleats

Diffusion to Cleats

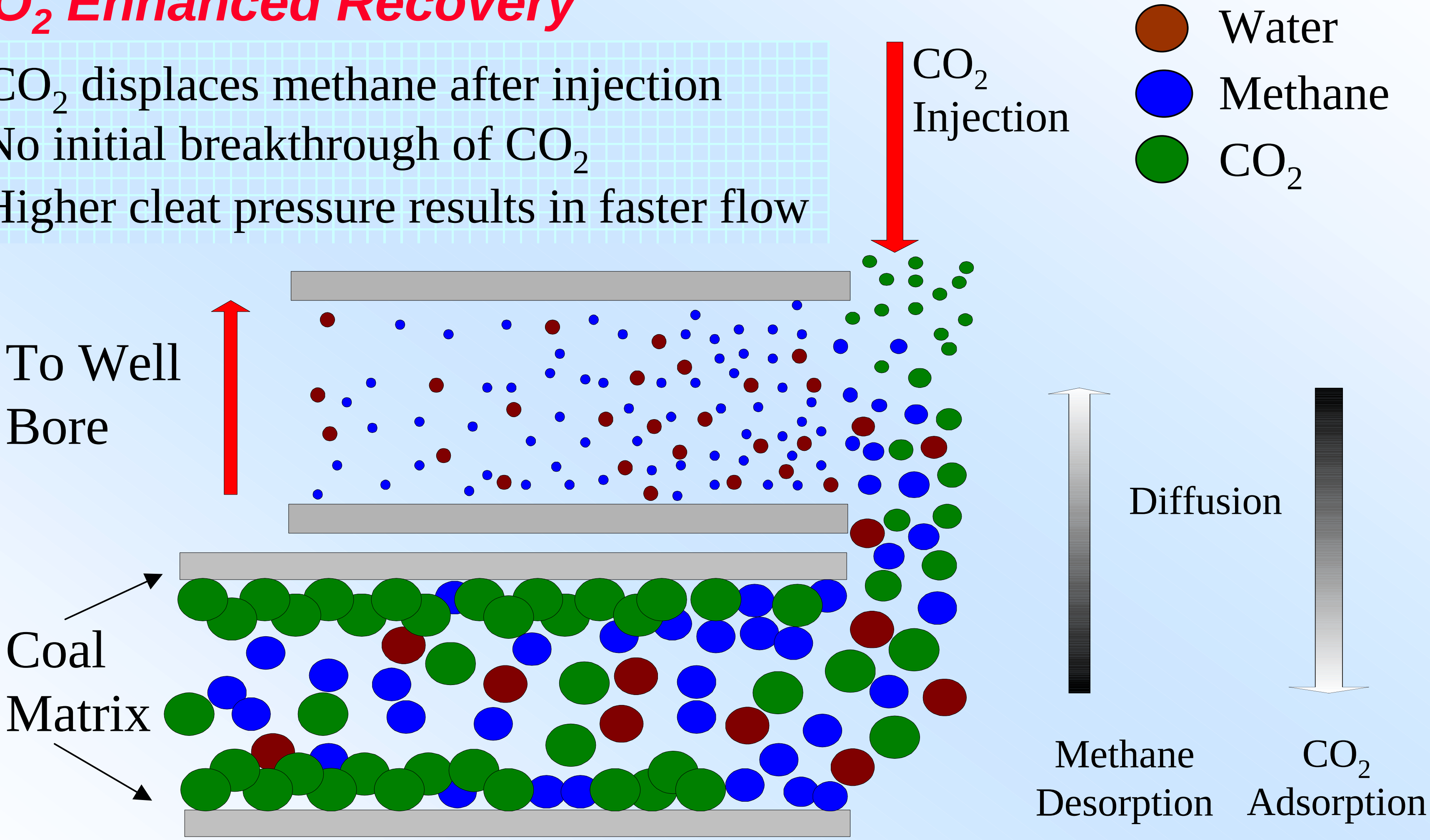
Desorption

Absolute Adsorption on Fruitland Coal at 115°F



CO_2 Enhanced Recovery

- CO_2 displaces methane after injection
- No initial breakthrough of CO_2
- Higher cleat pressure results in faster flow



Theory / Practice

- **Theory:** Improve our understanding of high-pressure adsorption through rigorous methodologies.
- **Practice:** Provide reliable equilibrium adsorption models for optimum CBM production and CO_2 sequestration.
- **Strategy:** Use rigorous methodologies to develop reliable adsorption models for industrial practice.
- **Goal:** Develop reliable coal-structure-based generalized predictions using simple, accessible characterizations.

Current Issues

- Adsorption modeling
- Coal characterization
- Coal structure-based model generalizations
- Estimates for adsorbed-phase density
- Effect of moisture on modeling adsorption capacity
- Matrix swelling
- Binary and ternary pvT data
- Balancing computational efficiency and reliability

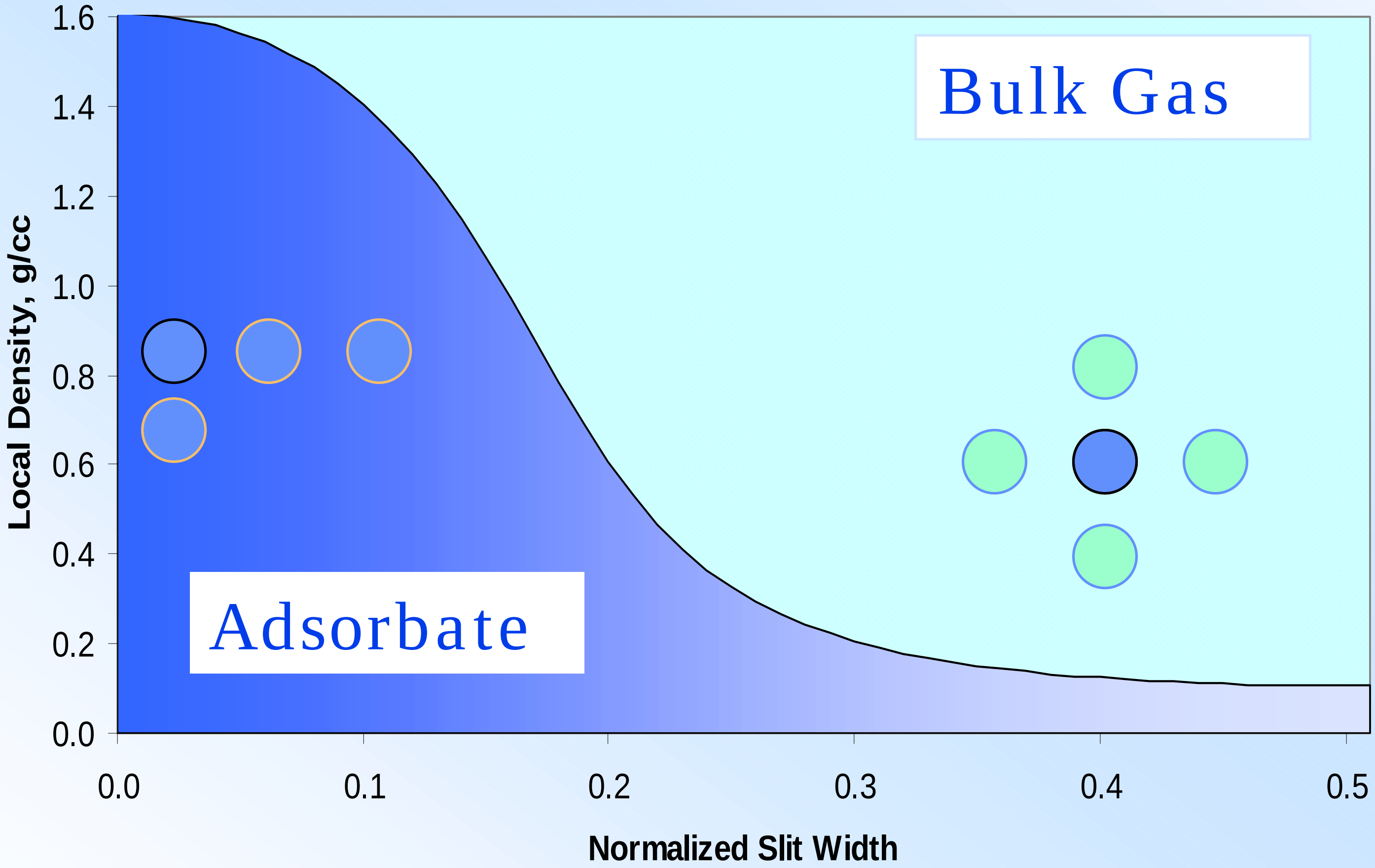
Current Issues: Adsorbed-Phase Density

- Why do we need adsorbed-phase density?
- Current estimation methods:
  - Traditional
  - Experimental approximation
  - Model-based:

    2D equations of state, SLD theory, Ono Kondo theory
- What is the impact?

Molecular Interactions:

Mean Field Approximation



Excess and Absolute Adsorption

- The excess adsorption is defined as follows

$$n_{Gibbs} = \oint_V \left(\rho_{ads} - \rho_{bulk}\right) dV$$

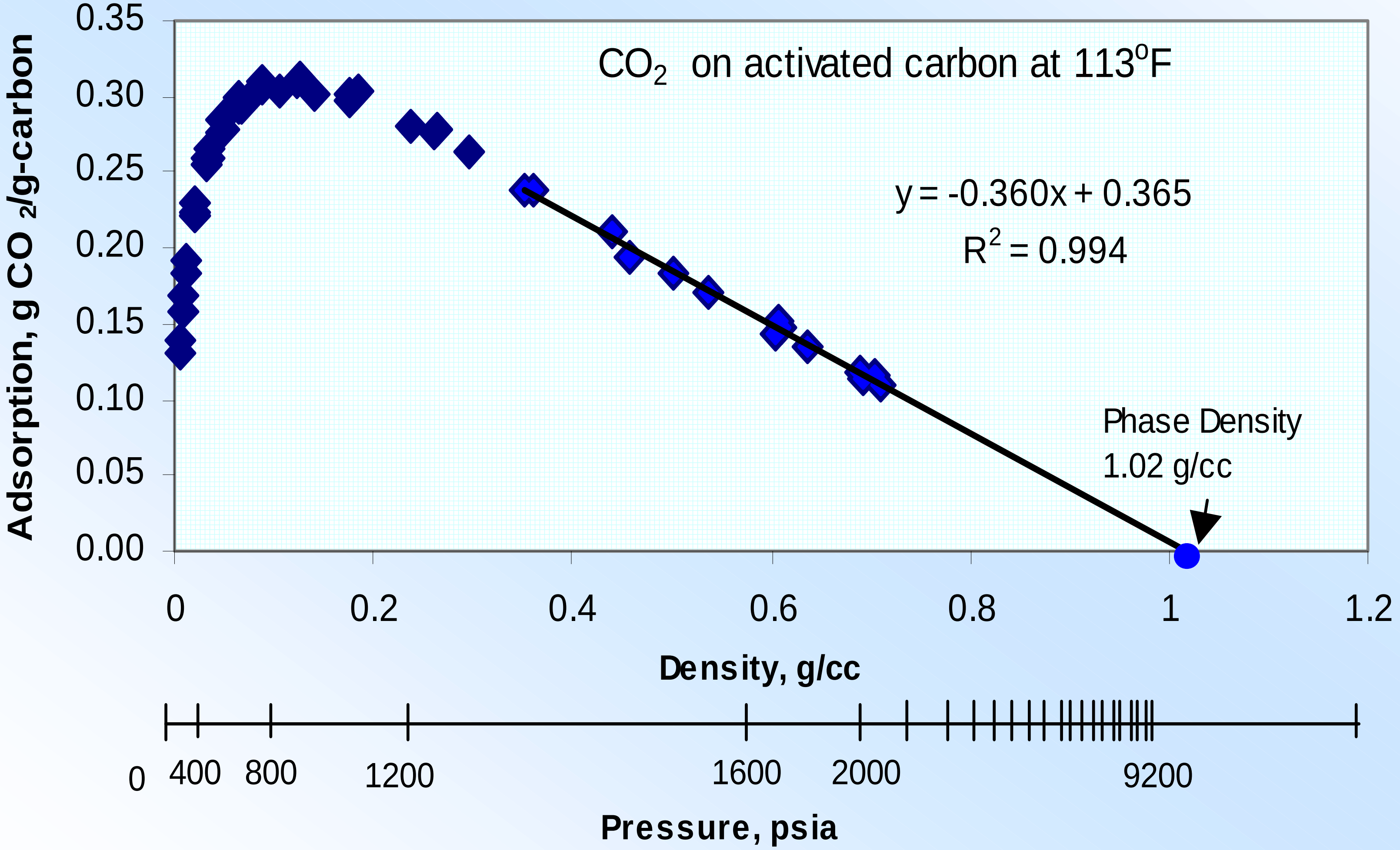
or

$$n_{Gibbs} = V\left(\overline{\rho}_{ads} - \rho_{bulk}\right)$$

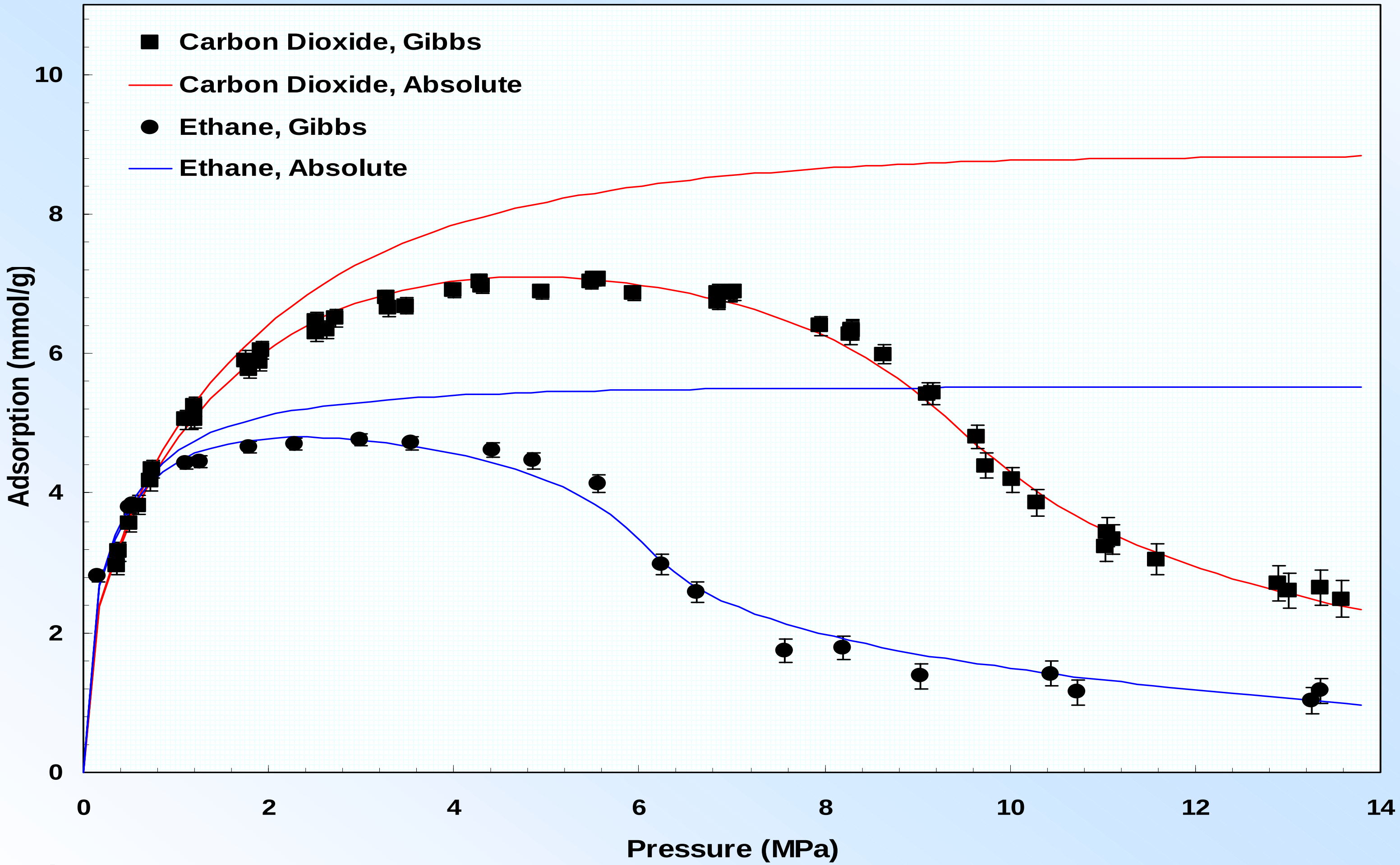
- The absolute adsorption is defined as

$$n_{abs} = V_{ads}\,\rho_{ads} = \frac{n_{Gibbs}}{1 - \dfrac{\rho_{bulk}}{\rho_{ads}}}$$

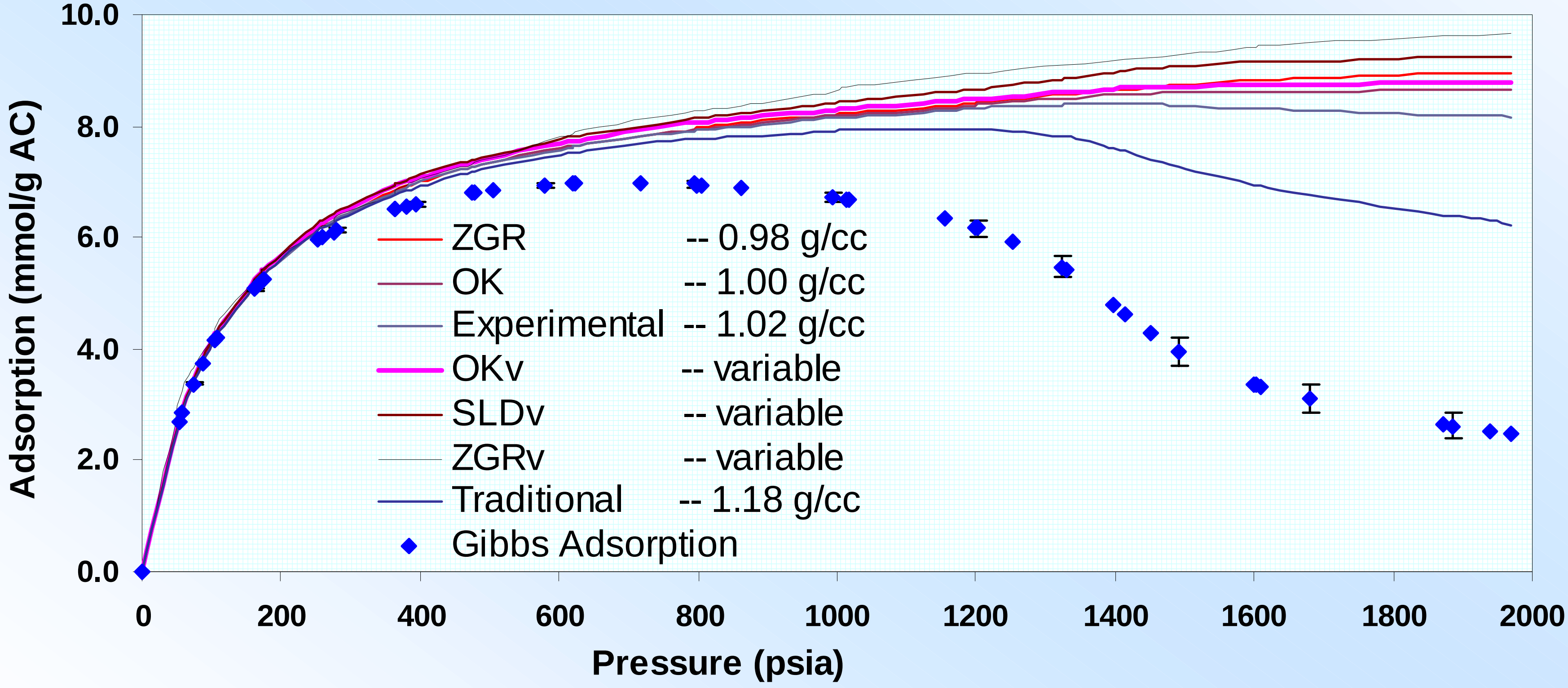
Estimation of Phase Volume and Density



CO_2 and Ethane Adsorption on Activated Carbon (OSU)



Impact of Adsorbed-Phase Density: CO_2 on Activated Carbon at 113 °F



Current Issues: Adsorption Modeling

- We seek simple, reliable adsorption equilibrium models that are suitable for generalized predictions and reservoir simulations.
- Such models should be capable of
  - Precisely representing pure and mixture isotherms
  - Facilitating *a priori* predictions

Equilibrium Modeling: Three Methods

1. Enhanced forms of the Langmuir isotherms

-- provide simple data correlation

2. Two-dimensional equations of state (2-D EOS)

(a) Cubic EOS (b) Segment-Segment EOS

-- facilitate generalized simulations

3. Simplified-Local-Density (SLD) models

-- account for surface structure and near-critical behavior

The Langmuir & Loading Ratio Correlation (LRC)

$$\frac{\omega_i}{L_i} = \frac{(B_i P y_i)^{\eta_i}}{1 + \sum_j (B_i P y_i)^{\eta_i}}$$

P = *pressure*

y_i = *gas phase mole fraction of component "i"*

η_i = *LRC exponent for component "i"*

ω_i = *amount adsorbed of component "i"*

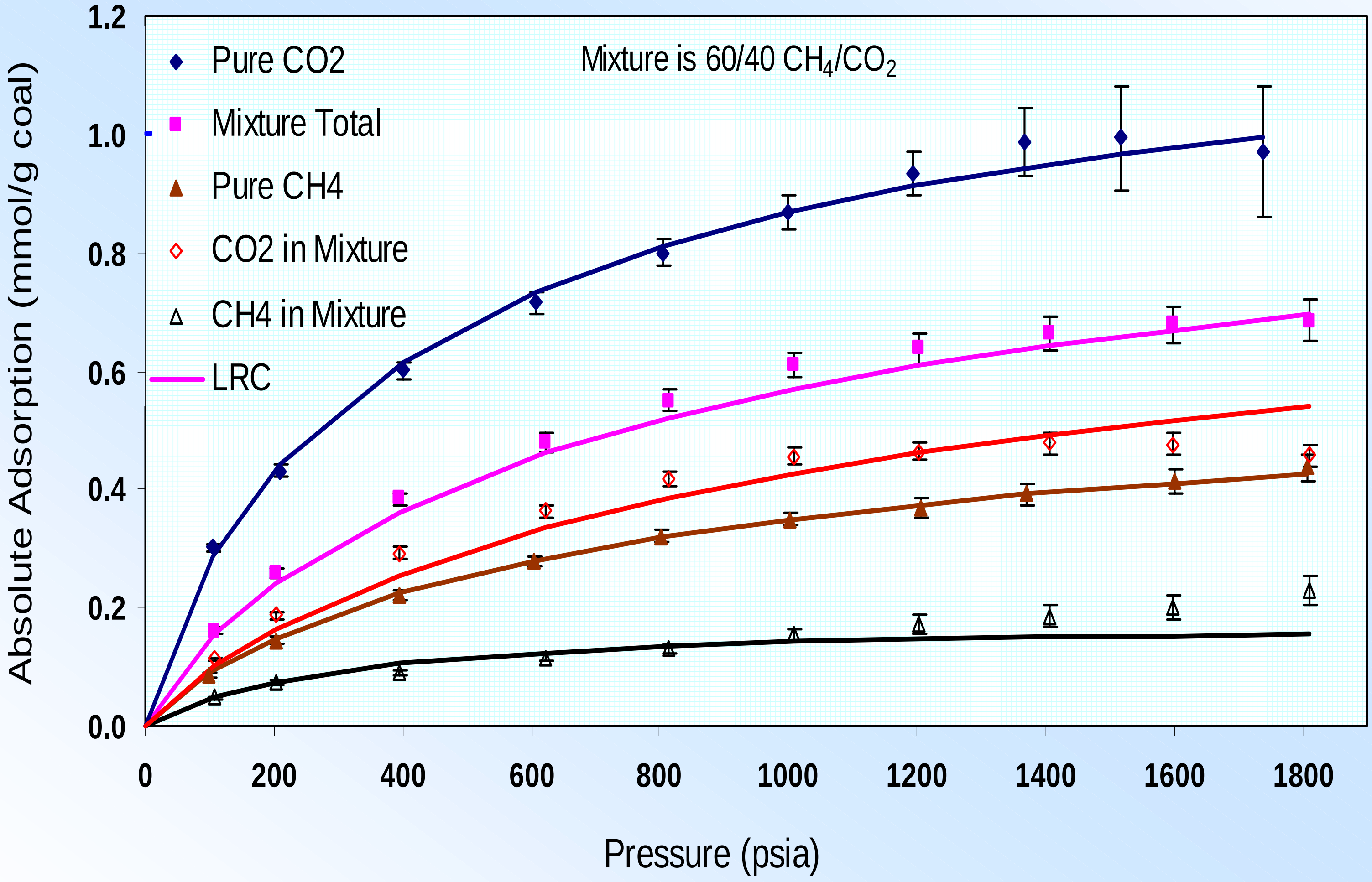
L_i, B_i = *Langmuir/LRC model coefficients*

LRC Current Capability

The loading-ratio correlations:

- Represent absolute pure-component and mixed-gas **total** adsorption precisely
- Yield reasonable predictions for these systems
- Represent individual-component adsorption in mixtures less precisely, especially the less-adsorbed ones
- Require adsorbed-phase density estimates

LRC Representations: Illinois-6 Coal



2-D Equations of State

(OSU, 1992)

$$\left[A\pi + \frac{\alpha\omega^2}{1 + U\beta\omega + W(\beta\omega)^2}\right]\left[1 - (\beta\omega)^m\right] = \omega RT$$

$$\alpha = \sum_i \sum_j x_i x_j \alpha_{ij} \qquad \beta = \sum_i \sum_j x_i x_j \beta_{ij}$$

$$\alpha_{ij} = (\alpha_i + \alpha_j)/2 \qquad \beta_{ij} = \sqrt{\beta_i \beta_j}$$

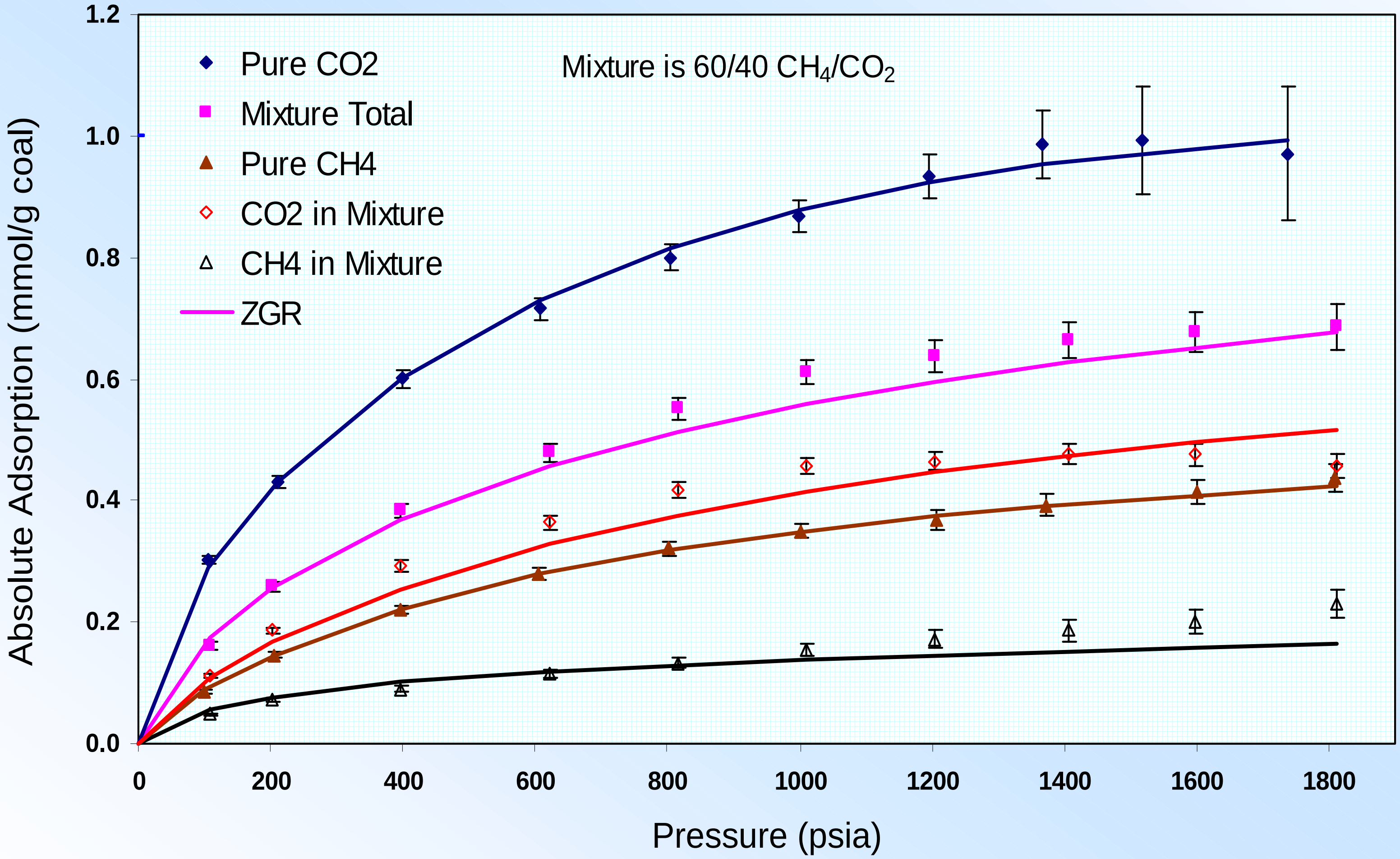
EOS	m	U	W
VDW	1	0	0
SRK	1	1	0
PR	1	2	-1
Eyring	1/2	0	0
ZGR	1/3	0	0

2D EOS Current Capability

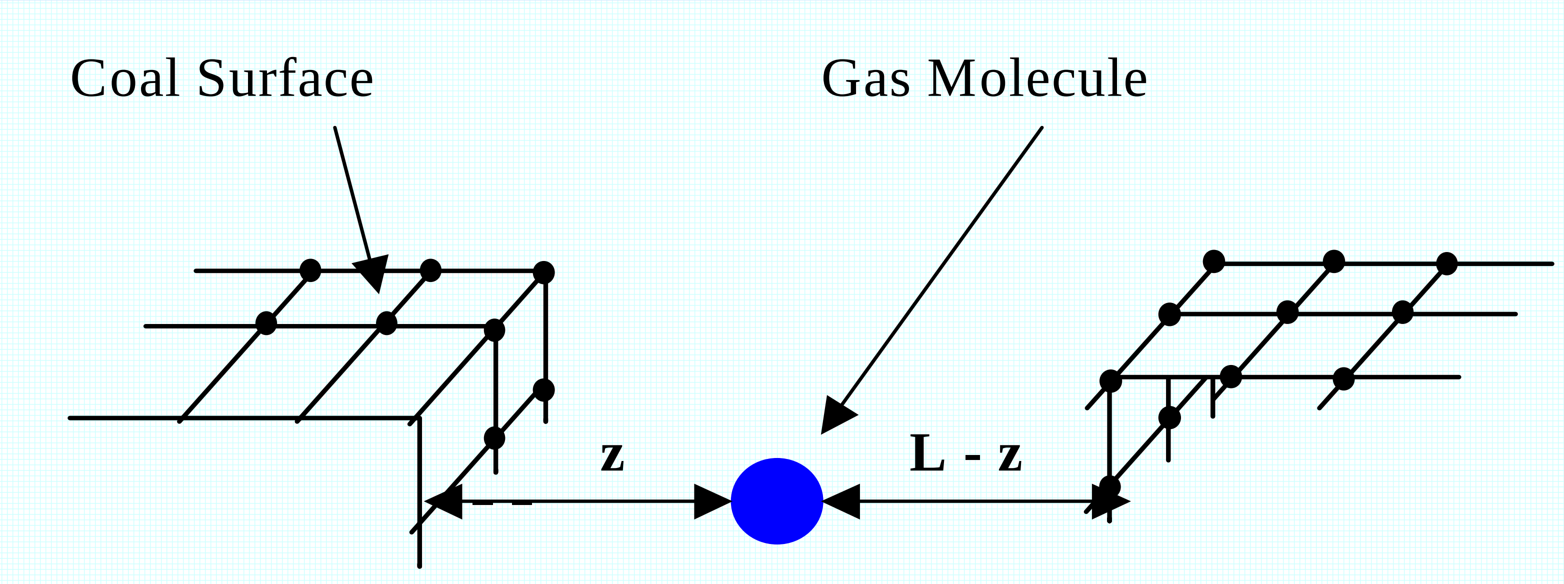
2-D EOS models:

- Describe CBM pure-component and mixed-gas **total** adsorption data with sufficient precision
- Yield reasonable predictions for these systems
- Represent individual-component adsorption less precisely, especially the less-adsorbed ones
- Employ inadequate repulsive terms
- Do not account for variations in coal structure

2D EOS Representations: Illinois-6 Coal



The EOS-SLD Adsorption Model



$$\mu_{fs}(z) = \mu_{fs1}(z) + \mu_{fs2}(L - z)$$

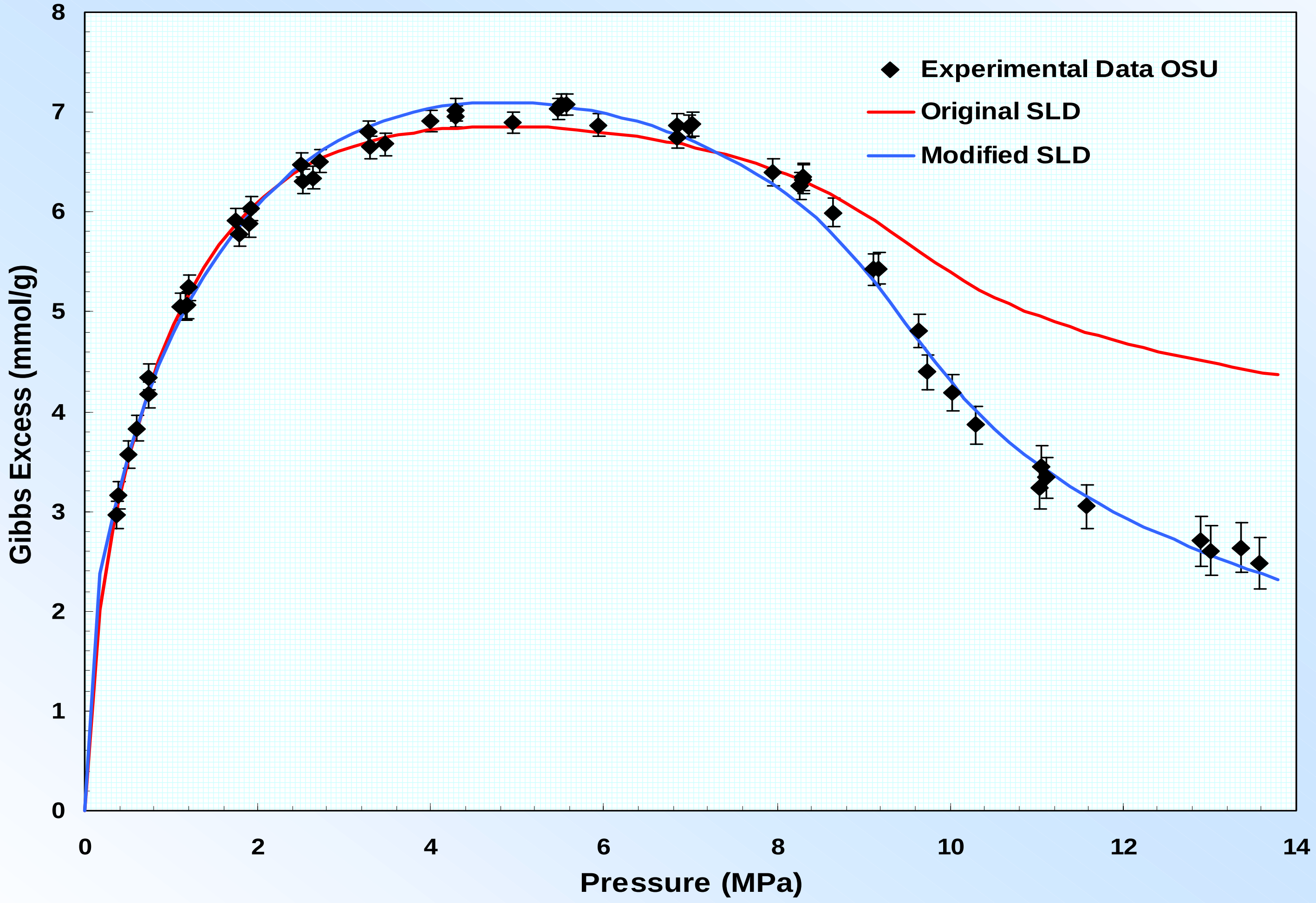
- The fluid-solid interaction potential equals the sum of the potentials between the gas molecule and the two sides of the slit.

EOS-SLD Current Capability

The EOS-SLD models:

- Account for variations in coal structure
- Provide a viable framework for generalized predictions
- Have produced promising preliminary results for mixture adsorption modeling
- Employ inadequate repulsive terms

CO_2 Adsorption Using Modified SLD-PR



Sample Pure-Gas Adsorption Model Results

	%AAD			
	Nitrogen	**Methane**	**CO_2**	**Ethane**
Dry Activated Carbon				
LRC	**0.3**	**0.6**	**6.1**	**5.8**
ZGR	**0.4**	**0.7**	**5.2**	**5.6**
ZGR Gibbs	**0.4**	**0.5**	**1.3**	**3.3**
Original SLD	**0.5**	**0.8**	**14.9**	**29.7**
Modified SLD	**0.4**	**0.6**	**2.2**	**6.1**
Wet Fruitland Coal				
LRC	**1.1**	**0.7**	**3.3**	
ZGR	**1.9**	**0.7**	**3.1**	
Original SLD	**1.5**	**0.6**	**3.9**	
Modified SLD	**1.1**	**0.6**	**3.6**	

Conclusions

- 2-D EOS and the EOS-SLD models are better equipped than Langmuir-type correlations for modeling CBM adsorption isotherms.
- The EOS-SLD models appear both accurate and amenable to structure-based generalization.
- Improved mixing rules and additional mixture data are required to improve predictions for individual-component adsorption.
- More efforts should be dedicated to structure-based model generalizations.

Modeling Work in Progress at OSU

- Extend the EOS-SLD and Ono Kondo models to mixture predictions.
- Implement other potential models for fluid-solid Interactions.
- Incorporate other geometries within the EOS-SLD framework.
- Develop theoretically-based equations of state that feature more accurate fluid-fluid repulsive terms.