Multiphase Transport Phenomena

C.T. Miller
University of North Carolina

Approach

- Interdisciplinary research and education challenges
- Learning theory and Zen on learning and confusion
- Engagement
- Build on background
- Connect to other lectures
- Some things classical and some things not
- Facilitate abstraction
- Provide for the needy

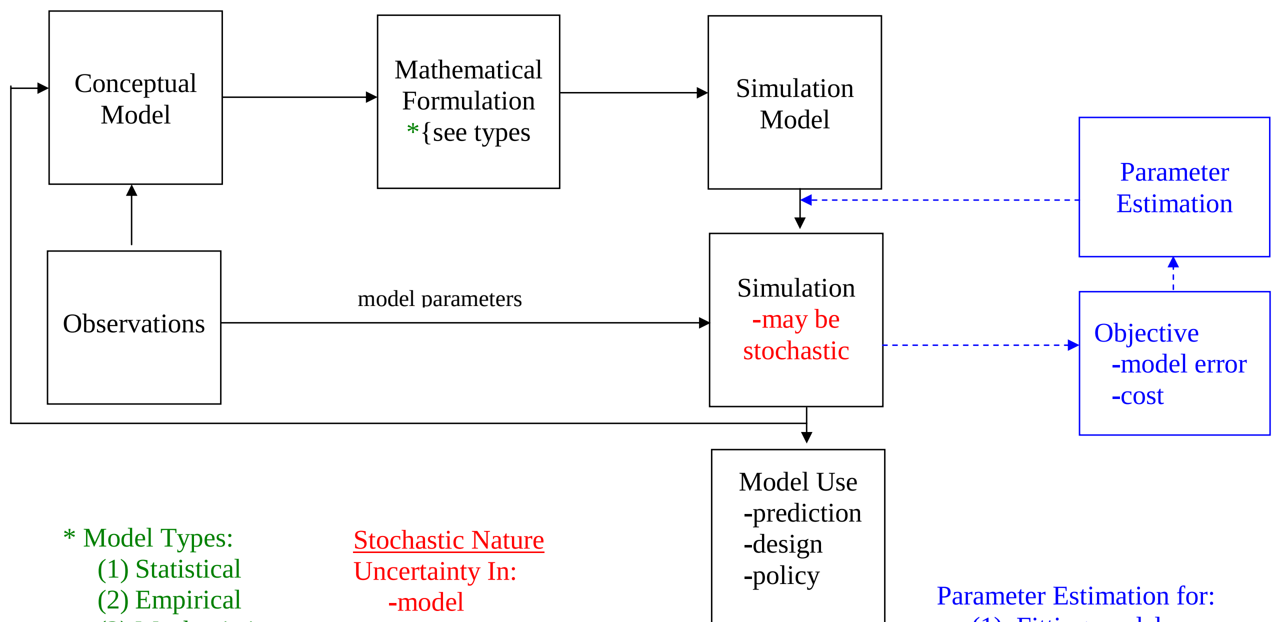
Some Terminology

- Scales: molecular, micro, macro, meso, and mega
- Phases: single-fluid phase, multiple fluid phase systems
- Flow versus species transport
- Continuum scale modeling
- Closure, or constitutive, relations
- Forward versus inverse problems

Overview

- Modeling process
- Conventional macroscale, or porous medium continuum scale, modeling approach
- Macroscale multiphase flow
- Macroscale multiphase flow and transport
- Multiscale modeling
- Microscale modeling approaches
- Example applications

Modeling Porous Medium Systems



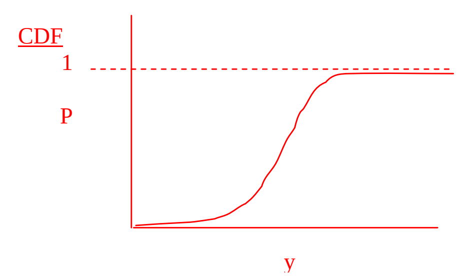
* Model Types:
- (1) Statistical
- (2) Empirical
- (3) Mechanistic
  - PDE's
  - ODE's
  - DAE's
  - AC's

<u>Stochastic Nature</u>

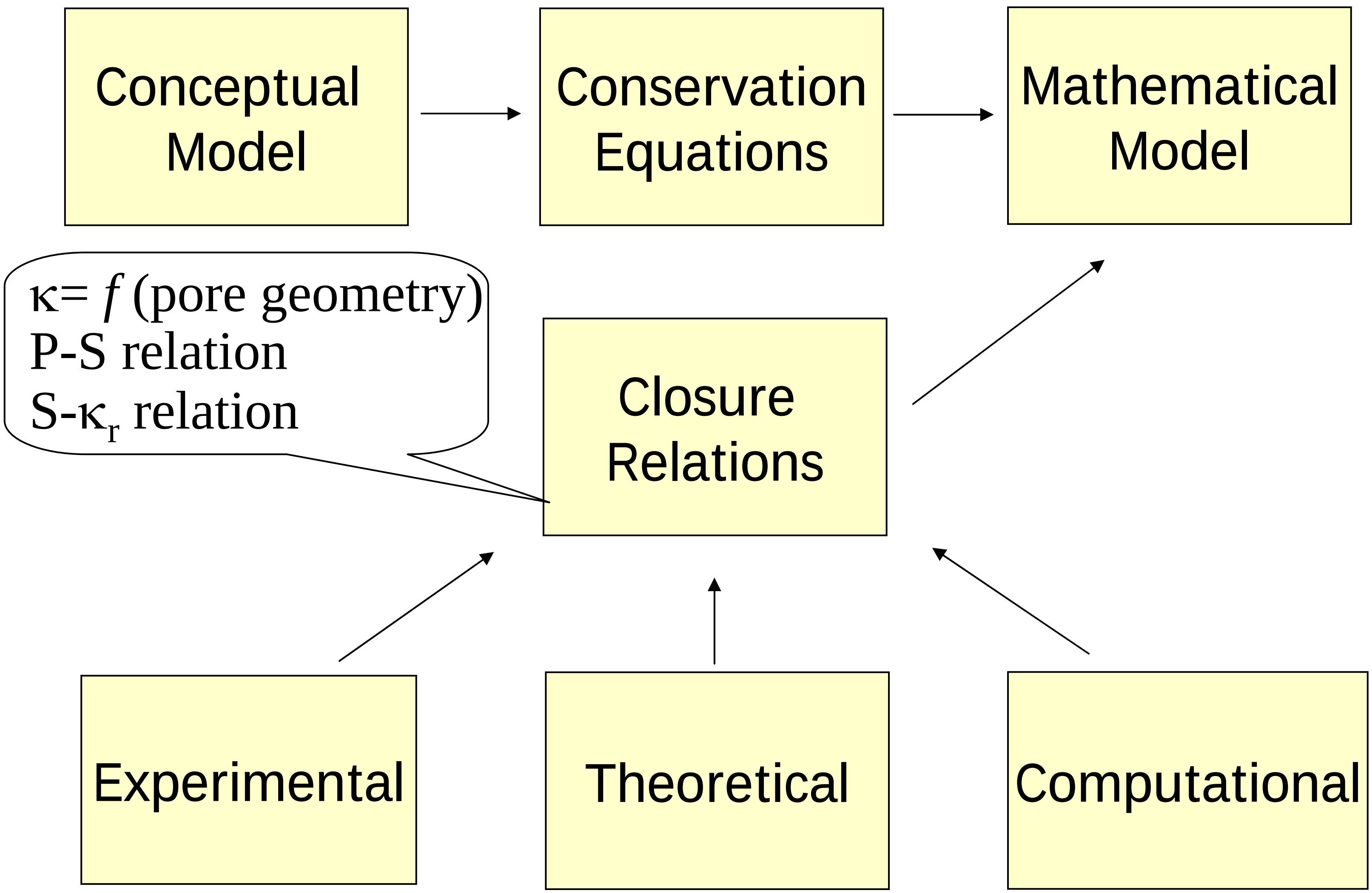
Uncertainty In:
- -model
- -parameters
- -auxiliary Conditions

Leads to uncertainty in predictions

Parameter Estimation for:
1. Fitting model
2. Minimizing objective function



Mechanistic Modeling Framework



Conservation Equations

- Averaging procedures were alluded to as a means to develop and close the single-phase flow equation
- Averaging procedures were also discussed as a means to develop a species transport equation

Species Balance Equation:

$$\frac{\partial}{\partial t}(\epsilon^\alpha \rho^\alpha \omega^{\iota\alpha}) = -\nabla\cdot(\mathbf{j}^{\iota\alpha} + \epsilon^\alpha \rho^\alpha \omega^{\iota\alpha}\mathbf{v}^\alpha) + \mathcal{I}^{\iota\alpha} + \mathcal{R}^{\iota\alpha} + \mathcal{S}^{\iota\alpha}$$

Species-Summed Flow Equation:

$$\frac{\partial}{\partial t}(\epsilon^\alpha \rho^\alpha) = -\nabla\cdot(\epsilon^\alpha \rho^\alpha \mathbf{v}^\alpha) + \mathcal{I}^\alpha + \mathcal{S}^\alpha$$

Ponderables

- What set of constraints can be developed with respect to the quantities that appear in the species conservation equation?
- Using these constraints, show how the flow equation can be derived from the species mass conservation equation

Conservation Equations and Constraints

Species Balance Equation:

$$\frac{\partial}{\partial t}(\epsilon^{\alpha}\rho^{\alpha}\omega^{\iota\alpha}) = -\nabla\cdot(\mathbf{j}^{\iota\alpha} + \epsilon^{\alpha}\rho^{\alpha}\omega^{\iota\alpha}\mathbf{v}^{\alpha}) + \mathcal{I}^{\iota\alpha} + \mathcal{R}^{\iota\alpha} + \mathcal{S}^{\iota\alpha}$$

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$$\sum_{\alpha}\epsilon^{\alpha} = 1, \ \sum_{\alpha}\mathcal{I}^{\iota\alpha} = 0,$$

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$$\sum_{\iota}\mathcal{I}^{\iota\alpha} = \mathcal{I}^{\alpha} \ \sum_{\iota}\mathcal{S}^{\iota\alpha} = \mathcal{S}^{\alpha}$$

Ponderables

- For single-phase flow, what is the closure problem?
- Consider Darcy's experiments and law and use as an alternative to computational or theoretical approaches to solve the closure problem and note all other assumptions used
- Derive the single-phase flow model for the case in which porosity is constant and the fluid is incompressible, note the consequences, and assess if these are reasonable

Conservation Equations and Constraints

Species Balance Equation:

$$\frac{\partial}{\partial t}(\epsilon^\alpha \rho^\alpha \omega^{\iota\alpha}) = -\nabla\cdot(\mathbf{j}^{\iota\alpha} + \epsilon^\alpha \rho^\alpha \omega^{\iota\alpha}\mathbf{v}^\alpha) + \mathcal{I}^{\iota\alpha} + \mathcal{R}^{\iota\alpha} + \mathcal{S}^{\iota\alpha}$$

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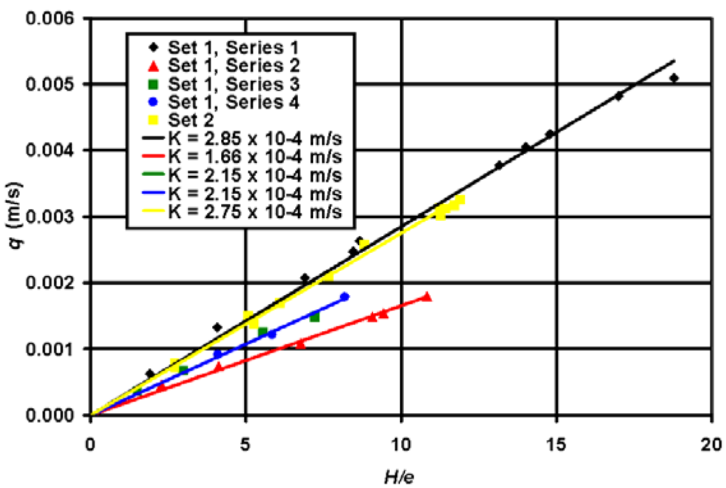
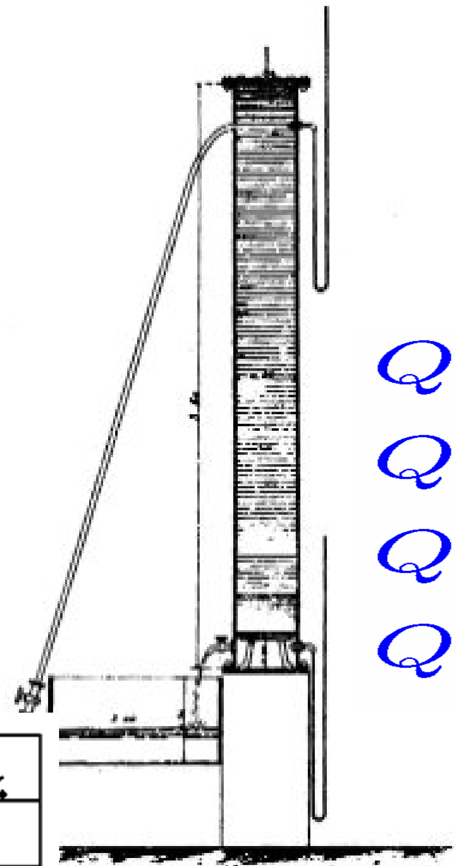
Darcy's Law

Henry Darcy (1803-1858)





$$Q \propto A_c$$
$$Q \propto L_c^{-1}$$
$$Q \propto \Delta h$$
$$Q = f(\text{media})$$

Darcy's Law:

$$\mathbf{q}^\alpha = \epsilon^\alpha \mathbf{v}^\alpha = -\frac{\mathbf{k}^\alpha}{\mu^\alpha} \cdot (\nabla p^\alpha + \rho^\alpha g \nabla z)$$

Traditional Single-Phase Flow Model

$$\frac{\partial}{\partial t}(\epsilon^\alpha \rho^\alpha) = -\nabla \cdot (\epsilon^\alpha \rho^\alpha \mathbf{v}^\alpha) + \mathcal{I}^\alpha + \mathcal{S}^\alpha$$

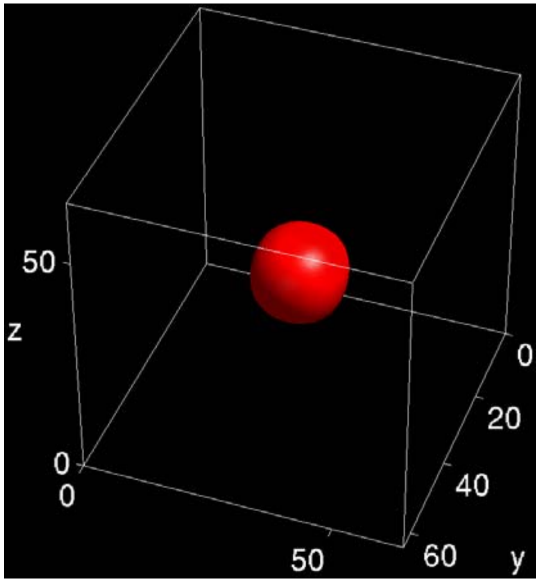
$$\rho^a = \rho^a(p^a)$$

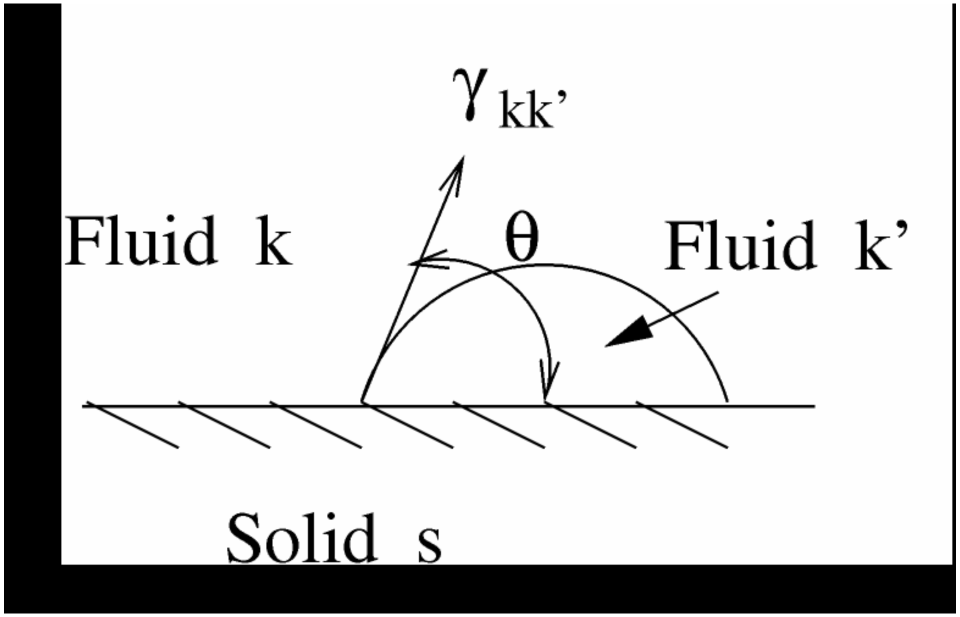
$$\mathbf{q} = -\mathbf{K} \cdot \nabla h$$

$$S_s \frac{\partial h}{\partial t} = \nabla \cdot (\mathbf{K} \cdot \nabla h) + \mathcal{S}$$

Microscale Multiphase Physics

Equilibrium state





$$p_n - p_w = \frac{2\gamma}{R}\cos\theta$$

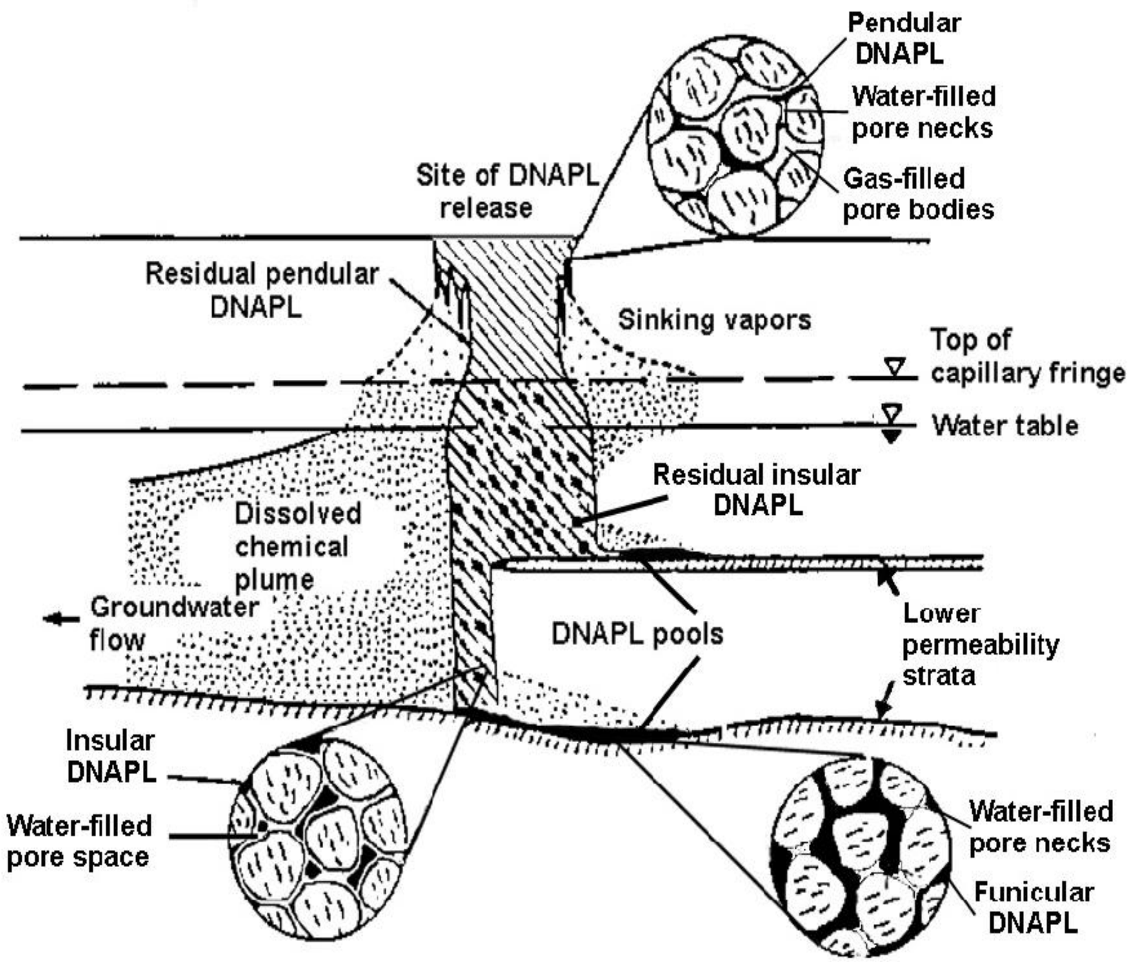
Physics of Multiphase Porous Medium Systems

- In a multiphase porous medium system, fluids move in response to viscous, capillary, and gravity forces
- This balance of forces is influenced by properties of the medium and the fluids: morphology of the pore space, contact angle, interfacial tensions, densities, and viscosities
- These forces result in very complex patterns of flow and entrapment of residual non-wetting phases can result

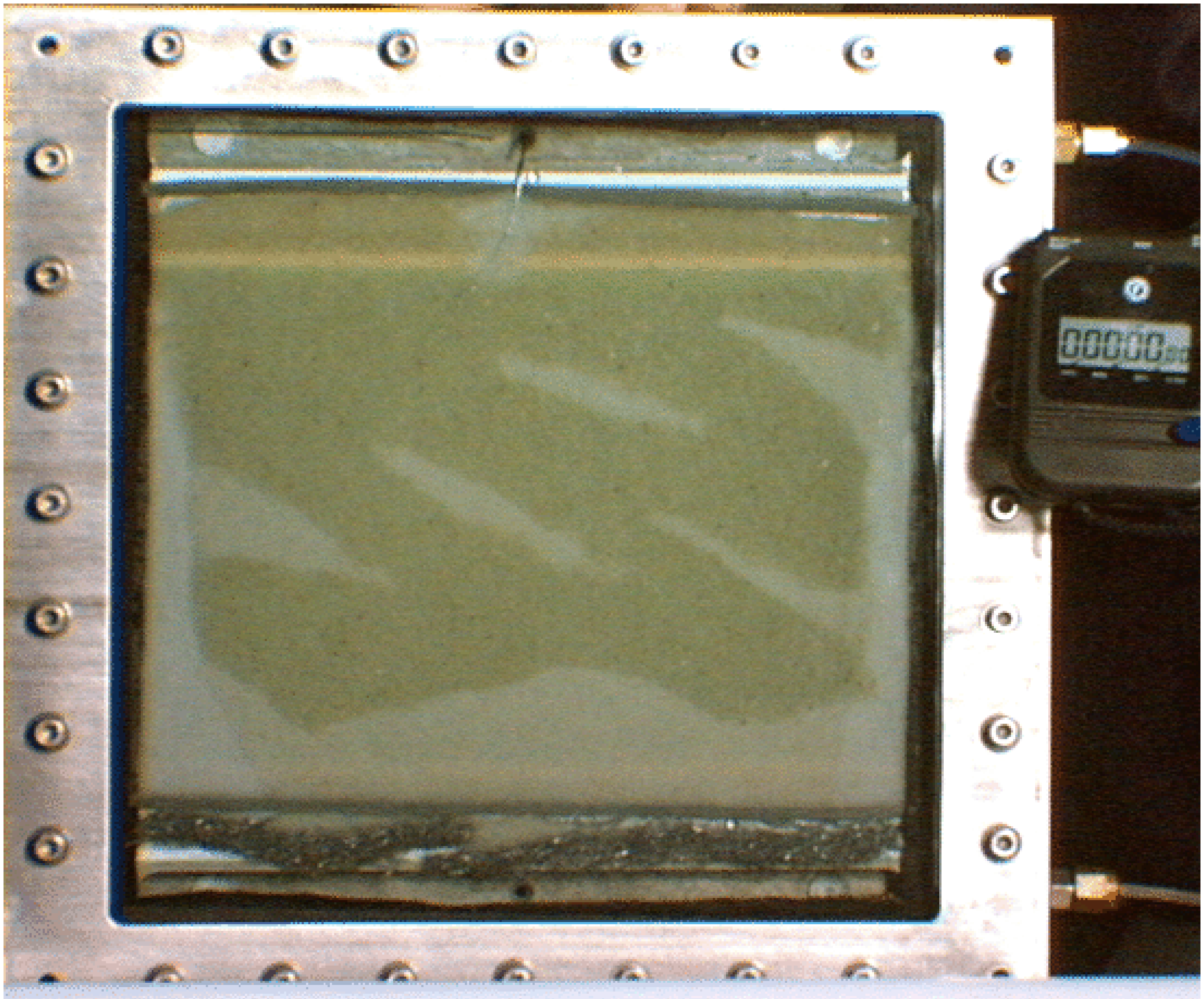
Multiphase Flow and Species Transport

- Multiphase flow---more than one fluid occupying the pore space
  - Water infiltration
  - Short time scale NAPL infiltration
  - Petroleum exploration
- Multiphase flow and species transport---more than one fluid and species mass fractions or concentrations are important
  - Pesticide transport
  - BTEX problems from petroleum spills

DNAPL Behavior in Heterogeneous Porous Media



Multiphase Flow Example



Multiphase Conservation Equations

Species Balance Equation:

$$\frac{\partial}{\partial t}(\epsilon^\alpha \rho^\alpha \omega^{\iota\alpha}) = -\nabla\cdot(\mathbf{j}^{\iota\alpha} + \epsilon^\alpha \rho^\alpha \omega^{\iota\alpha} \mathbf{v}^\alpha) + \mathcal{I}^{\iota\alpha} + \mathcal{R}^{\iota\alpha} + \mathcal{S}^{\iota\alpha}$$

Species-Summed Flow Equation:

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$$\sum_\iota \mathcal{I}^{\iota\alpha} = \mathcal{I}^\alpha \ \ \sum_\iota \mathcal{S}^{\iota\alpha} = \mathcal{S}^\alpha$$

Ponderables

- Define the closure problem for two-phase flow in a macroscale porous medium system
- How might one investigate approaches to produce a closed model?
- What sorts of assumptions are implicit in traditional closure approaches?

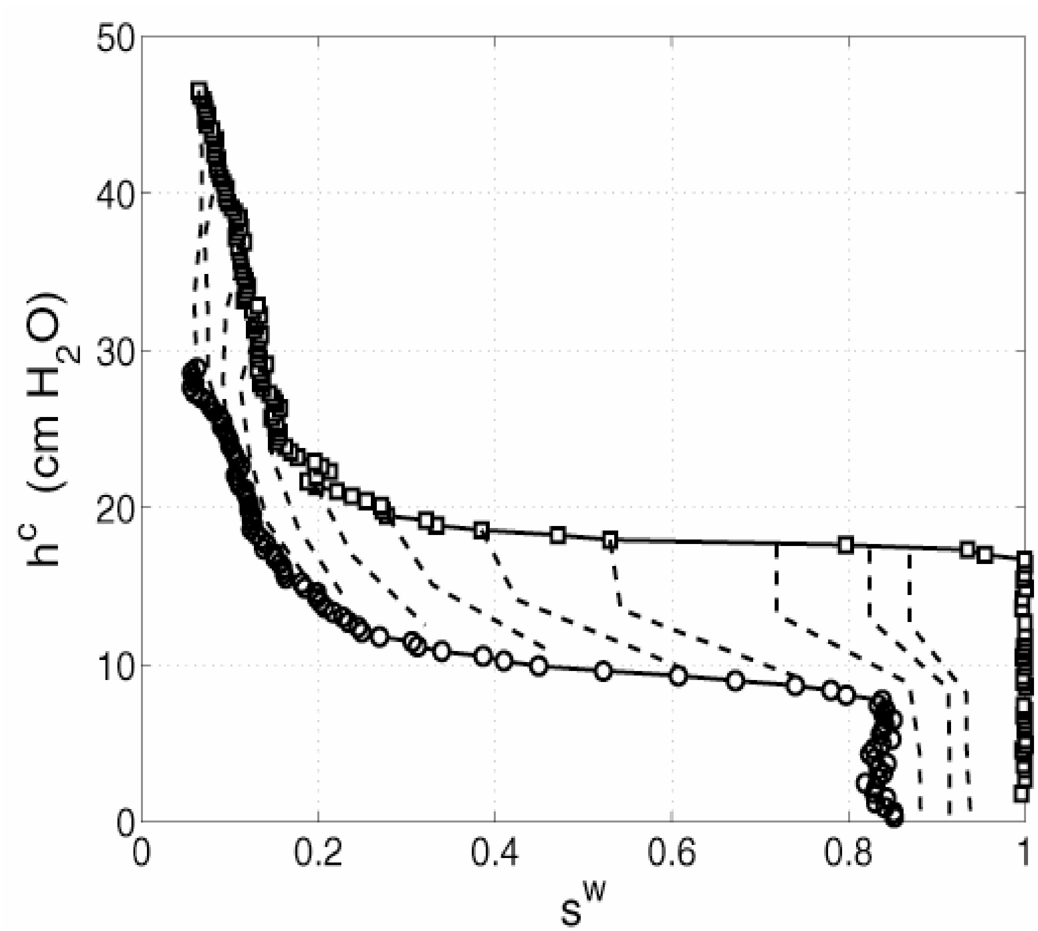
Closure Problem for Two-Phase Flow

Assuming an immobile solid phase

$$\frac{\partial}{\partial t}(\epsilon^\alpha \rho^\alpha) = -\nabla \cdot (\epsilon^\alpha \rho^\alpha \mathbf{v}^\alpha) + \mathcal{I}^\alpha + \mathcal{S}^\alpha$$

For a two-fluid system, this results in five unknowns for each phase or a total of ten unknowns in two equations

Capillary Pressure Saturation Relations



- C-109 sand experiment
- Key features to note:
  - Primary drainage
  - Entry pressure
  - Uniformity effects
  - Main imbibition
  - Non-wetting phase trapped
  - Wetting scanning curves
  - Hysteresis
  - Quasi-static experiments

Examples of Common Closure Assumptions

- Saturation is solely determined based upon capillary pressure and its history in a quasi-static sense
- Darcy's law can be extended with modification to multiphase systems
- Relative permeability is solely dependent upon the saturation of the respective phase and its history
- Rigorous connection with microscale quantities can be ignored

Ponderables

- Write a general form for a closed multiphase flow model
- Consider an air-water system and write a closed model for this special case noting the reasoning steps used in the simplification

Closed Multiphase Flow Model

$$\frac{\partial}{\partial t}(\epsilon^\alpha \rho^\alpha) = -\nabla \cdot (\epsilon^\alpha \rho^\alpha \mathbf{v}^\alpha) + \mathcal{I}^\alpha + \mathcal{S}^\alpha$$

$$\mathbf{q}^\alpha = \epsilon^\alpha \mathbf{v}^\alpha = -\frac{k k^{r\alpha}}{\mu^\alpha} \nabla \left(p^\alpha + \rho^\alpha g z\right)$$

$$S^\alpha = f\left(p^\beta(t)\right), \ \text{for } \beta = 1, ..., n_f$$

$$k^{r\alpha} = f\left(S^\beta(t)\right), \ \text{for } \beta = 1, ..., n_f$$

$$\mathbf{q}^\alpha = \epsilon^\alpha \mathbf{v}^\alpha = -\frac{\mathbf{k}^\alpha}{\mu^\alpha} \cdot \left(\nabla p^\alpha + \rho^\alpha g \nabla z\right)$$

$$\rho^\alpha = \rho^\alpha(p^\alpha)$$

$$\sum_\alpha \epsilon^\alpha = 1$$

Example Closure Relations

van Genuchten P-S Relation:

$$S_e = \frac{\epsilon^a - \epsilon^r}{\epsilon^s - \epsilon^r} = (1 + |\alpha_v \psi|^{n_v})^{-m_v} \text{ for } \psi < 0$$
$$= 1 \text{ for } \psi \geq 0$$

Mualem S-K Relation:

$$k^{rw}(S_e) = S_e^{1/2}\left[1 - \left(1 - S_e^{1/m_v}\right)^{m_v}\right]^2$$

$$k^{rn}(S_e) = (1 - S_e)^{1/2}\left(1 - S_e^{1/m_v}\right)^{2m_v}$$

Air-Water System

- Air is much more mobile than water, therefore pressure gradients must be small for the air phase--assume zero
- Porosity is assumed constant, thus changes in water and air volume fractions are inversely related
- Common multiphase extension of Darcy's law applies
- Quasi-static pressure-saturation-relative permeability relations apply
- Spatial gradients of aqueous-phase density can be ignored

Richards' Equation

$$\frac{\partial}{\partial t}(\epsilon^a \rho^a) = -\nabla \cdot (\rho^a \mathbf{q}^a)$$

$$\left(\frac{\epsilon^a}{\rho^a}\right)\frac{\partial \rho^a}{\partial t} + \frac{\partial \epsilon^a}{\partial t} = -\nabla \cdot \mathbf{q}^a$$

$$S_s S^a \frac{\partial \psi}{\partial t} + \frac{\partial \epsilon^a}{\partial t} = \nabla \cdot [K^a \nabla(\psi + z)]$$

$$S_s S^a \frac{\partial \psi}{\partial t} + \frac{\partial \epsilon^a}{\partial t} = \frac{\partial}{\partial z}\left[K^a\left(\frac{\partial \psi}{\partial z} + 1\right)\right]$$

$$\left(S_s S^a + \frac{\partial \epsilon^a}{\partial \psi}\right)\frac{\partial \psi}{\partial t} = \frac{\partial}{\partial z}\left[K^a\left(\frac{\partial \psi}{\partial z} + 1\right)\right]$$

Multiphase Flow and Transport

- Often the problem of concern
- Commonality with single-phase systems that transport model requires solution of the flow model for closure
- Commonality with single-phase flow model as well for implications of reaction form on size and formal type of resultant system of conservation equations

Ponderables

- Formulate a model to describe the transport and fate of contaminants resulting from the spill of a refined petroleum product in the unsaturated zone
- Describe the flow model
- What transport processes are of concern?
- Without simplifying assumptions, what is the size of the system of conservation equations?

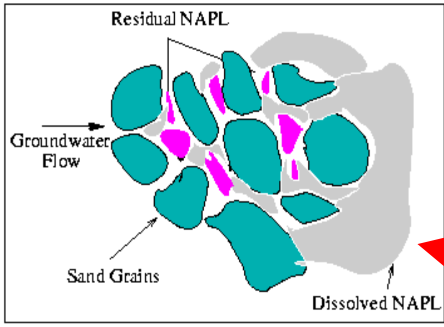
Ponderables

- How can separation of time scales be used to simplify the system of equations?
- How can the number of species be reduced?
- What assumptions are used to support the notion of natural attenuation for this class of problem?

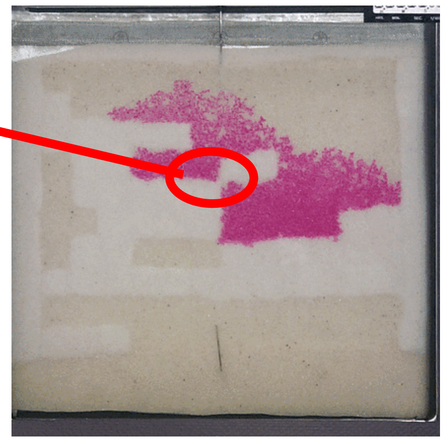
Examples of Current Multiphase Research

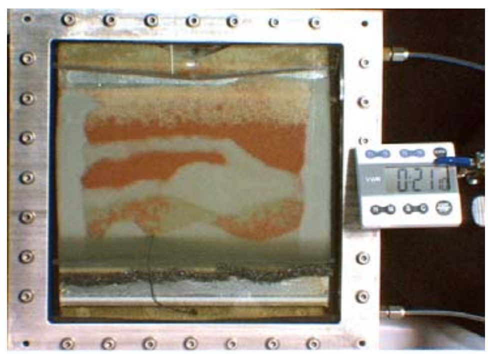
- Multiscale inspired
- Single-phase flow
- Pressure-saturation relations
- NAPL dissolution fingering
- Viscous coupling of fluids
- Multiscale NAPL dissolution
- Thermodynamically constrained averaging theory
- DNAPL remediation revisited

Multiscale Porous Medium Systems

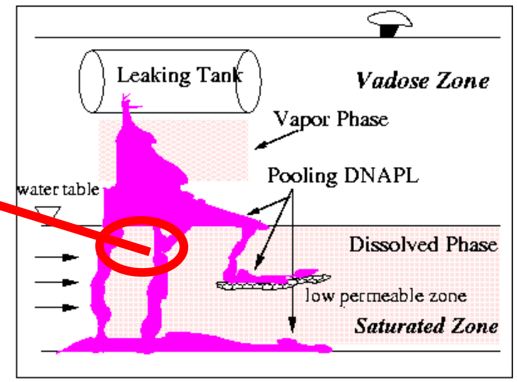


Pore scale





Lab scale

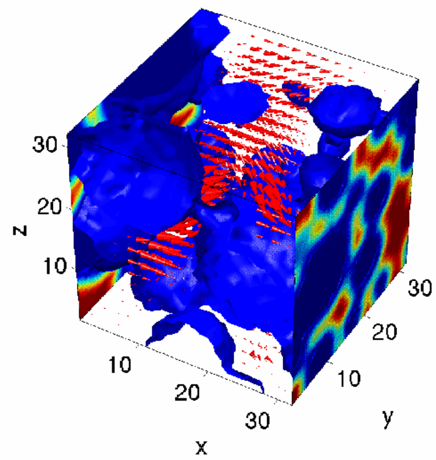


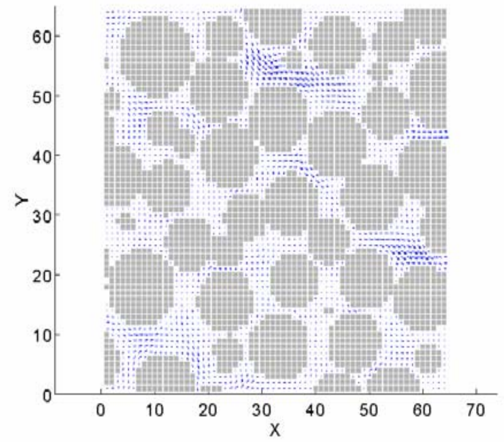
Field scale

Motivation for Pore-Scale Modeling

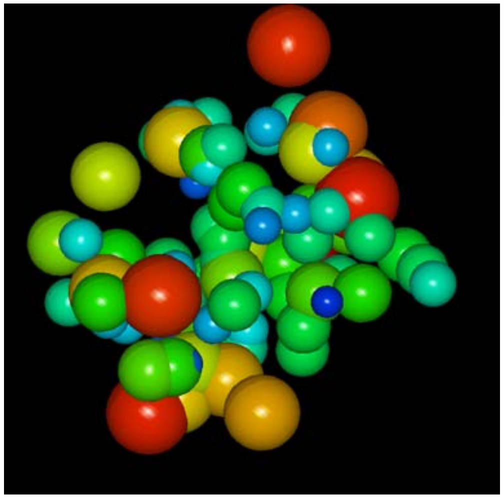
- A predictive tool to determine constitutive relations for standard continuum-scale models
- A significant means to close new continuum-scale theories for multiphase flow
- An important way of understanding the fundamental pore-scale processes

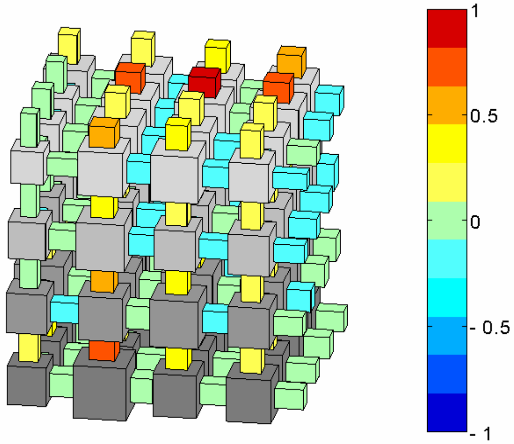
Single-Phase Flow





LB models





Pore-network models

Lattice-Boltzmann Method (LBM)

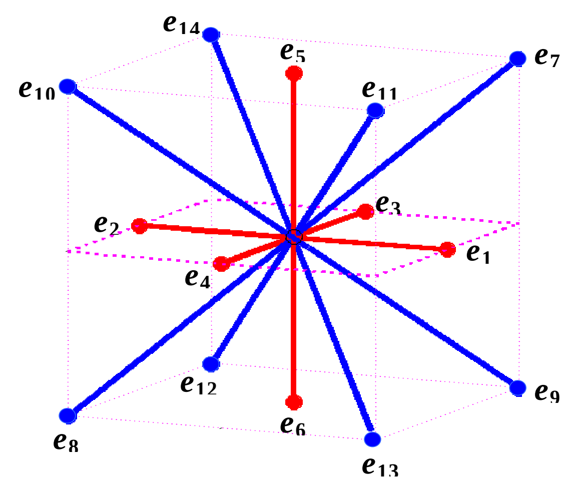
- Simulate fluids as microscopic particles that move along a lattice and collide with each other
- Fully recover Navier-Stokes equation
- Relatively easy implementation of boundary condition on complex geometries
- Suitable for massively parallel computers

Lattice-Boltzmann Method

$$f_i(\vec{x}+\vec{e}_i, t+1) - f_i(\vec{x}, t) = \frac{1}{\tau}\left[f_i^{(eq)}(\vec{x}, t) - f_i(\vec{x}, t)\right]$$

$$\rho' = \sum_i f_i \quad \text{: density}$$

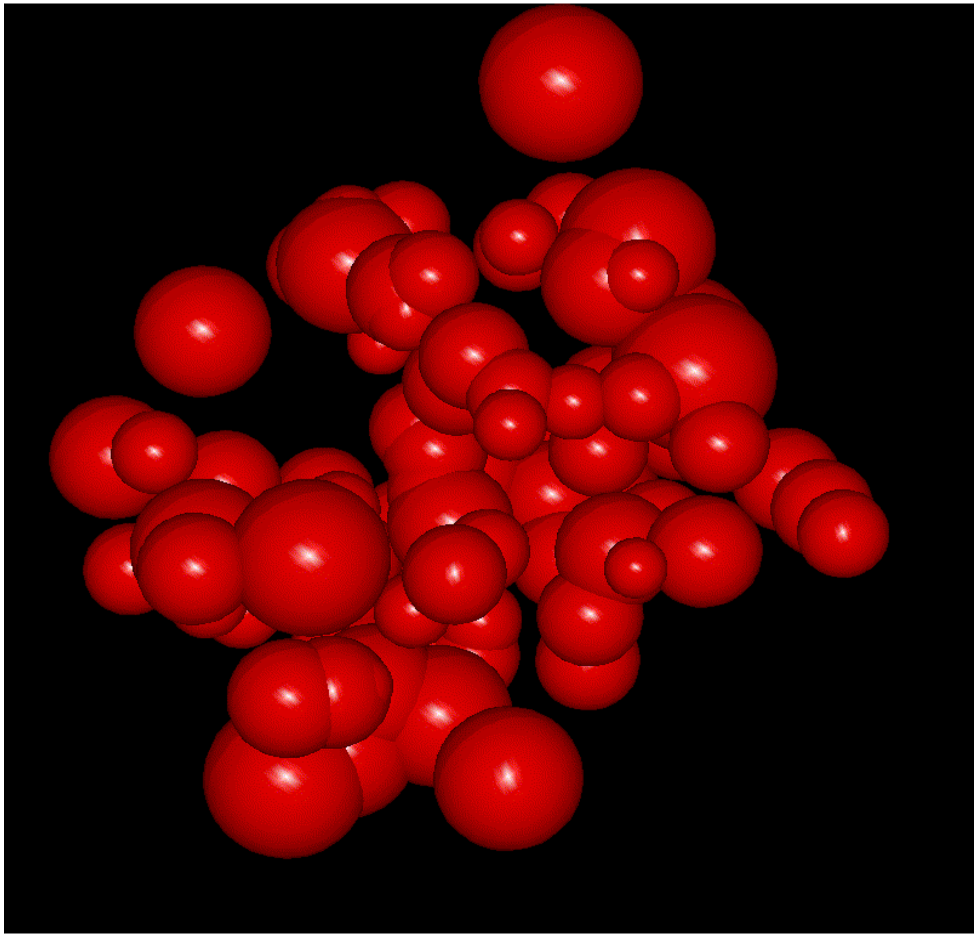
$$\rho' \vec{u} = \sum_i f_i \vec{e}_i \quad \text{: momentum}$$



Simulated Porous Media

	RSP1	RSP23
$\langle D \rangle$ (mm)	0.20	0.19
$\sigma/\langle D \rangle$	0.5%	66%
L(mm)	4.250	6.192
ϕ	0.442	0.334
N_s	10328	14380

Random-Size Sphere Packing



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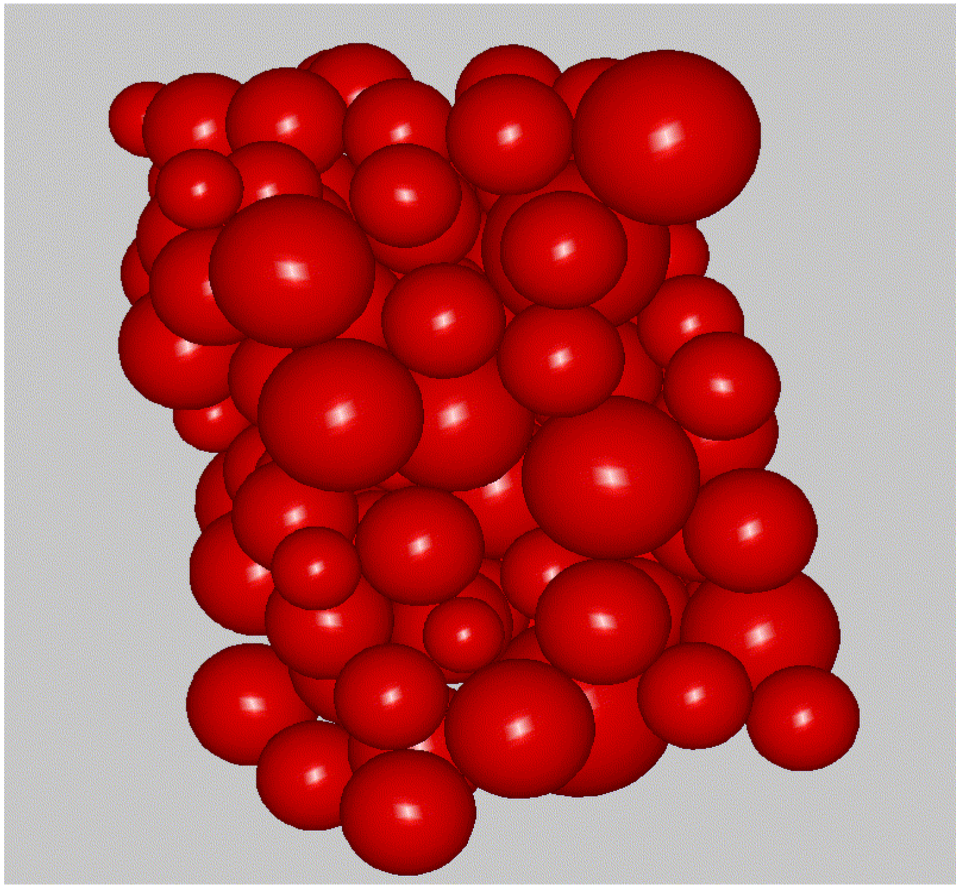
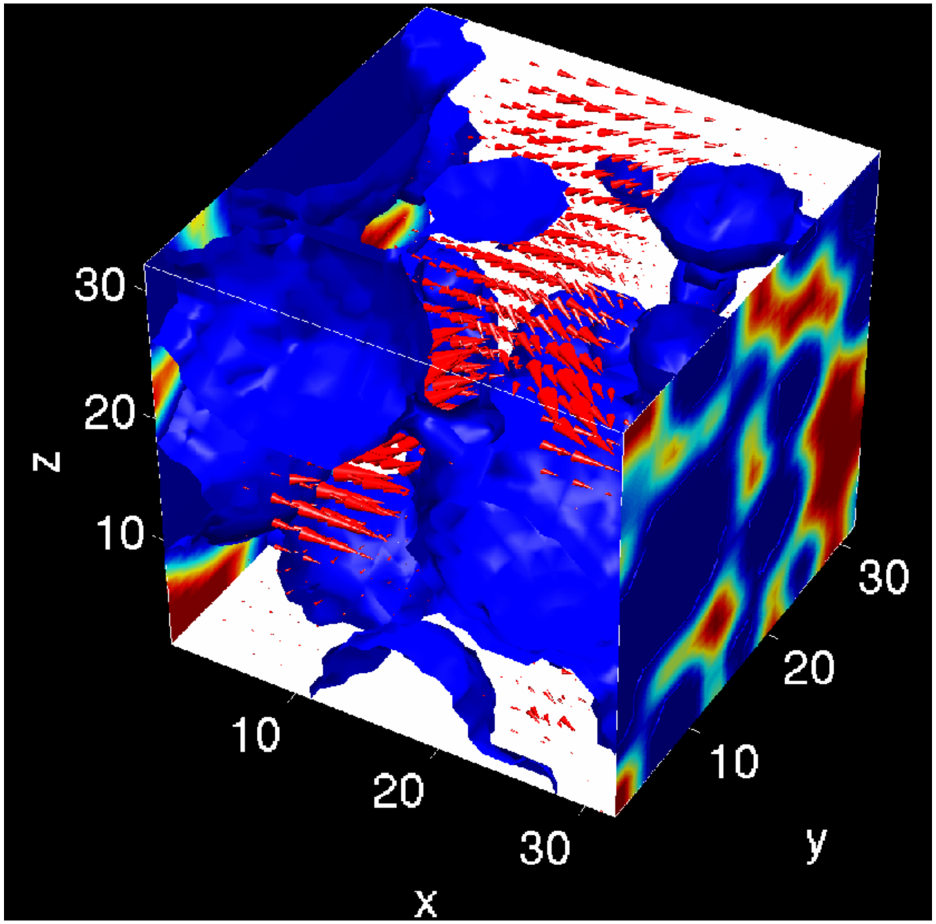
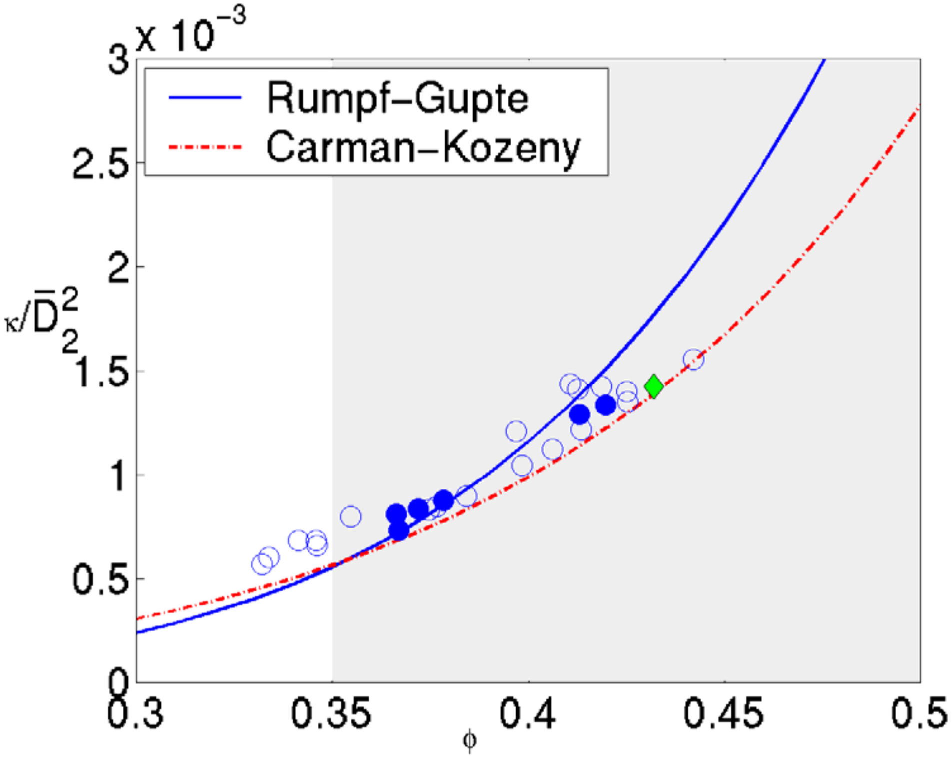


LBM-Simulated Microscale Flow



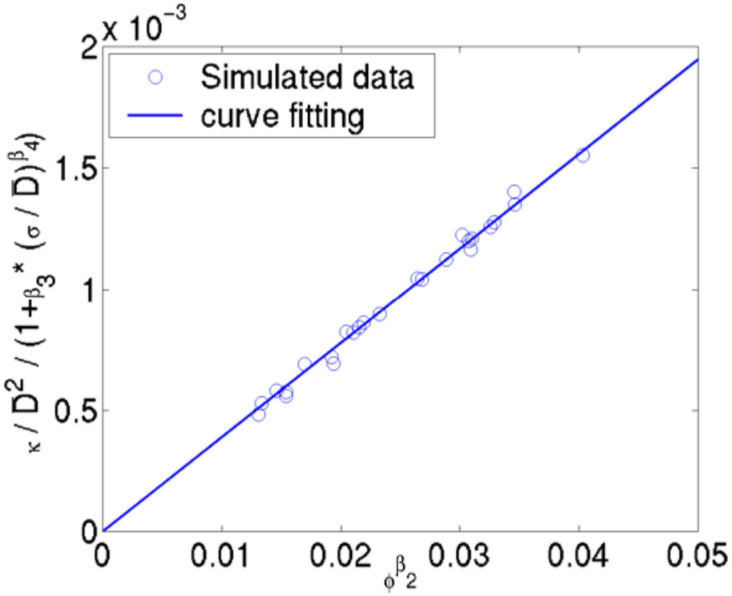
Simulation Results for κ



$$\kappa_{RG} = \frac{\overline{D}_2^2}{5.6}\phi^{5.5}$$

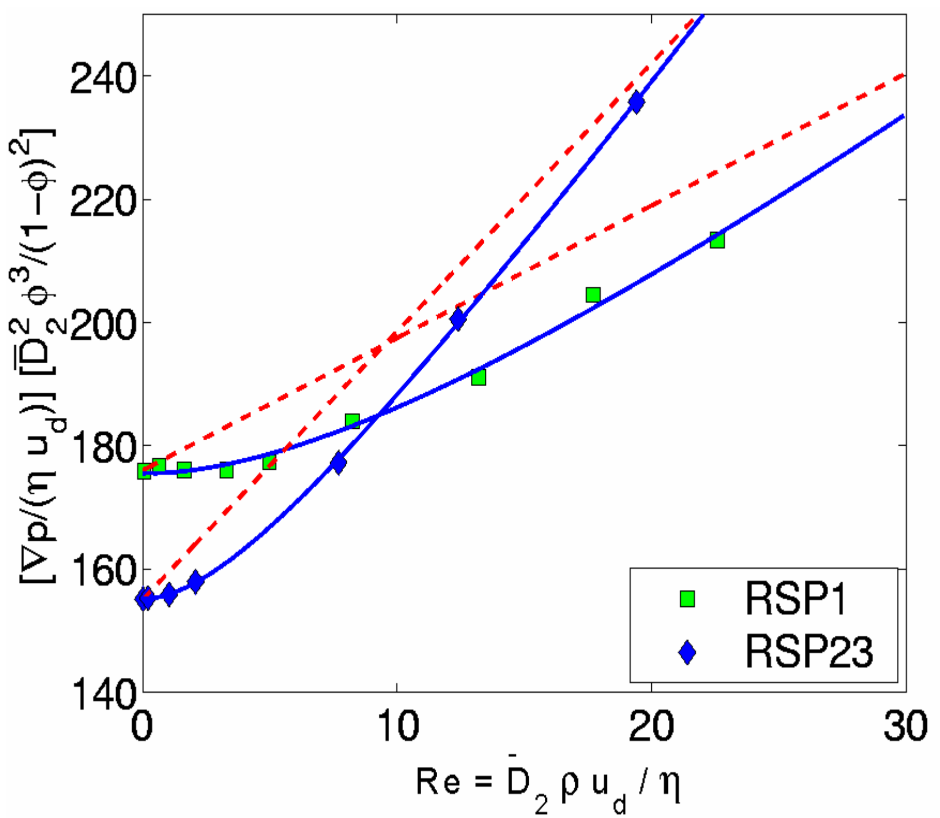
$$\kappa_{CK} = \frac{\overline{D}_2^2}{180}\frac{\phi^3}{(1-\phi)^2}$$

Simulation Results for κ



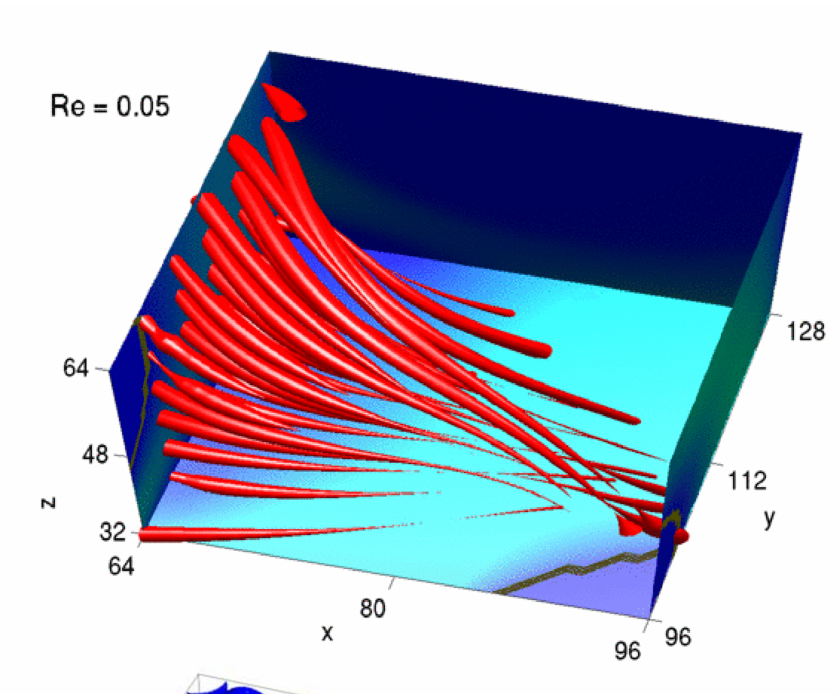
$$\frac{\kappa}{\overline{D}^2} = \beta_1 \phi^{\beta_2} \left[1 + \beta_3 \left(\frac{\sigma}{\overline{D}} \right)^{\beta_4} \right]$$

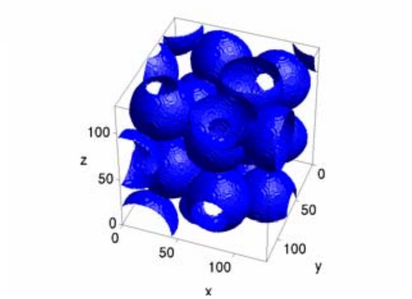
Non-Darcy Flow from LB Simulation

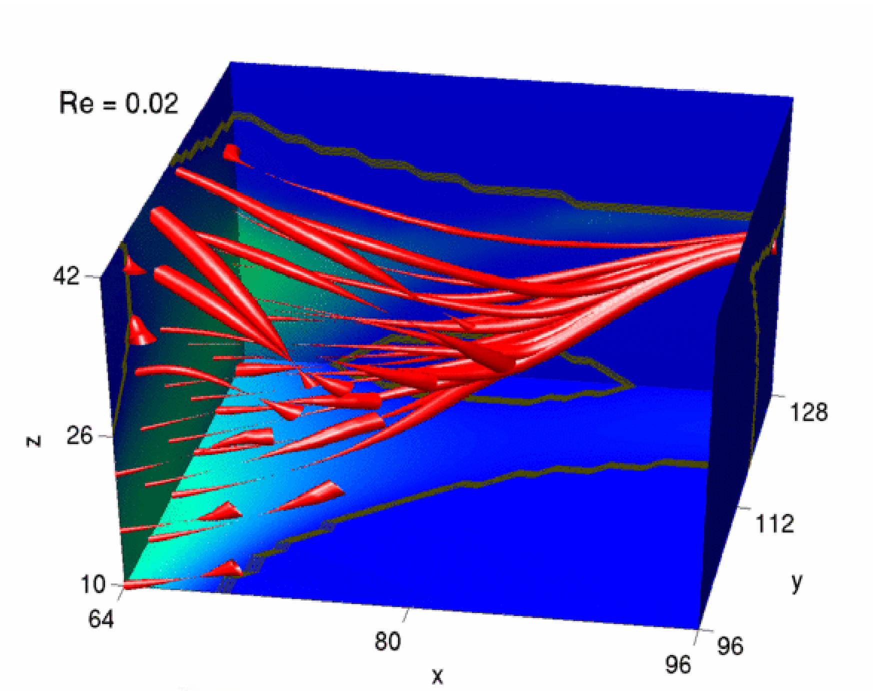


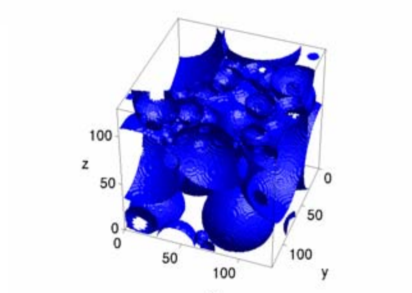
Non-Darcy Flow

Onset of Non-Darcy flow







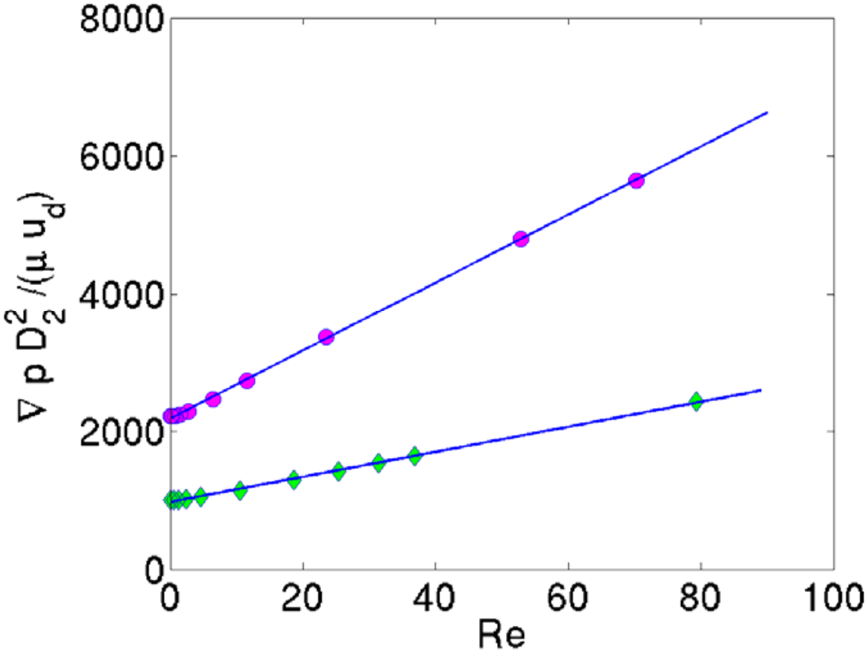


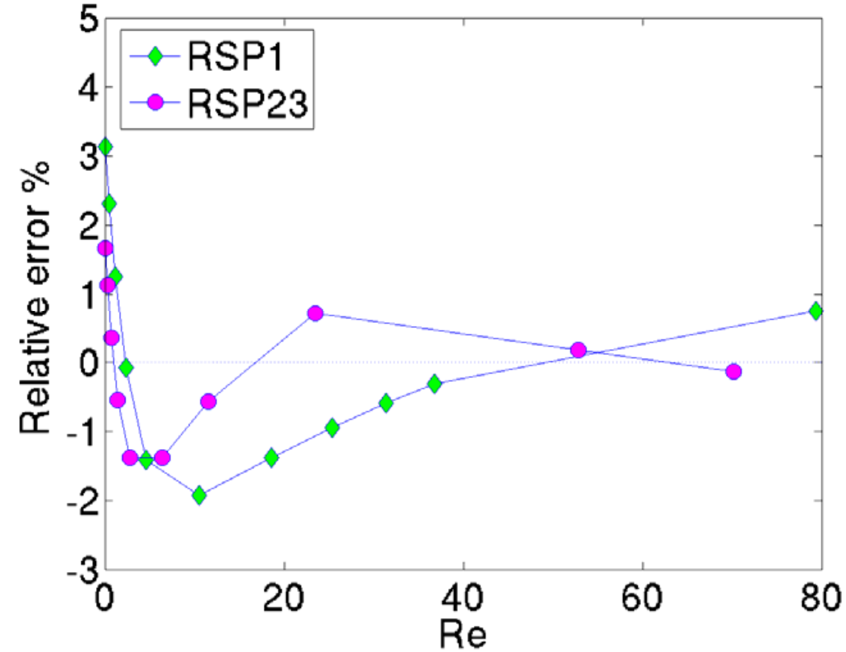
Non-Darcy Flow

Forchheimer equation:

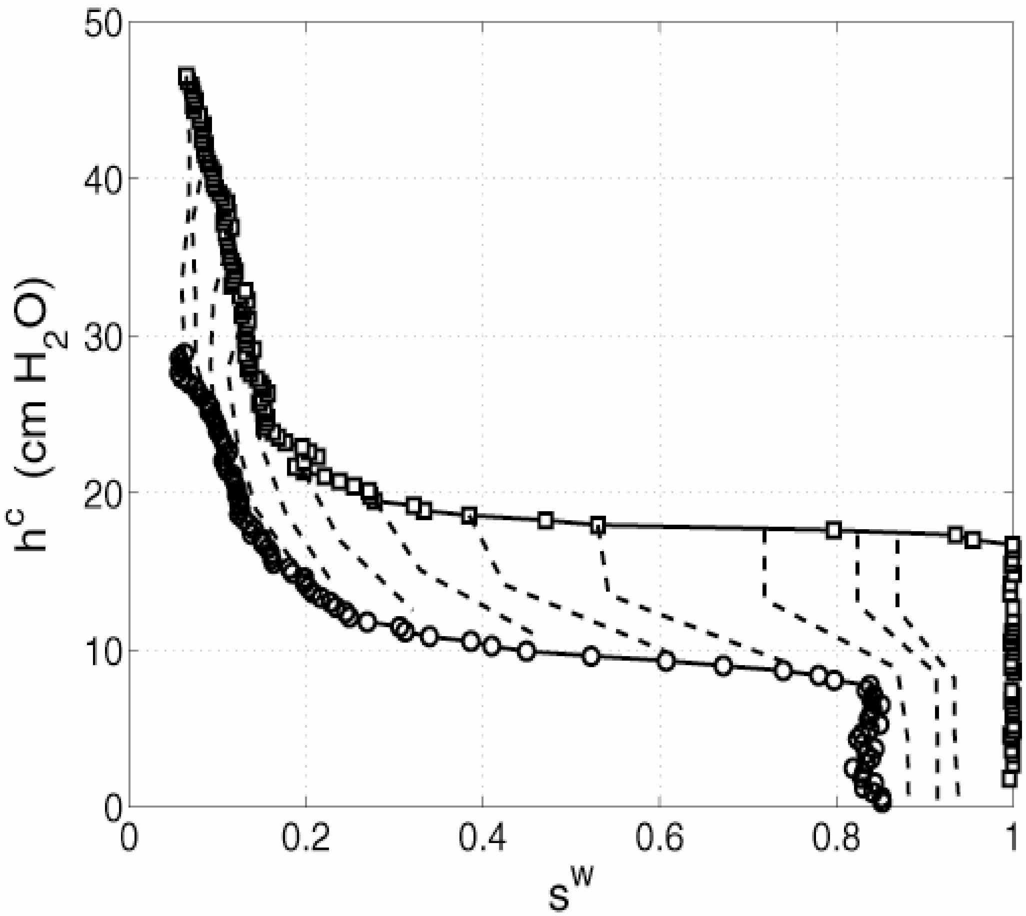
$$-\nabla p + \rho g = \frac{\mu}{\kappa_f} u_d + \beta \rho u_d^2,$$

$$\frac{(-\nabla p + \rho g)\bar{D}_2^2}{\mu u_d} = \frac{\bar{D}_2^2}{\kappa_f} + \beta \mathrm{Re} \bar{D}_2,$$





Two-Phase Pressure Saturation Relations



- C-109 sand experiment
- Key features to note:
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  - Entry pressure
  - Uniformity effects
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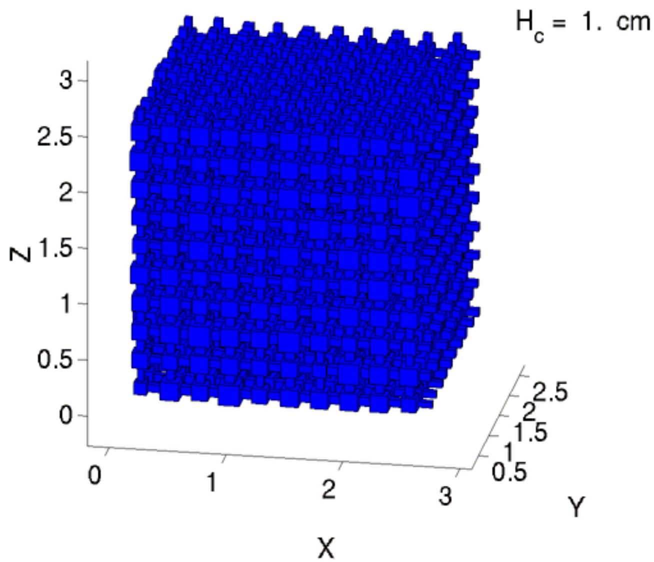
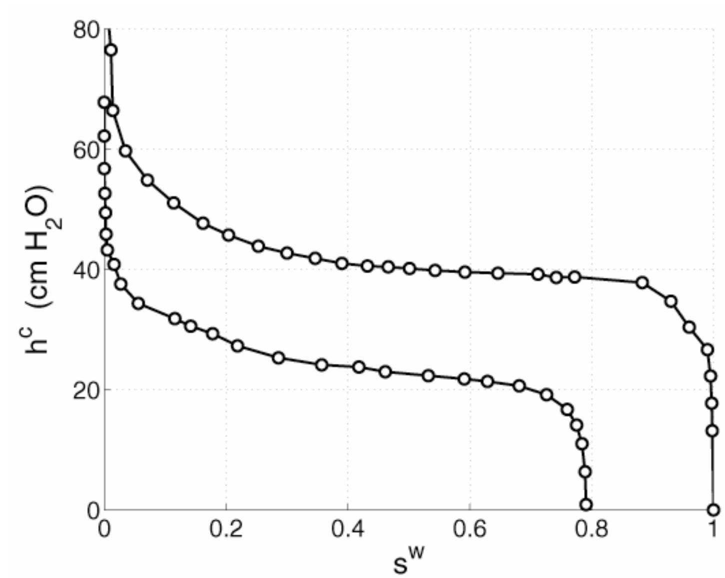
  - Non-wetting phase trapped
  - Wetting scanning curves
  - Hysteresis
  - Quasi-static experiments

Pore-Scale Modeling





Experimental and Simulated Properties

	GB1b	Simulated GB1b
<D> (mm)	0.1156	0.1149
σ_D (mm)	0.0121	0.0116
Porosity ϕ	0.356 ± 0.002	0.356
Domain Length L (mm)	2.35	2.35
Number of Spheres	------	9532
NWP-WP	Dyed PCE- water	------

<D>: Arithmetic mean diameter

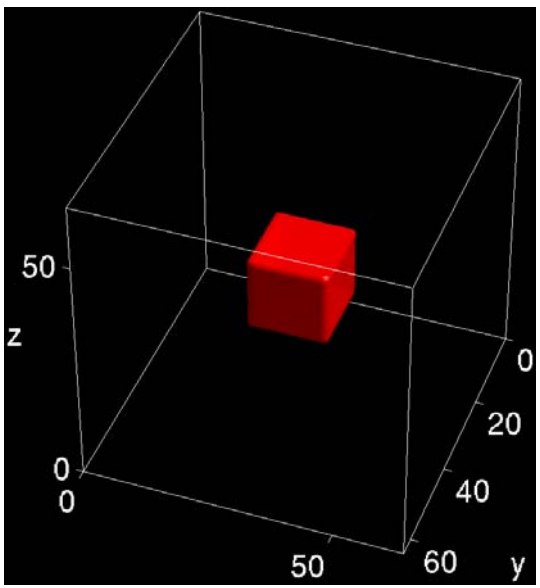
σ_D : Arithmetic standard deviation of grain diameter

Calibration of LB Multiphase Model

- Density ratio between fluids
- Viscosity ratio
- Interfacial tension (fluid - fluid interaction)
- Wettability (fluid - solid interaction)
- Boundary conditions

Bubble Test

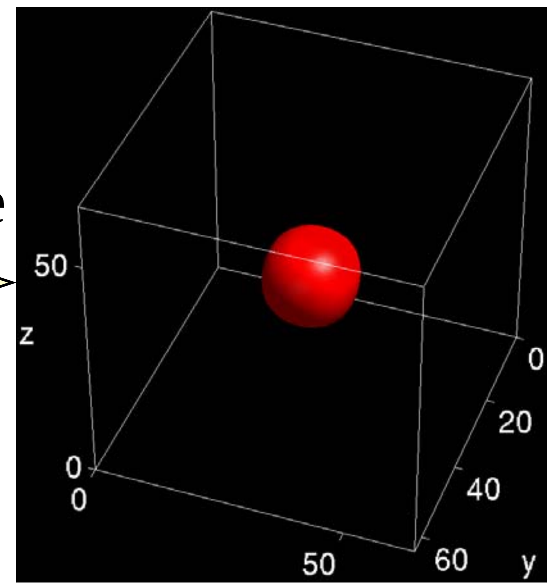
Initial state



No solid phase

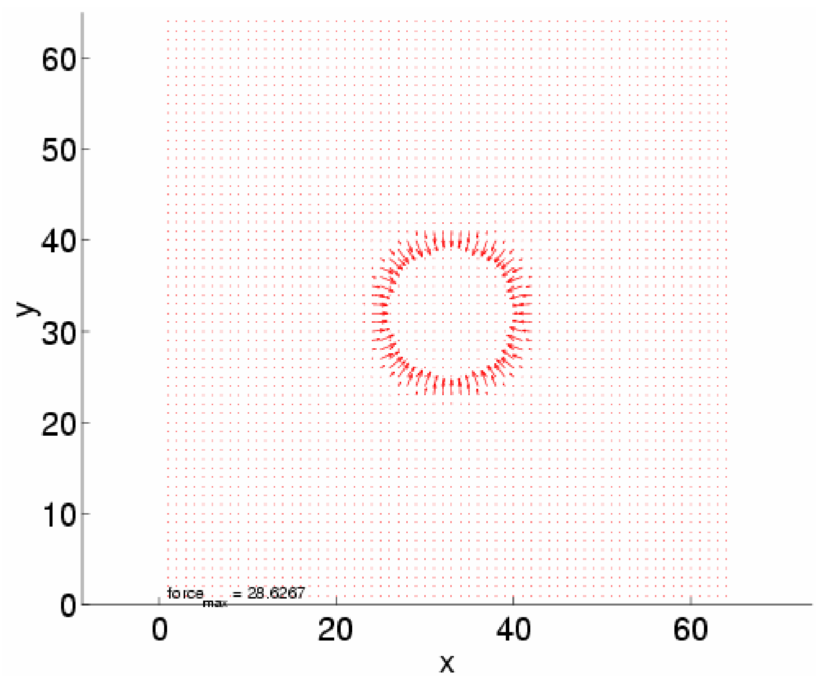
No body force

Equilibrium state

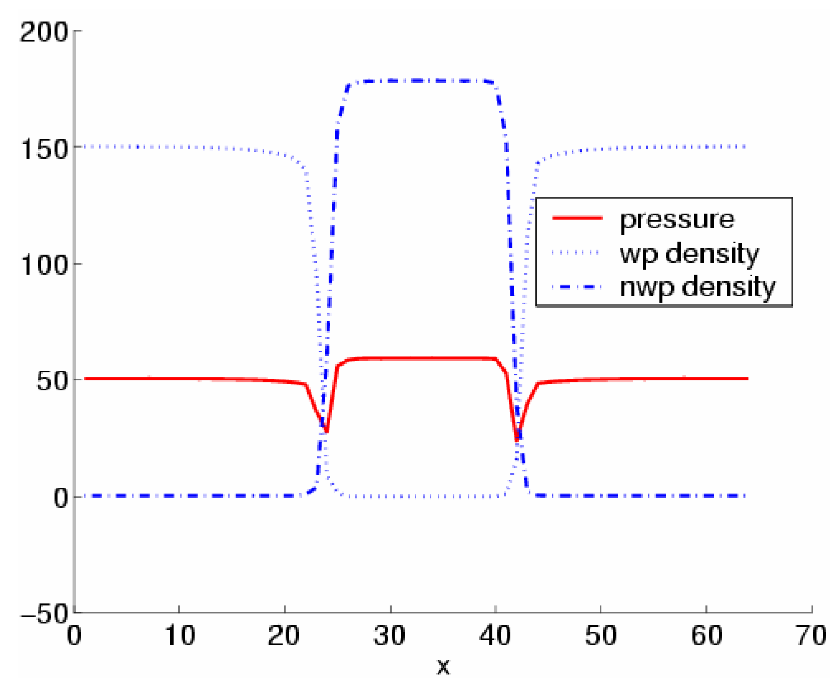


Bubble at the Equilibrium State

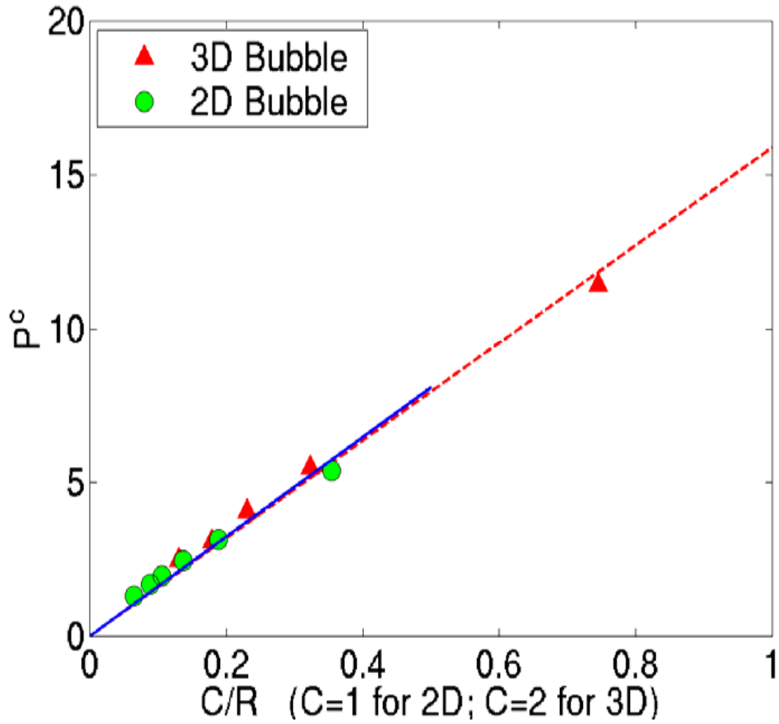
Interfacial tension force profile



Pressure profile



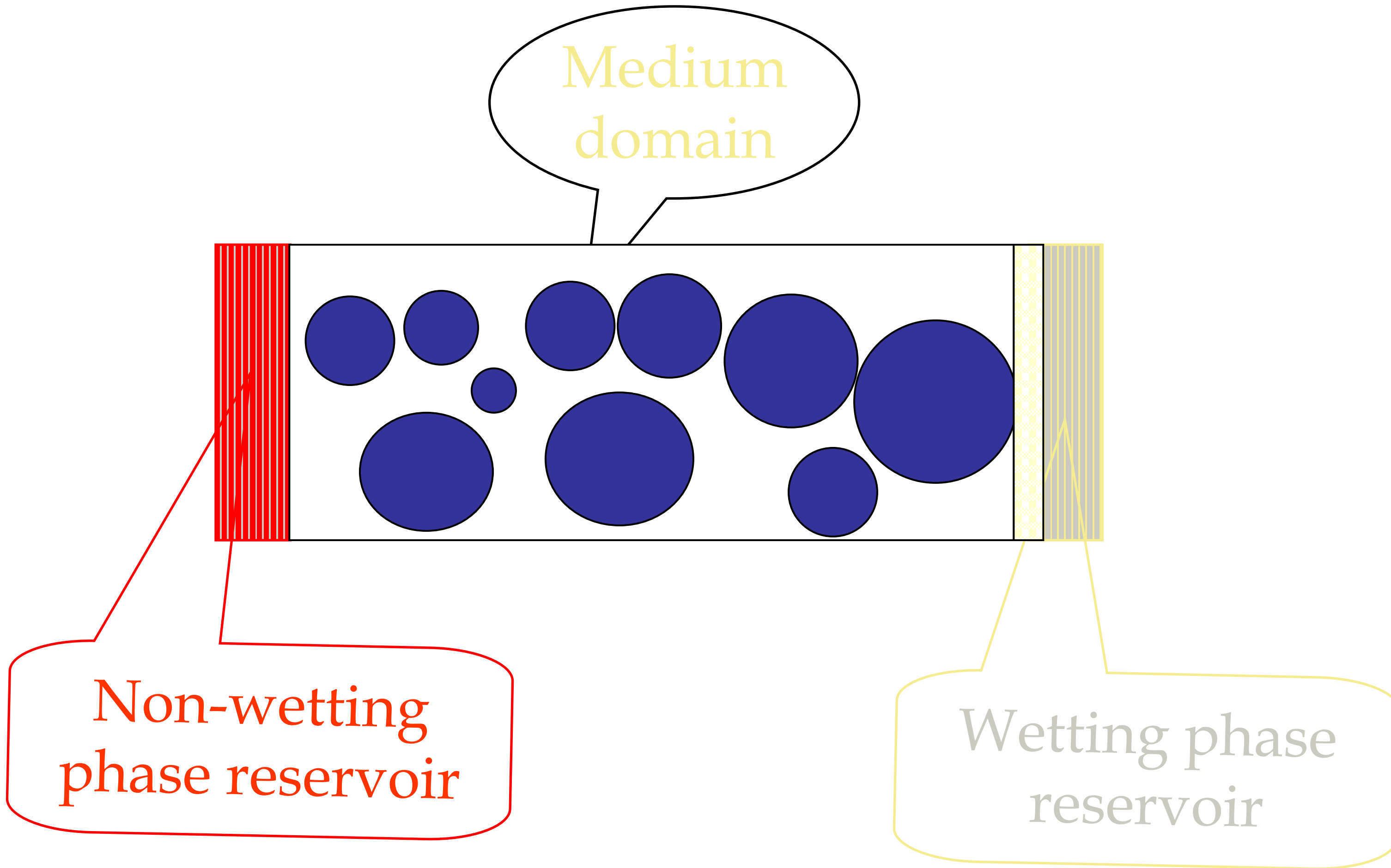
Test of Laplace's Law



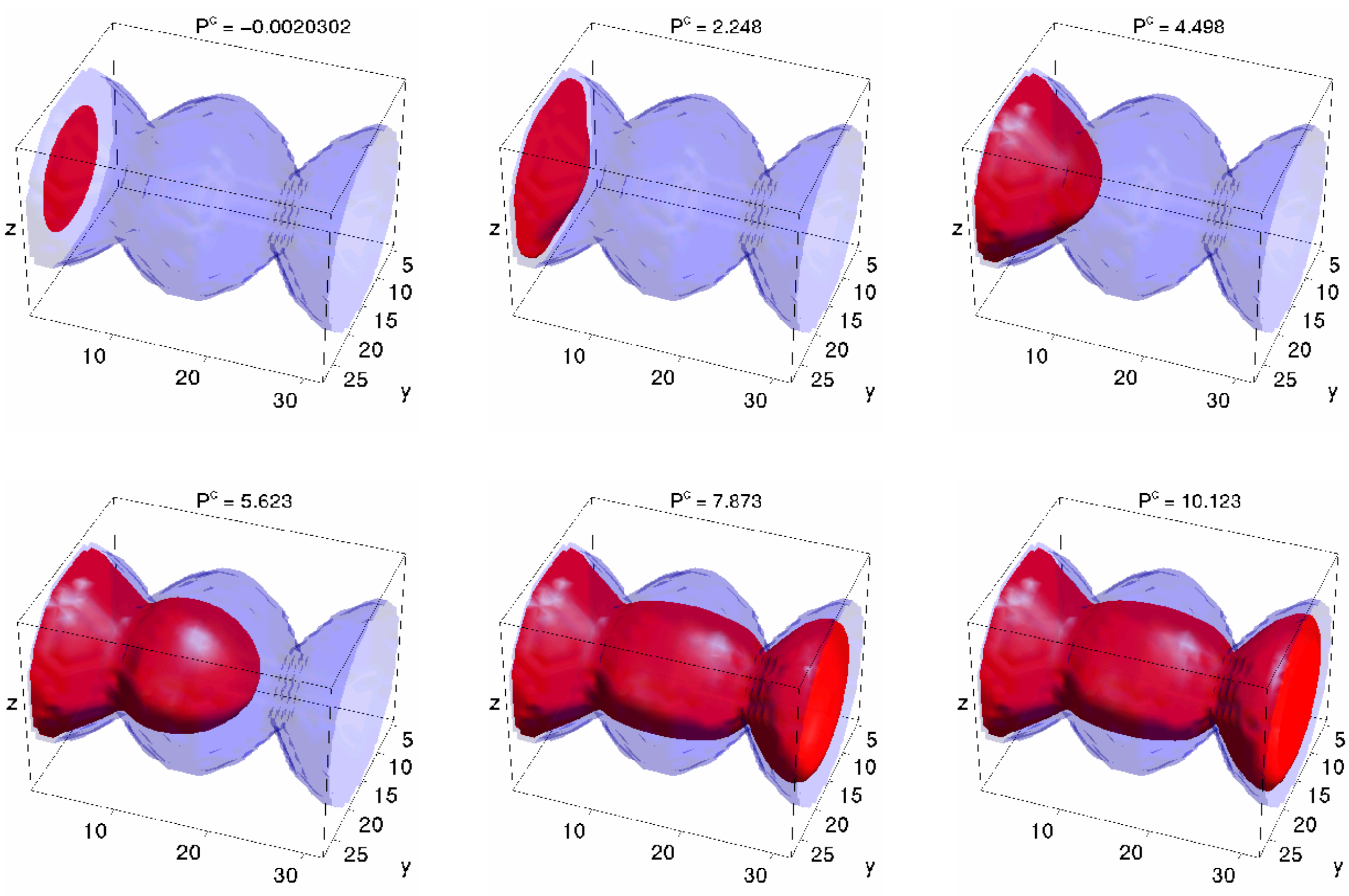
Laplace's Law:

$$p_n - p_w = \frac{2\gamma}{R}\cos\theta$$

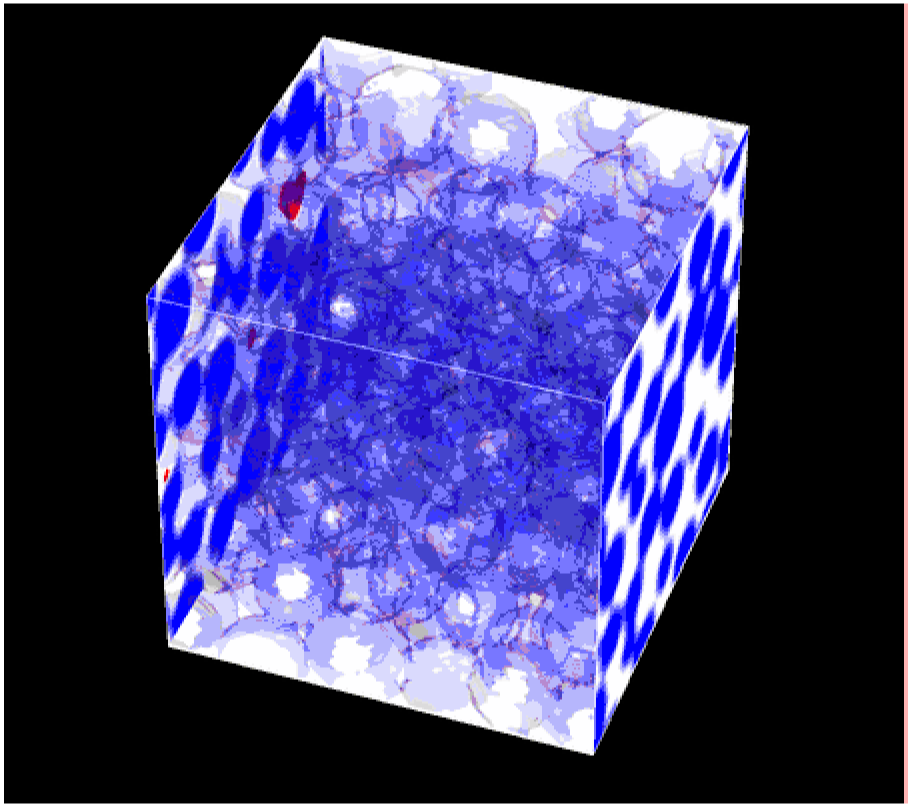
Displacement Simulation



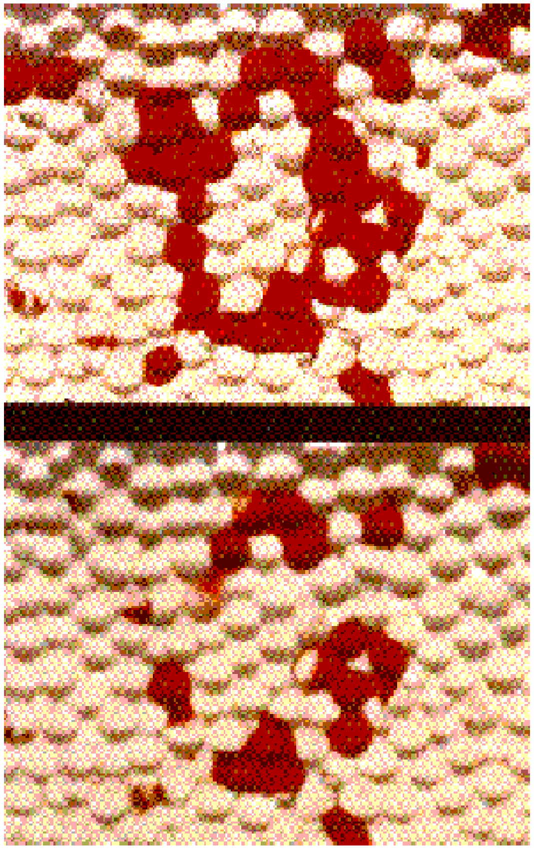
Displacement Simulation

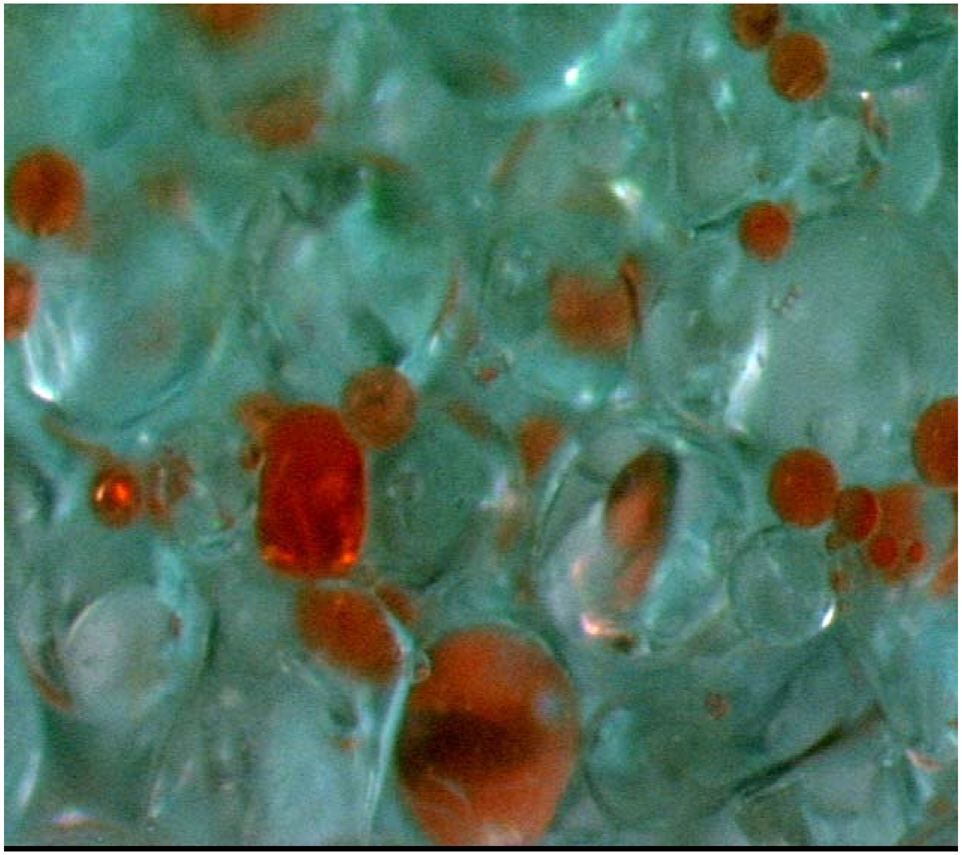


Drainage and Imbibition Simulation

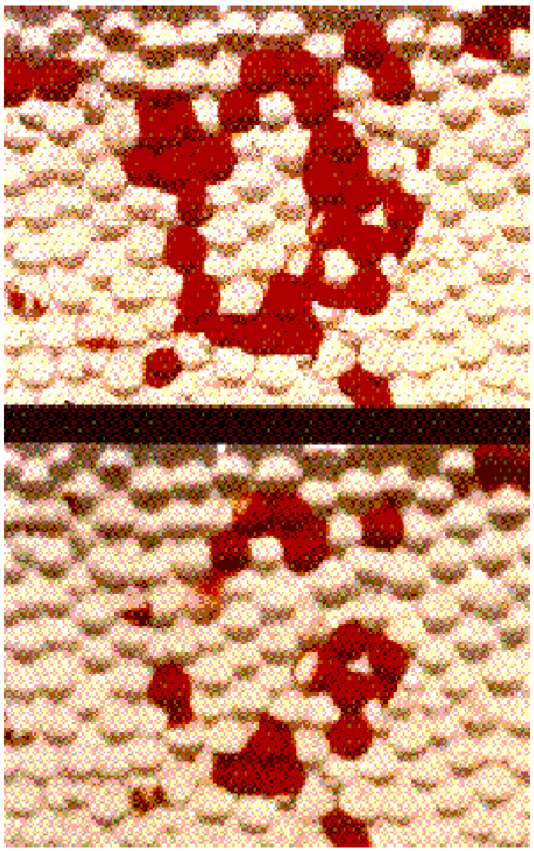


Pore-Scale DNAPL Entrapment



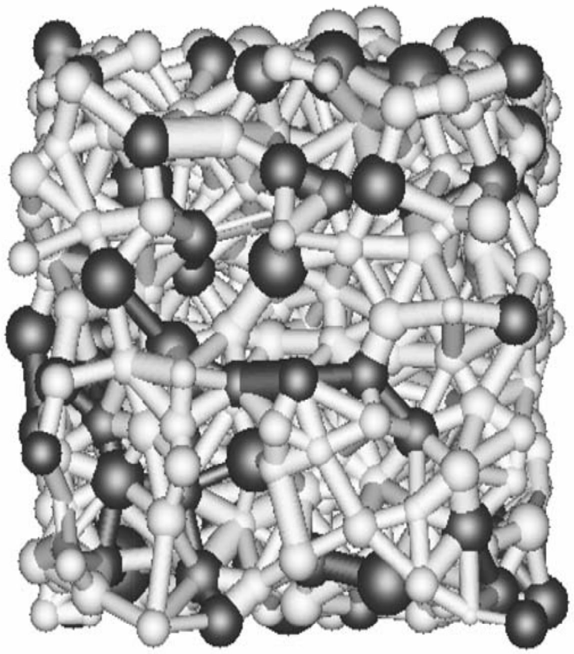


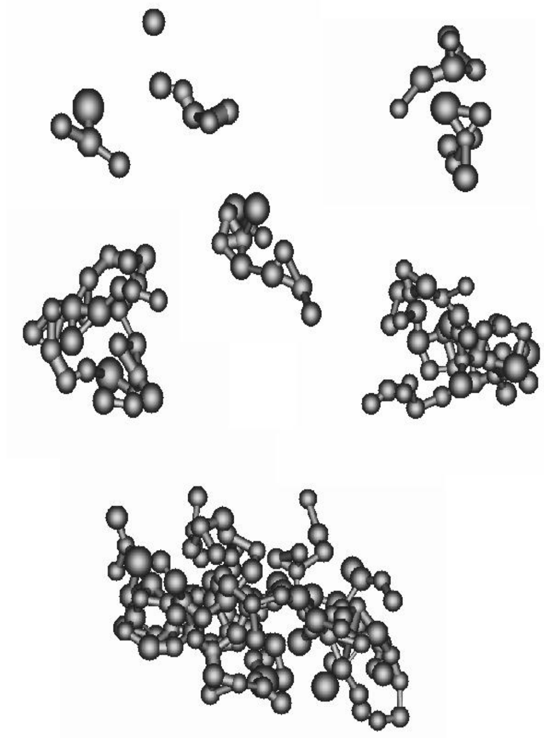
Micromodel TCE Residual



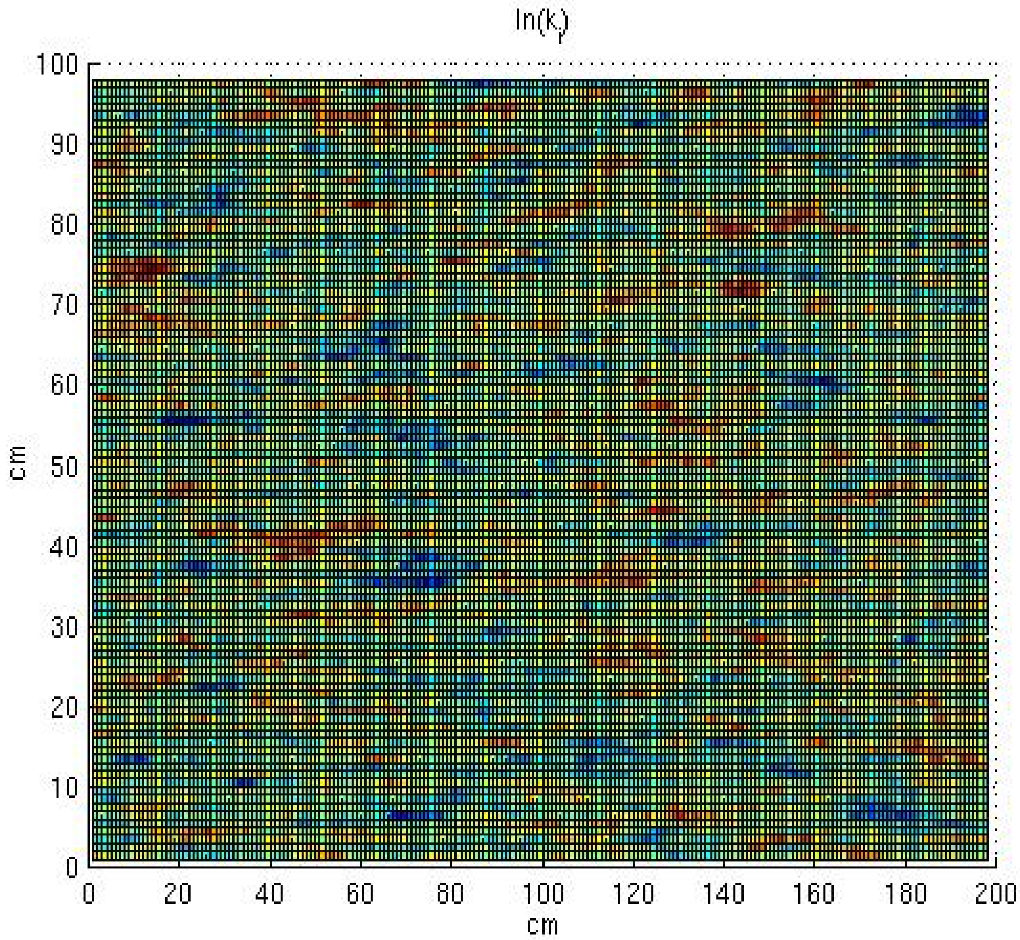
- Two-dimensional glass bead micromodel
- TCE dyed with Oil Red O
- Water saturated followed by DNAPL displacement and then water flushing
- TCE residual saturation results
- Large range of sizes of trapped TCE
- Largest features contain the majority of the TCE mass and are the most difficult to remove

Pore-Scale Network Model of NAPL Entrapment

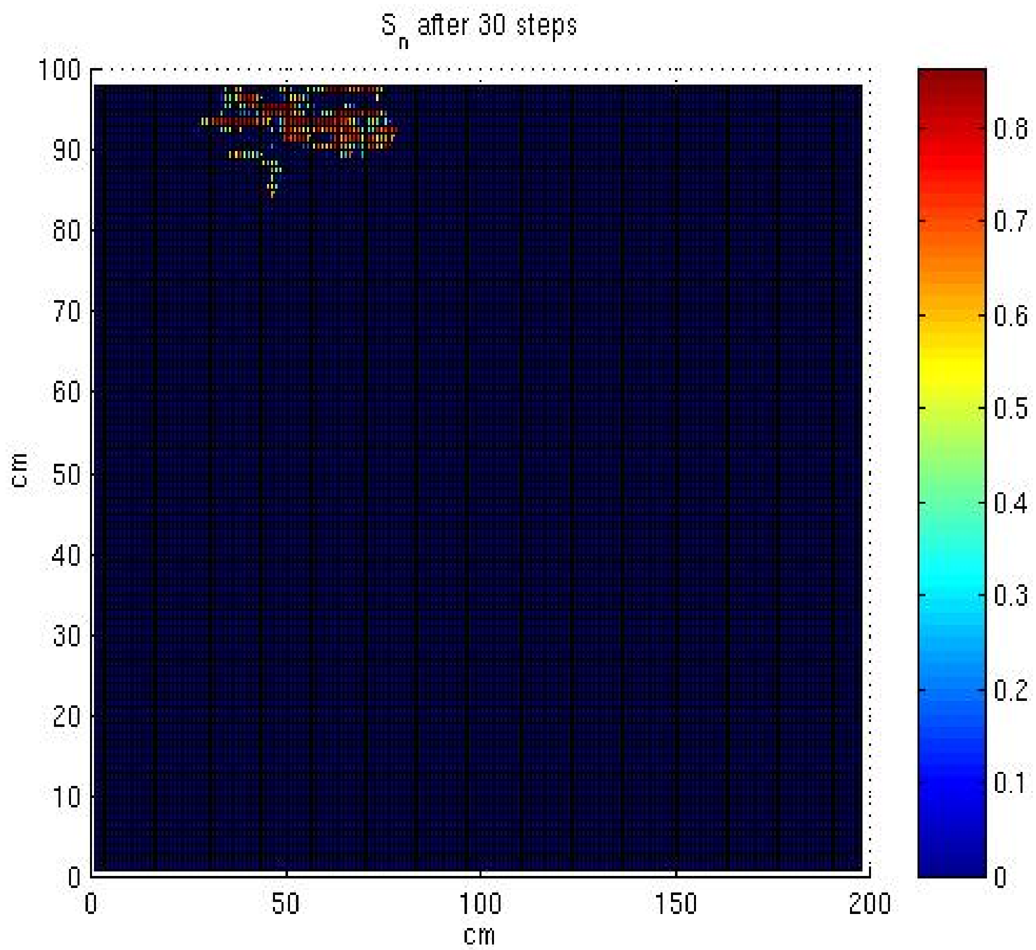




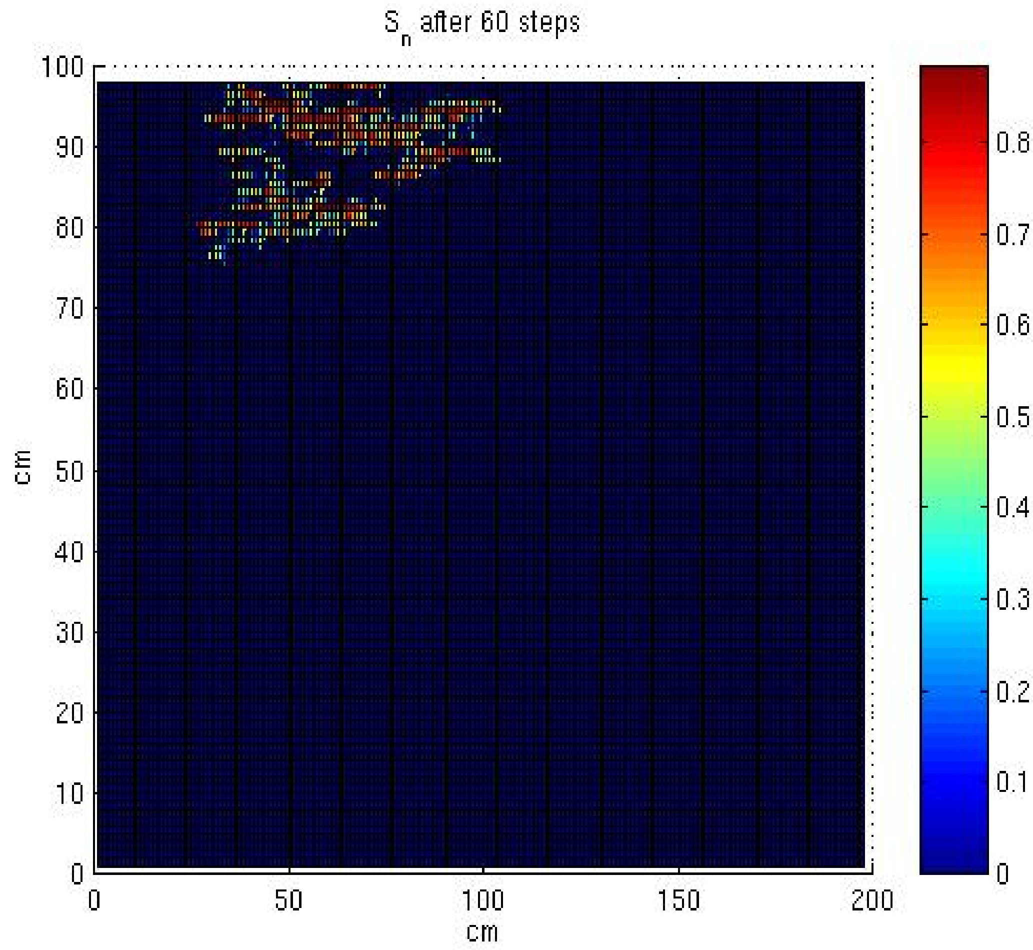
Percolation Simulation: K Field



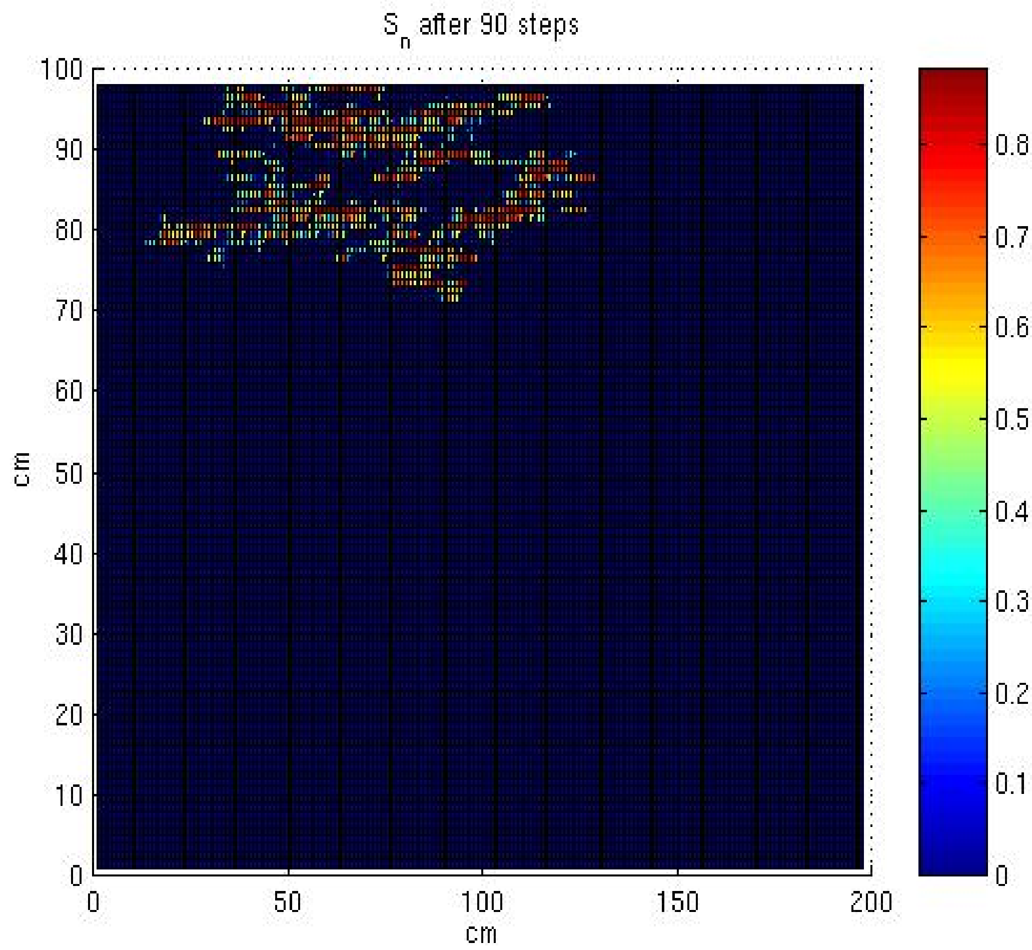
Percolation Simulation of DNAPL



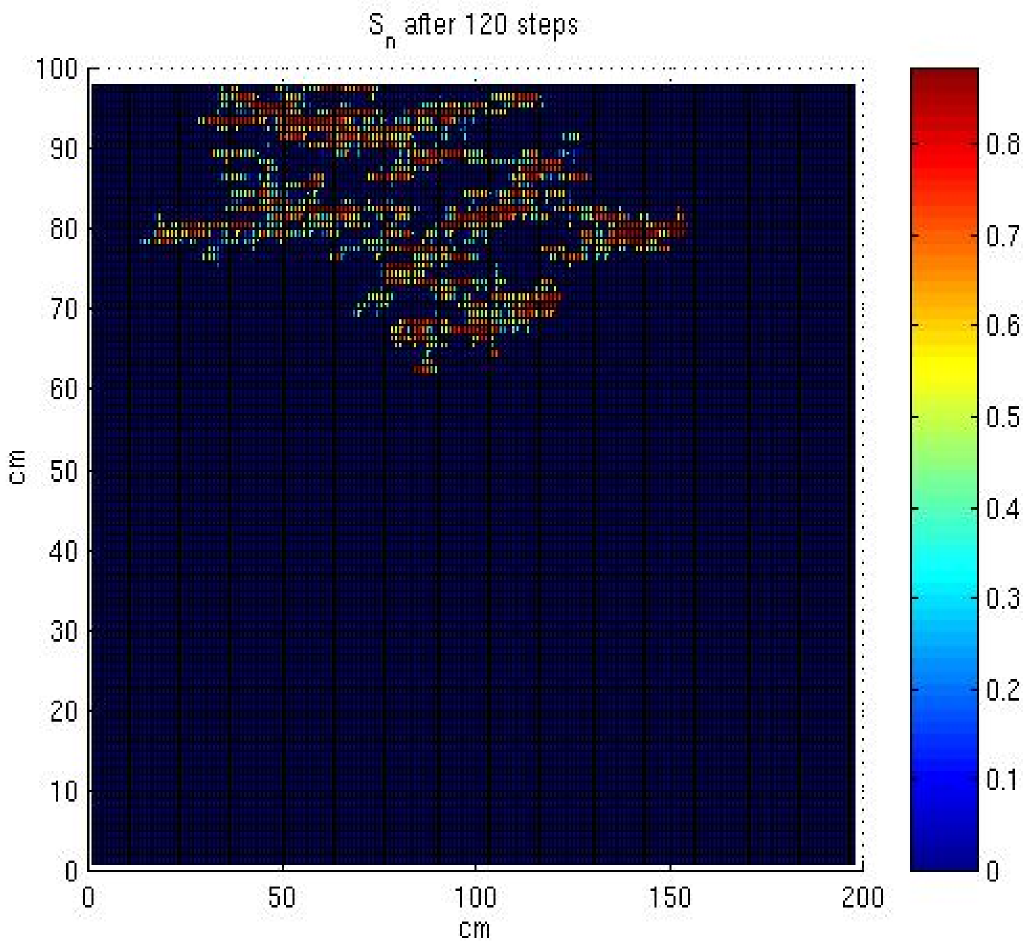
Percolation Simulation of DNAPL



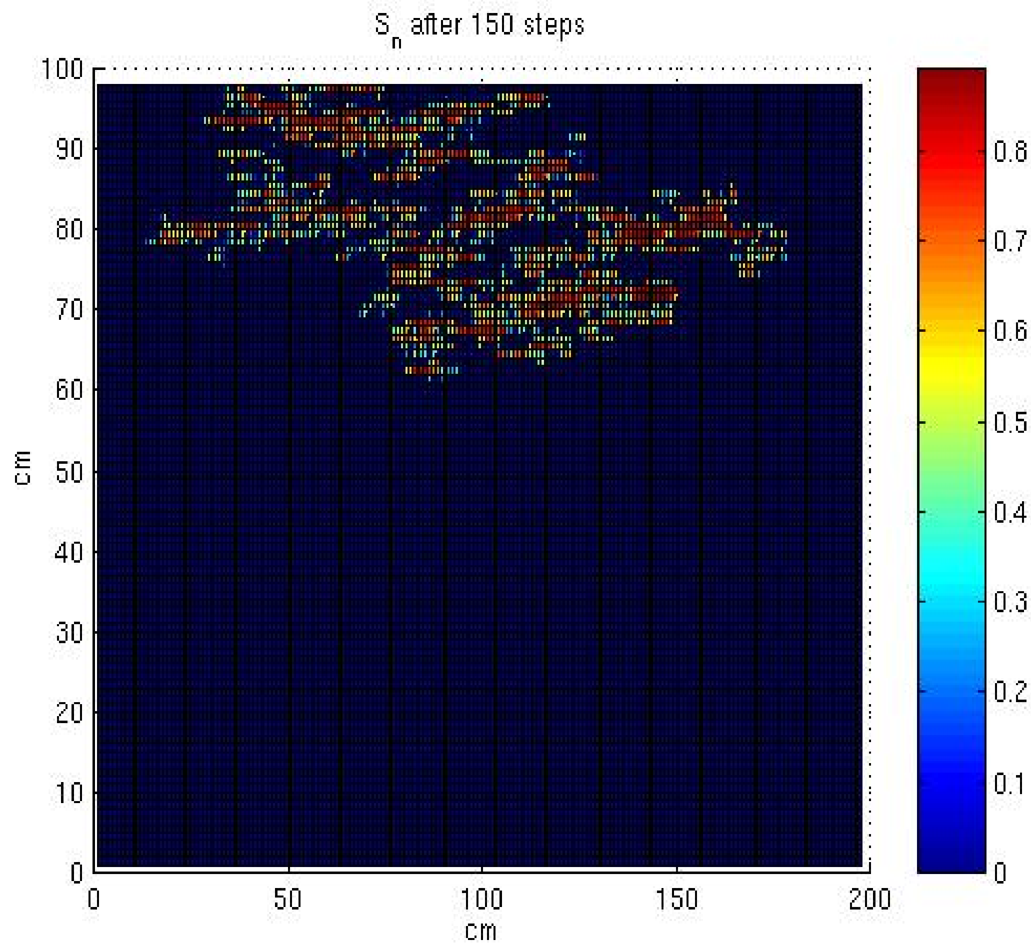
Percolation Simulation of DNAPL



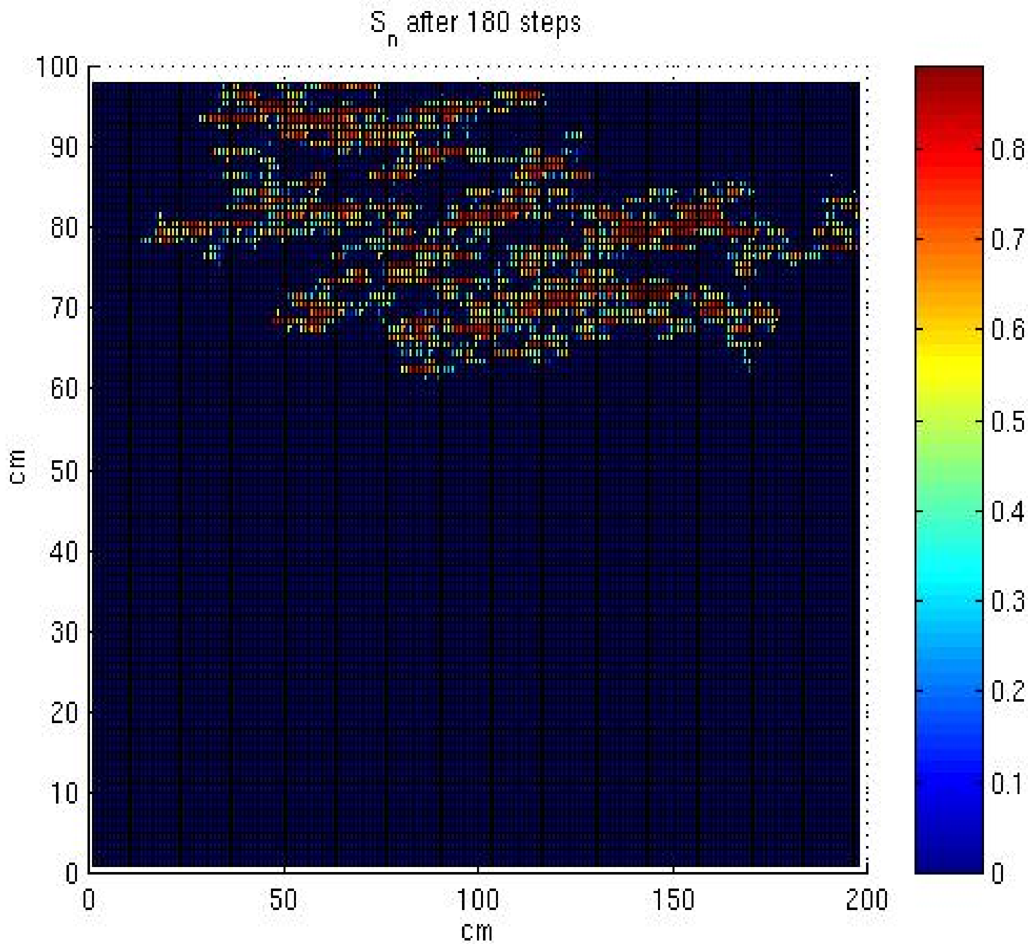
Percolation Simulation of DNAPL



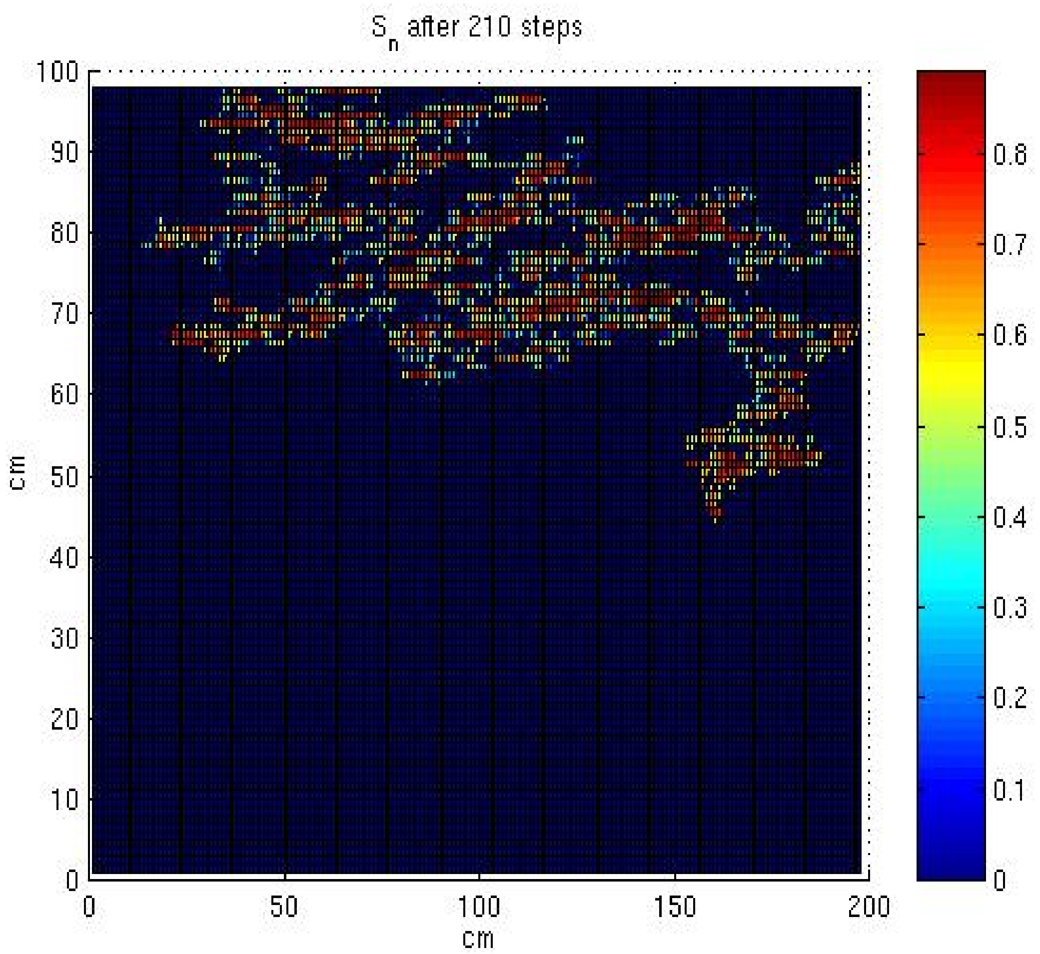
Percolation Simulation of DNAPL



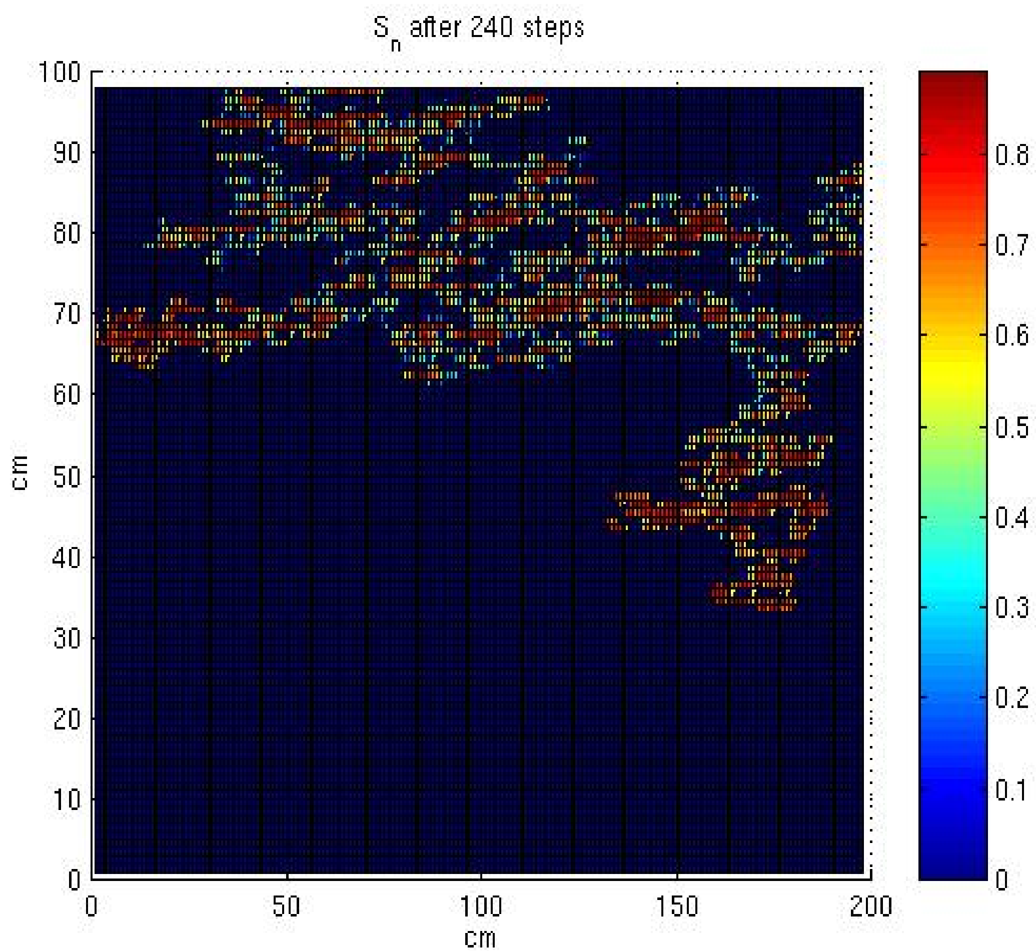
Percolation Simulation of DNAPL



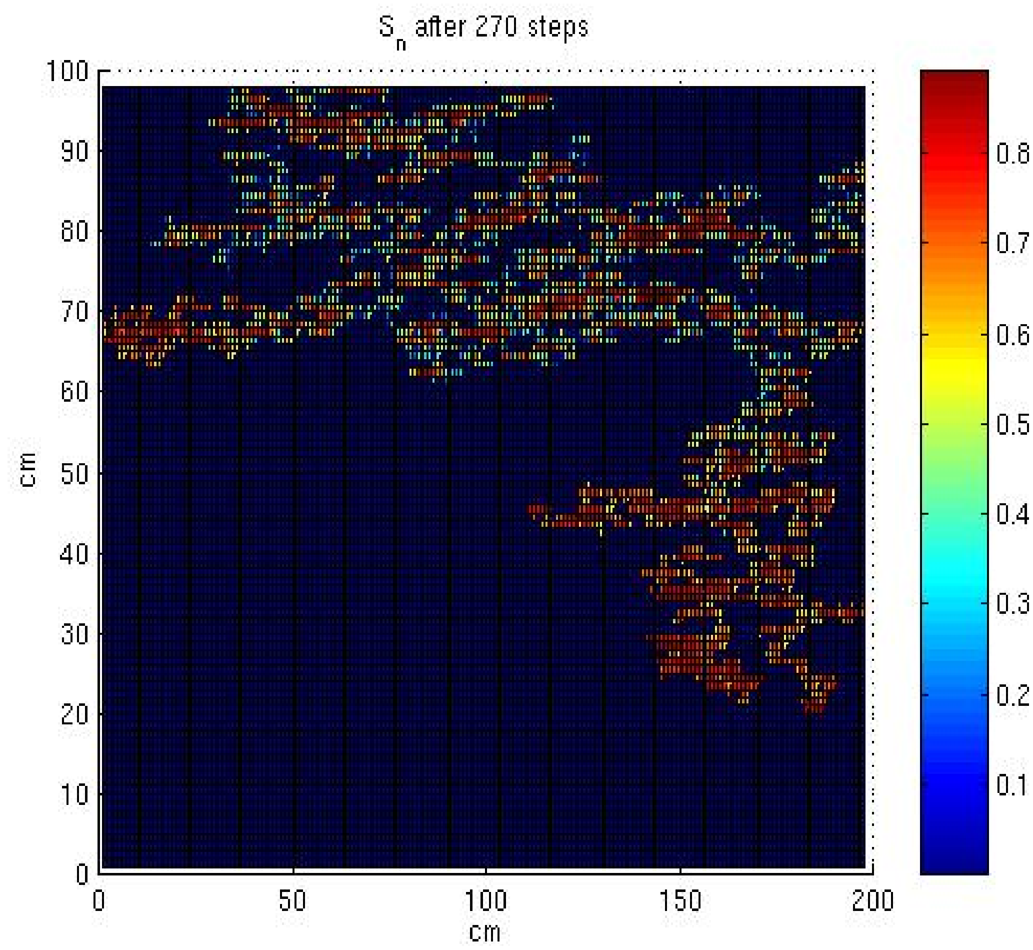
Percolation Simulation of DNAPL



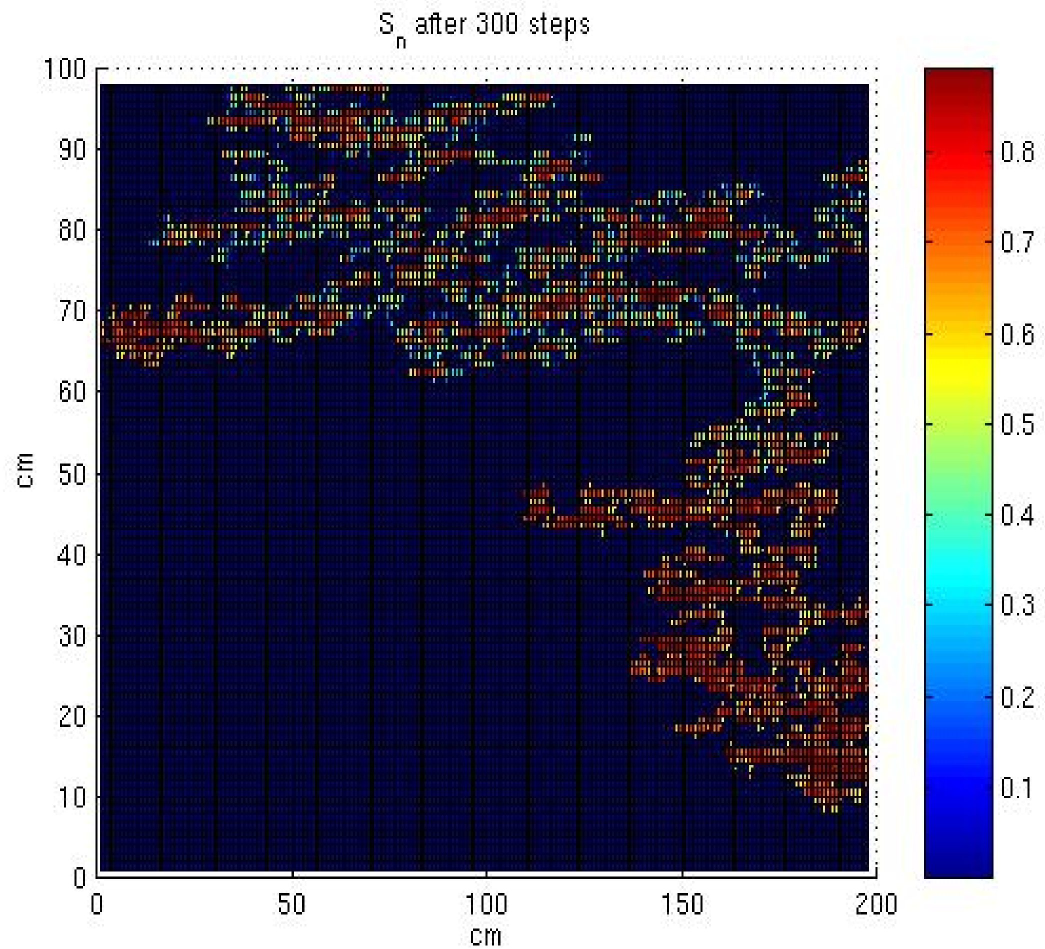
Percolation Simulation of DNAPL



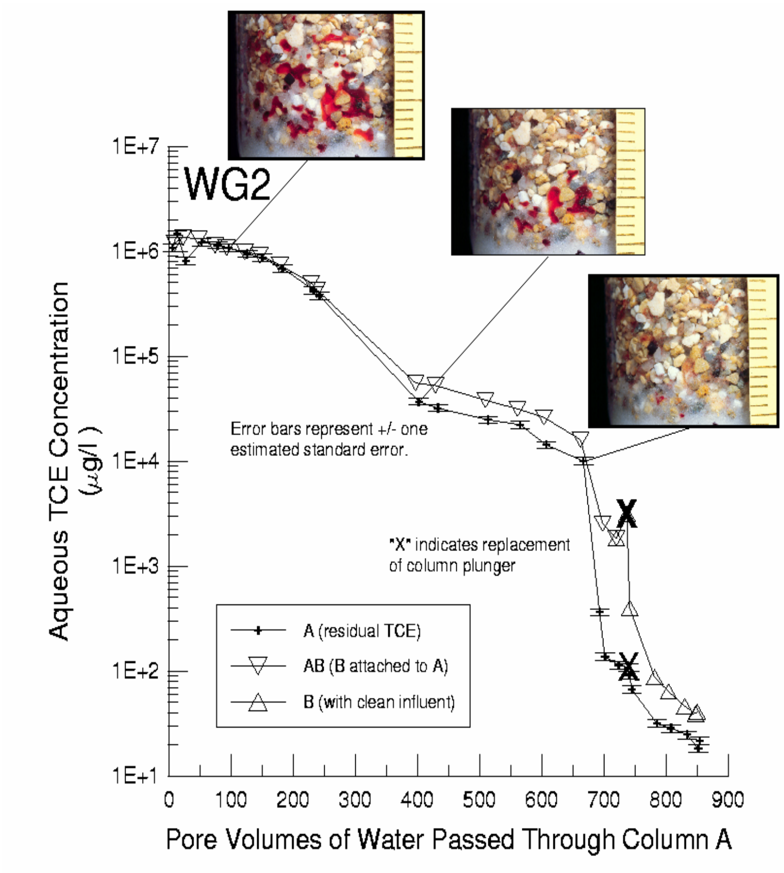
Percolation Simulation of DNAPL



Percolation Simulation of DNAPL



NAPL Dissolution Tailing for TCE



- •Column brought to residual saturation with TCE
- •Water flusing in an attempt to obtain drinking water standard concentrations of TCE
- •Large TCE residual feature determines clean-up time
- •Eventually complex TCE region breaks up and drinking water standards reached
- •Reference: Imhoff et al. [ES&T, 32(16), 1998]

Mass Transfer Fundamentals

- Linear model

$$\text{MassFlux} = k_l a_{na} (C_s - C)$$

$$K_l = k_l a_{na}$$

- Important dimensionless groupings

$$Sh = \frac{K_l d_p^2}{D_m}, \quad Re = \frac{v_a \rho_a d_p}{\mu_a}, \quad Sc = \frac{\mu_a}{\rho_a D_m}, \quad \theta_n$$

Experiment in 3-D Cell

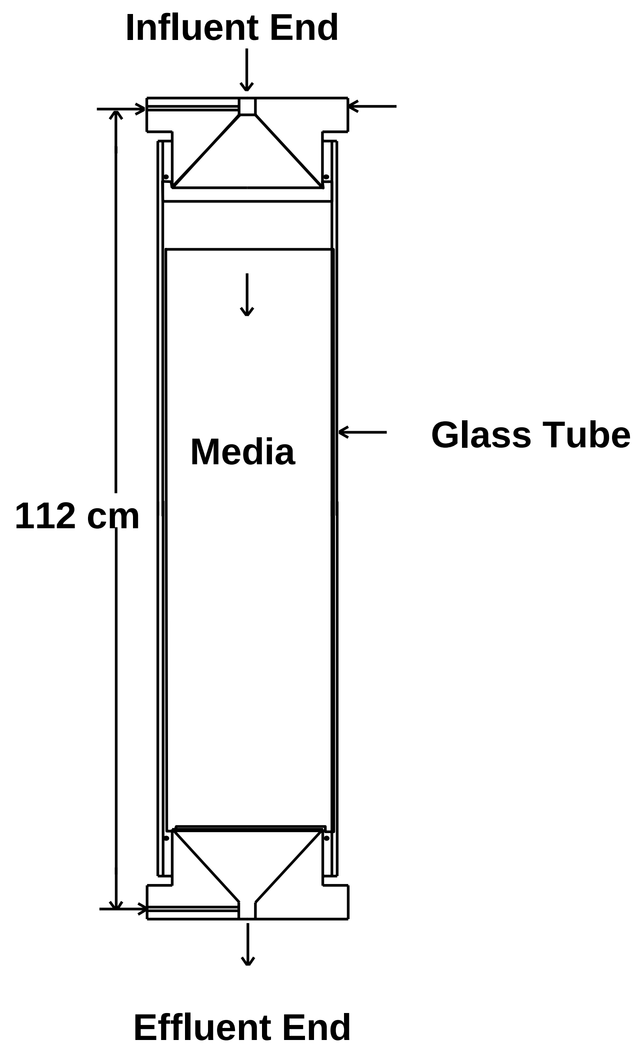
- Column: 9-cm dia. and 1.2-m long

V_a

- S_n = 2.2 m/day initial
- = 0.14

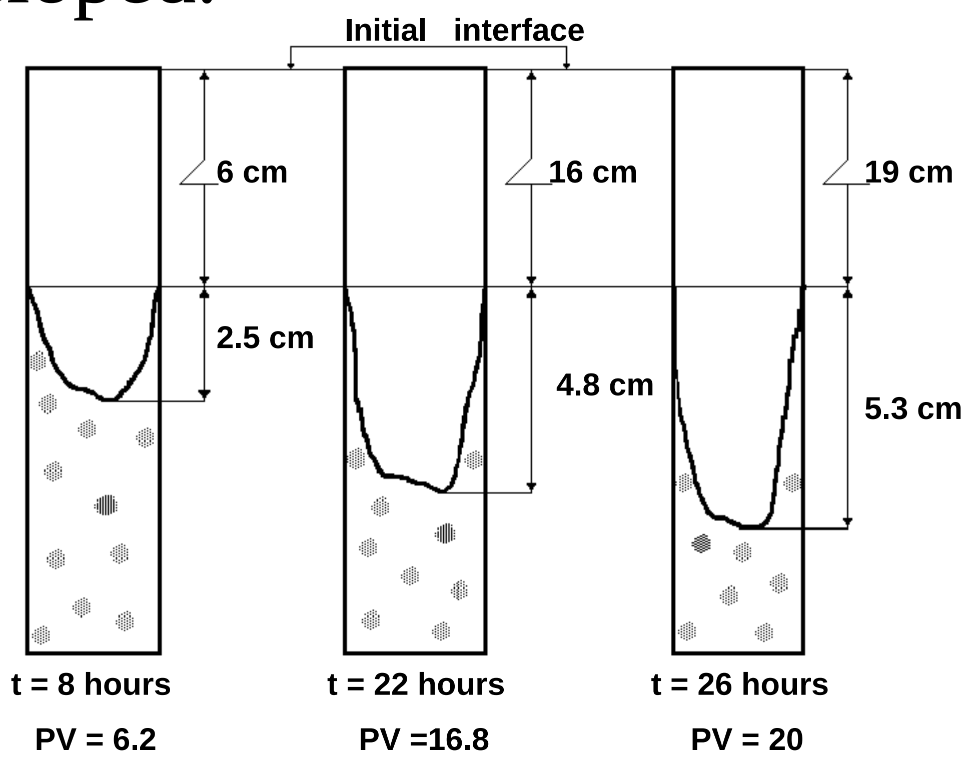
d_{50}

- NAPL - Dyed TCE
- = 0.035 cm



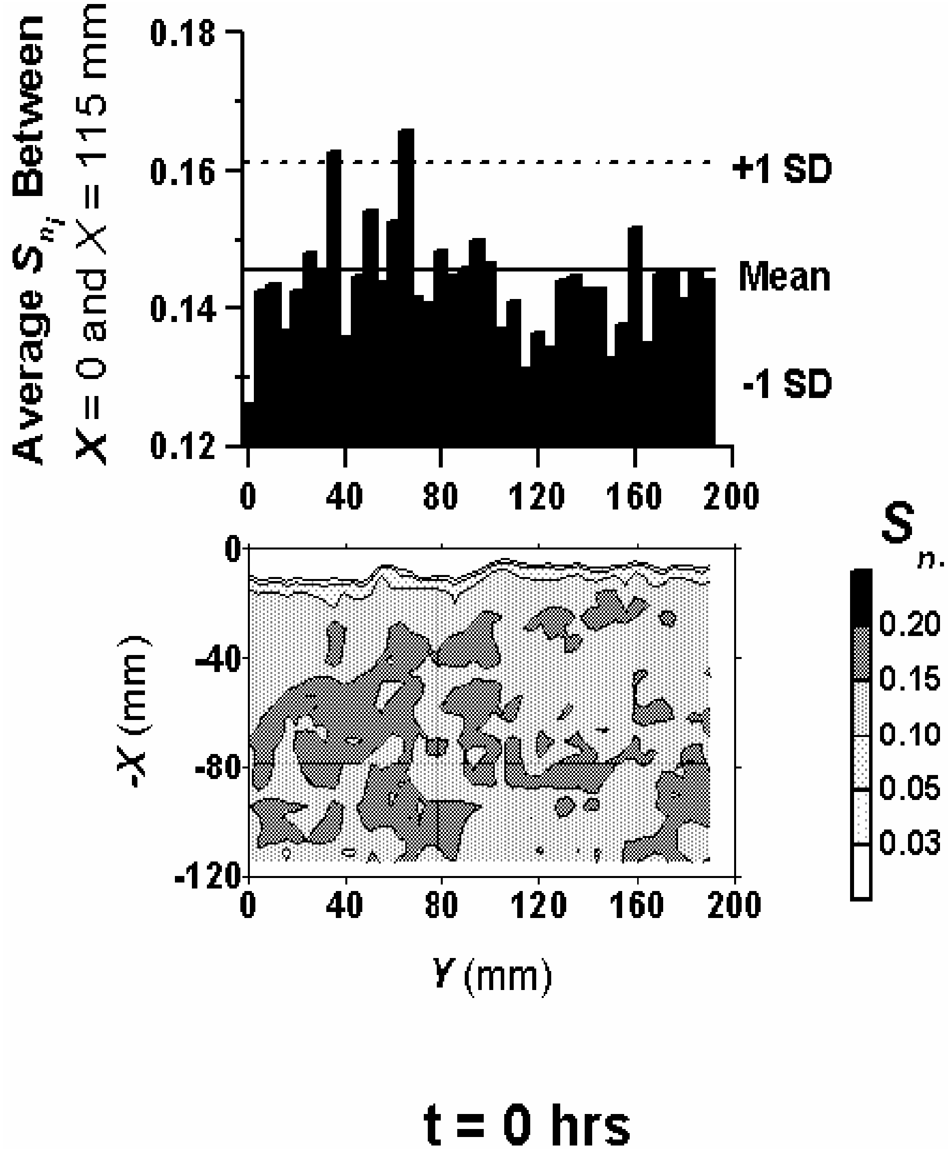
1-D Experiments: Fingering

- As the dissolution front moved downward through the medium, preferential flow paths developed.



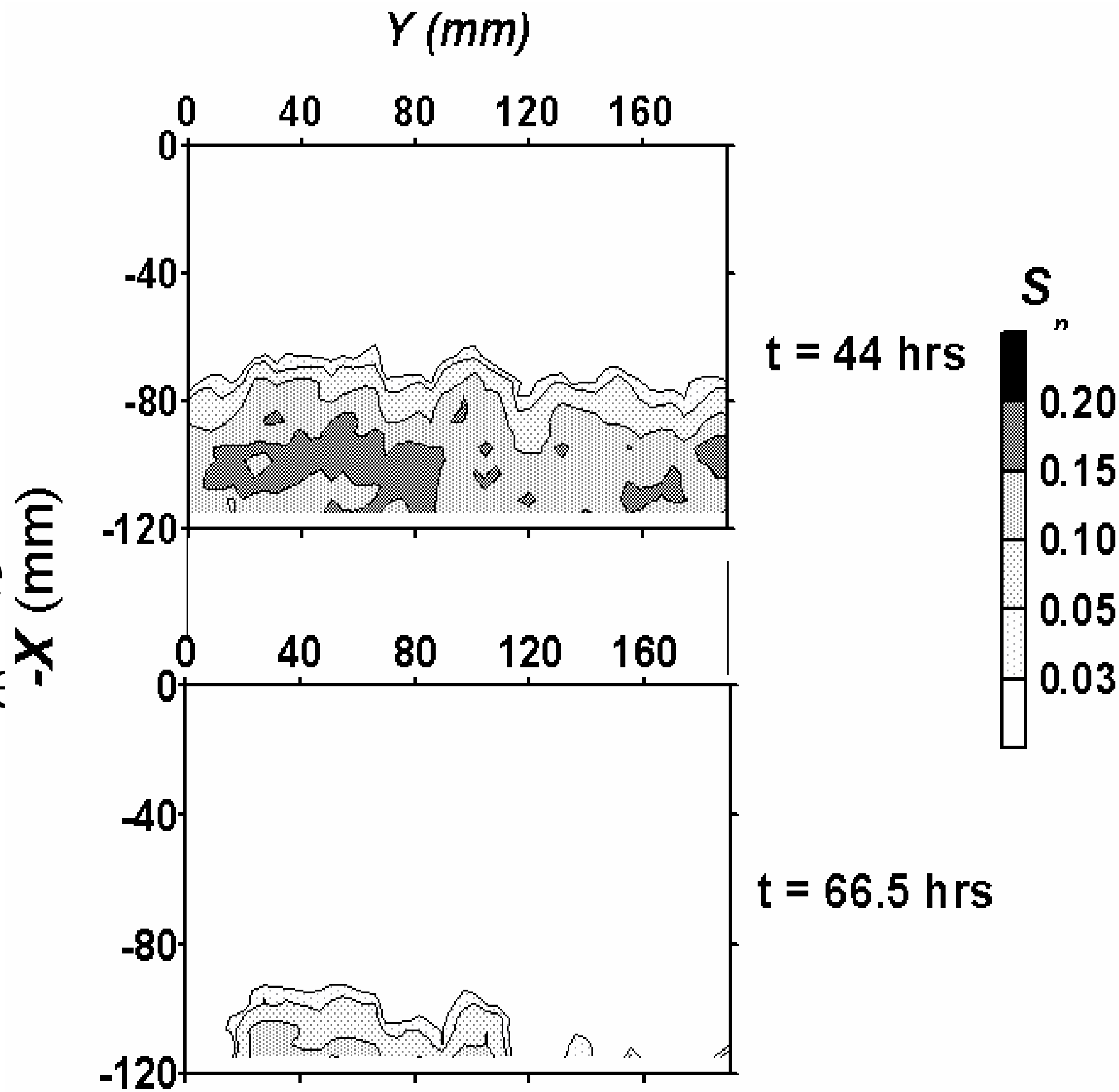
Dissolution Experiment Results

X-ray measurements at t = 0 h

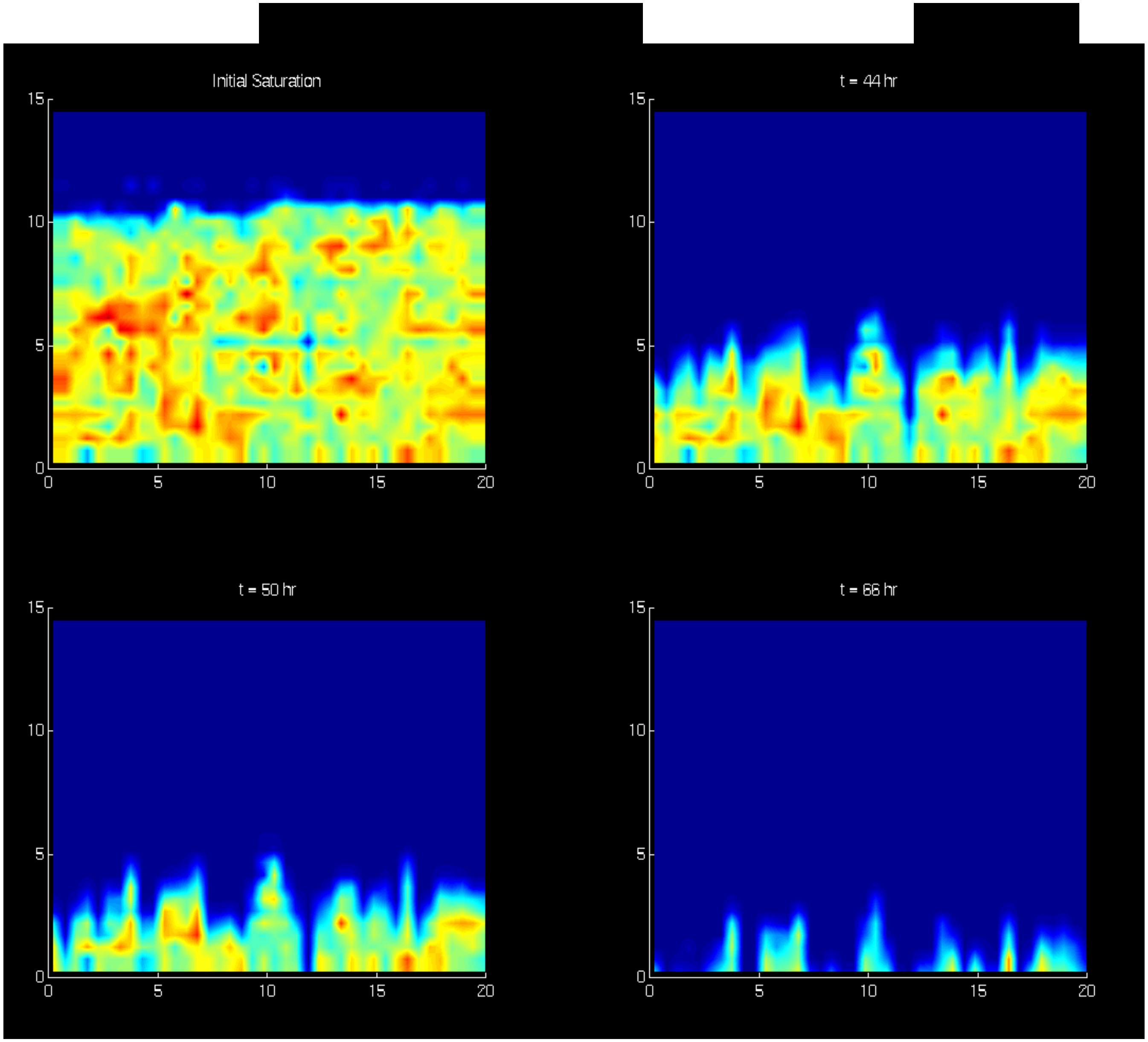


Dissolution Experiment Results

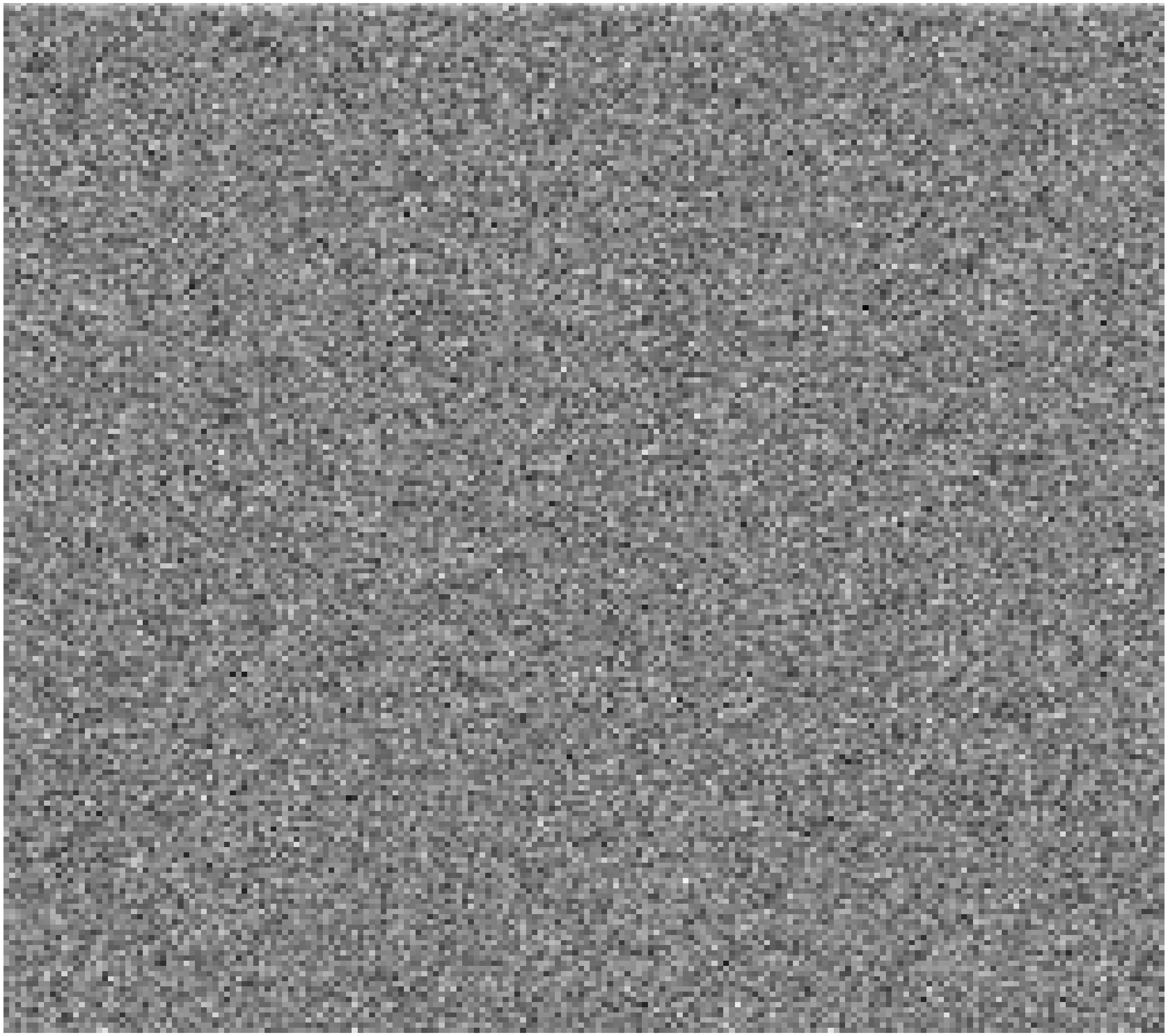
- X-ray measureme at later time



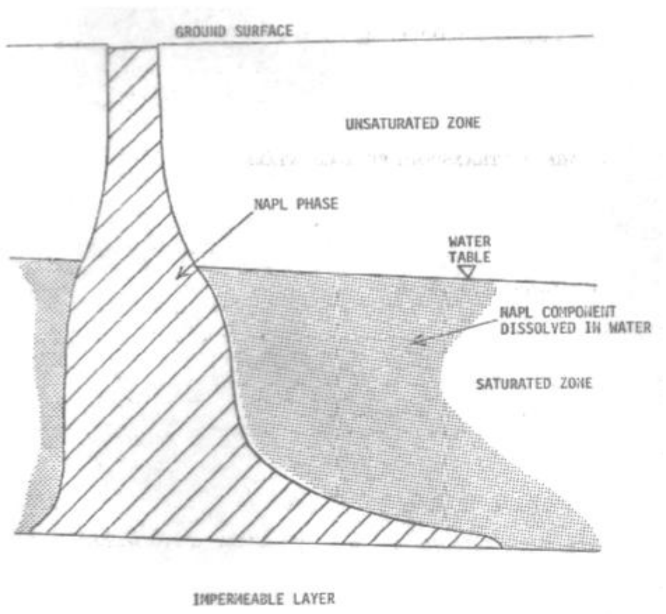
Dissolution Experiment: Simulated Results

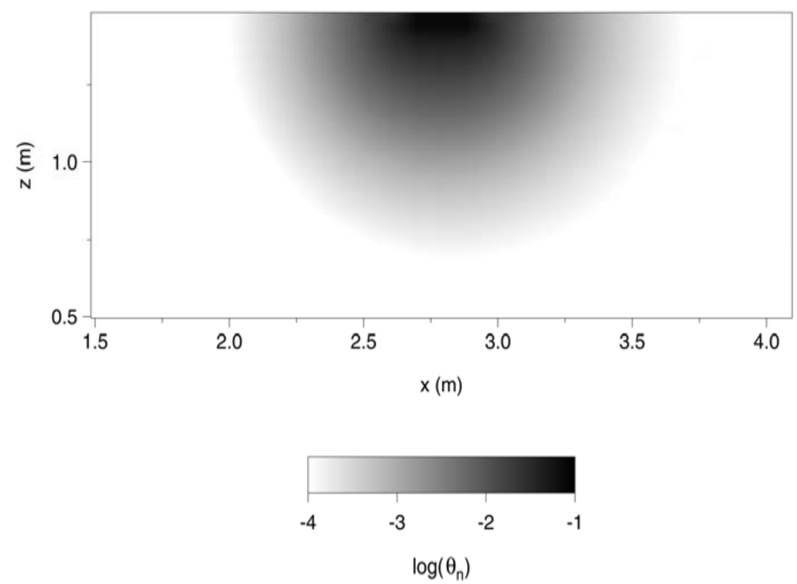


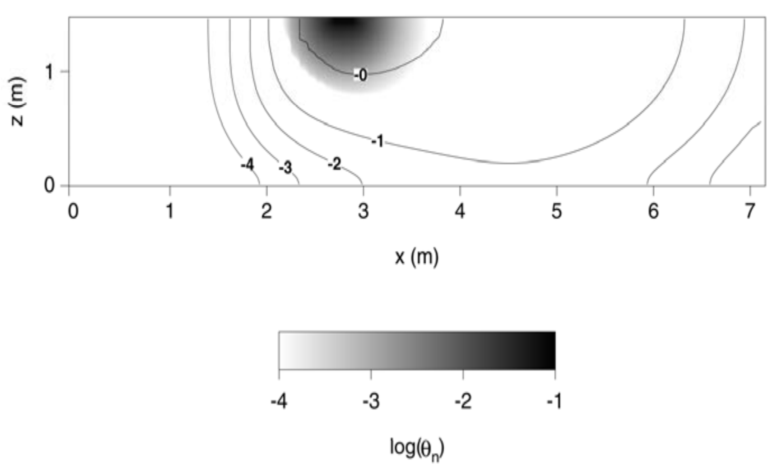
Dissolution Fingering Simulation

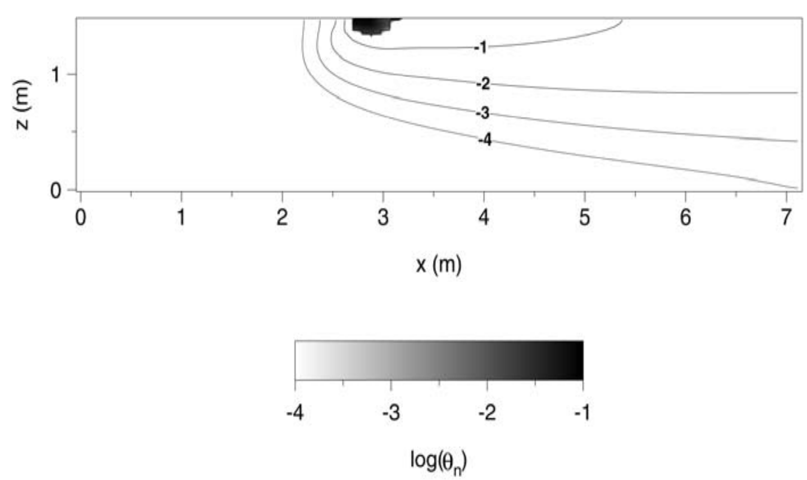


DNAPLs in Homogeneous Systems

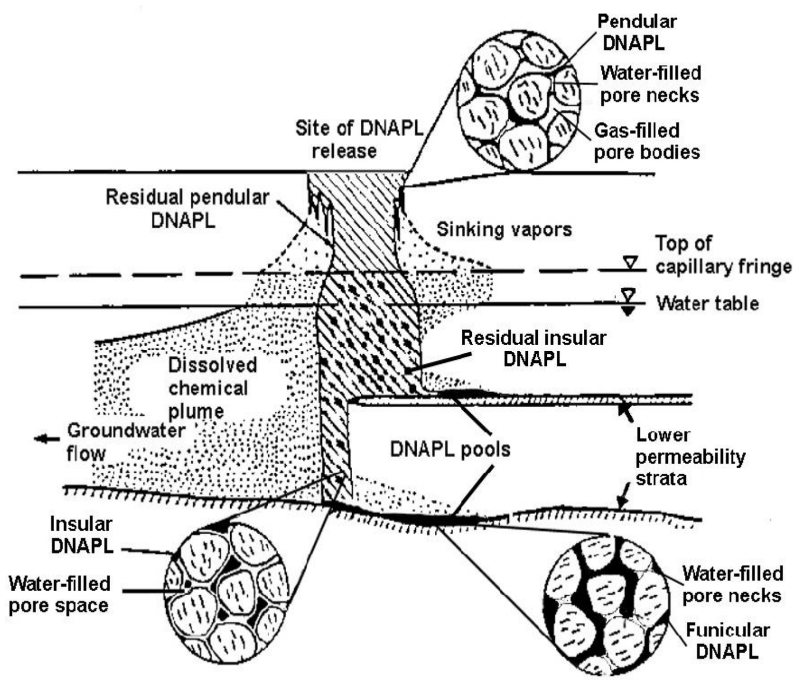


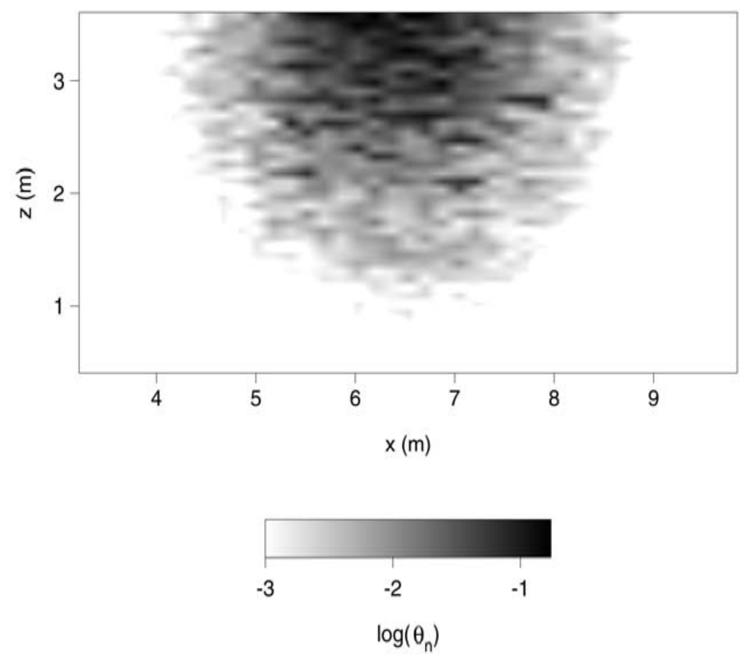






DNAPLs in Heterogeneous Systems



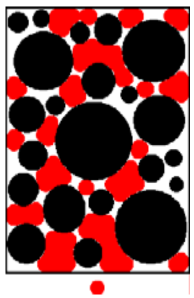


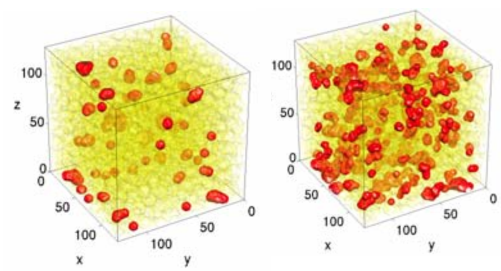
Nonaqueous Phase Dissolution

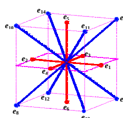
1

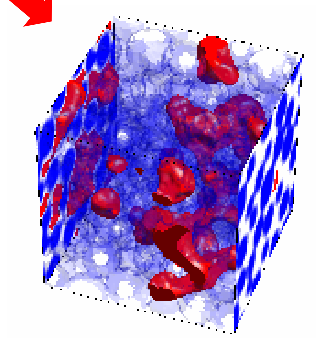
Pore morphology and topology

Morphological analysis of pore space









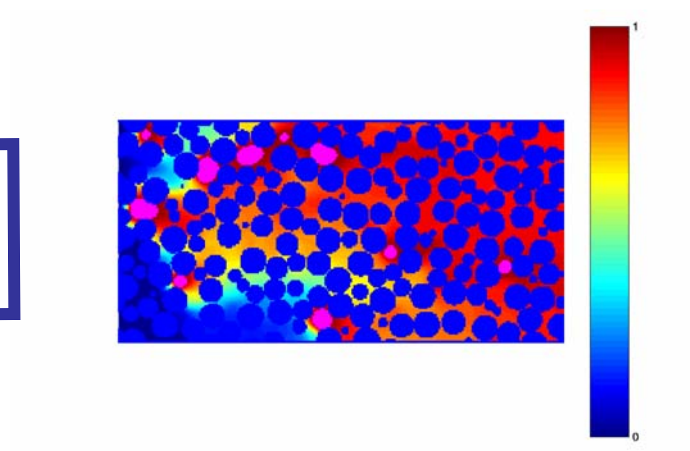
Residual NAPL distribution

2

LB two-fuid phase simulation

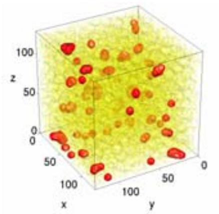
3

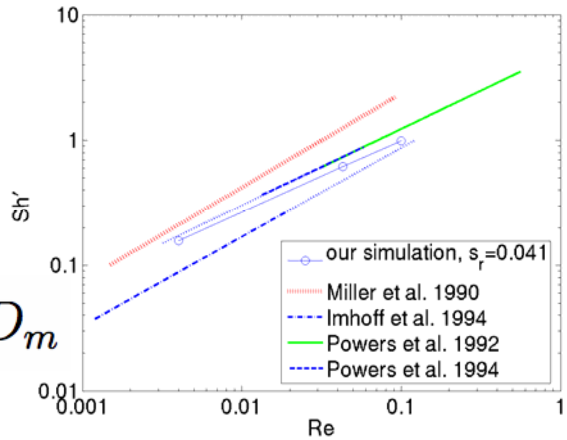
NAPL dissolution



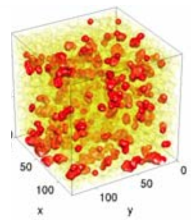
Pore-scale ADE solver with adaptive-stencil finite-volume scheme

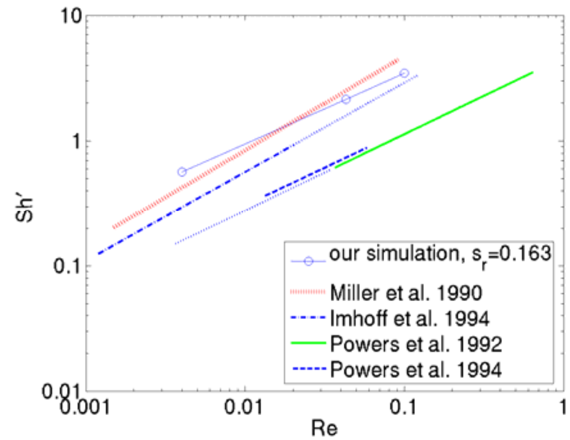
Nonaqueous Phase Dissolution



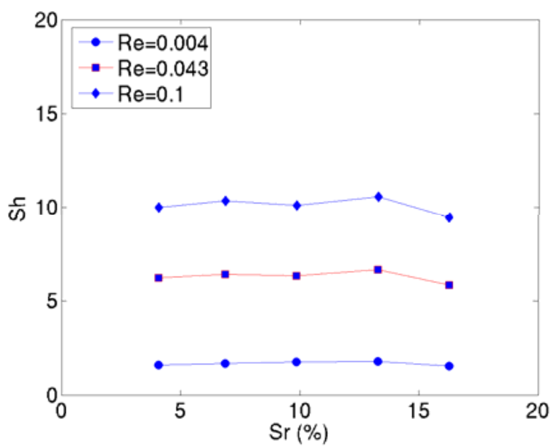


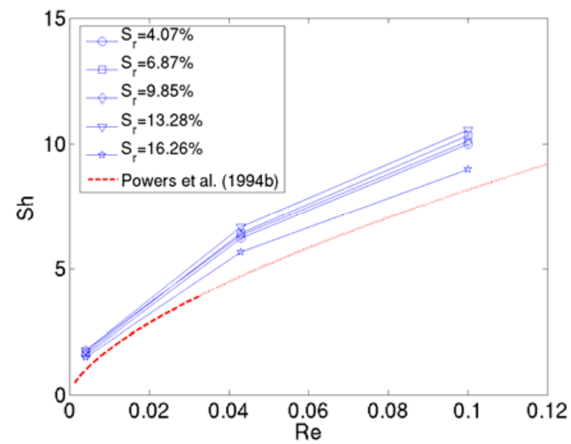
$$Sh' = K_l d_g^2 / D_m$$





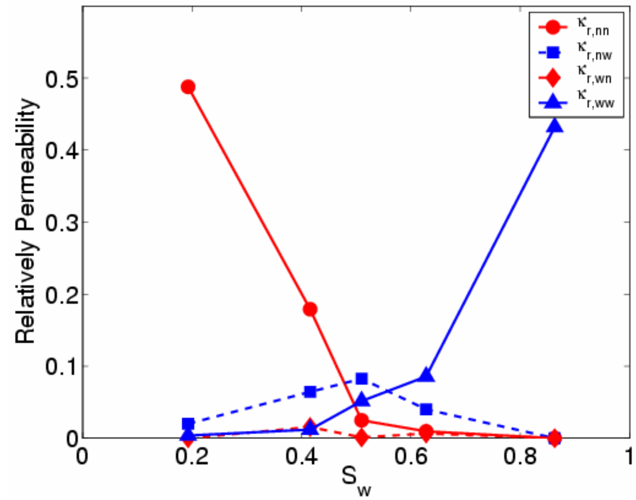
$$Sh = k_l d_g / D_m$$



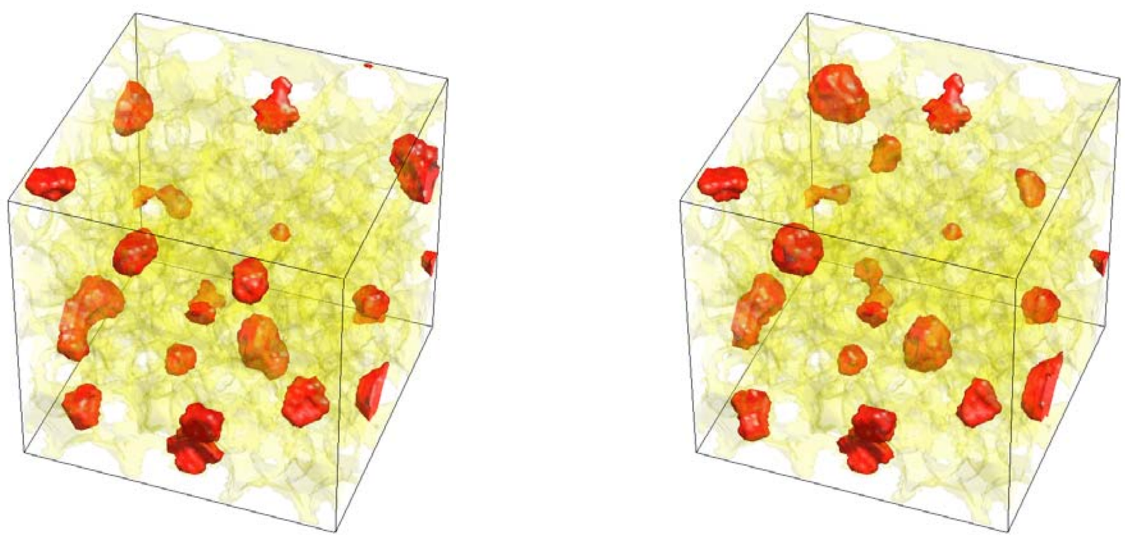


Viscous Coupling

Relative permeability-saturation (*ks*) relation:



Viscous coupling effect



Deficiencies in Traditional Models

- Models are often based upon ill-defined variables and empirically derived closure approximations lacking in theoretical support and precise knowledge of limitations
- Empirical closure relations are routinely extended beyond their level of experimental support

Deficiencies in Traditional Models

- Rigorous linkages among scales is usually absent
- Important phenomena are often not included naturally in multiphase models (e.g., wettability)
- Standard porous medium models are not typically constrained to obey the second law of thermodynamics

Deficiencies in Traditional Models

- Quantities of interest, such as interfacial areas, do not explicitly arise in standard models
- Standard models are often built upon assumptions well-known to be violated (e.g. quasi-equilibrium states)

Deficiencies in Traditional Models

- Standard approaches lack a rigorous structure in which to examine simplifying assumptions

TCAT Approach

- Form general conservation equations
- Use general conservation equations to formulate specific conservation equations for mass, momentum, angular momentum, energy, and entropy
- Specify thermodynamic dependence of internal energy and independent system variables

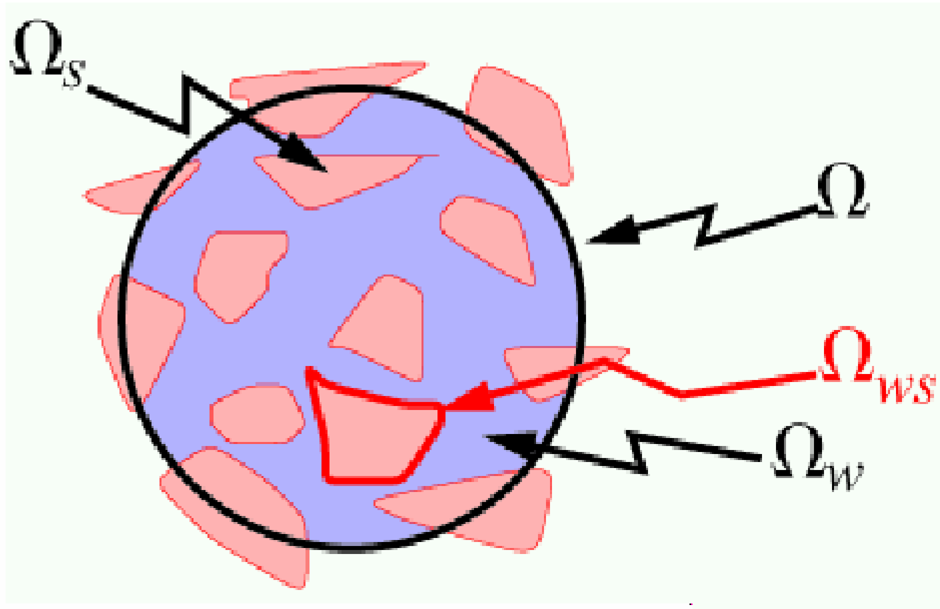
TCAT Approach

- Derive a total system entropy inequality
- Constrain the entropy inequality with the product of Lagrange multipliers and specific conservation equations, thermodynamic relations, and other constraints
- Solve for Lagrange multipliers to simplify entropy inequality

TCAT Approach

- Exploit entropy inequality to guide development of closure relations
- Use sub-scale theory, computation, or experiment to guide final form of closure relations
- Compare model systems to experimental observations and use to guide experimental design

TCAT Approach for Single-Phase Flow



$$\mathcal{E} = \{\Omega_\iota | \iota \in \mathcal{I}\} = \{\Omega_w, \Omega_s, \Omega_{ws}\}$$

$$\mathcal{I} = \{w, s, ws\}$$

$$\mathcal{E}_{c\iota} = \{\Omega_\kappa | (\bar{\Omega}_\iota \cap \bar{\Omega}_\kappa \neq \emptyset) \wedge (\bar{\Omega}_\iota \neq \bar{\Omega}_\kappa), \forall \Omega_\kappa \in \mathcal{E}\}$$

$$\mathcal{E}_{cw} = \{\Omega_{ws}\}$$

$$\mathcal{E}_{cs} = \{\Omega_{ws}\}$$

$$\mathcal{E}_{cws} = \{\Omega_w, \Omega_s\}$$

TCAT---Entropy Balance

$$\frac{\mathrm{D}^{\overline{\iota}}\eta^{\overline{\overline{\iota}}}}{\mathrm{D}t} + \eta^{\overline{\overline{\iota}}}\mathbf{l}{:}\mathbf{d}^{\overline{\iota}} - \nabla\cdot\left(\epsilon^{\iota}\boldsymbol{\varphi}^{\overline{\overline{\iota}}}\right) - \epsilon^{\iota}b^{\iota} - \sum_{\kappa\in\mathfrak{J}_{c\iota}}\left(\overset{\kappa\rightarrow\iota}{M_\eta} + \overset{\kappa\rightarrow\iota}{\Phi}\right) = \Lambda^{\overline{\overline{\iota}}}, \quad \text{for } \iota\in\mathfrak{J}$$

$$\langle \mathcal{P}_i\rangle_{\Omega_j,\Omega_k,w} = \frac{\int_{\Omega_j} w\mathcal{P}_i\,\mathrm{d}\mathfrak{r}}{\int_{\Omega_k} w\,\mathrm{d}\mathfrak{r}}$$

$$\eta^{\overline{\overline{\iota}}} = \langle\eta_\iota\rangle_{\Omega_\iota,\Omega}$$

$$\mathbf{v}^{\overline{\iota}} = \langle\mathbf{v}_\iota\rangle_{\Omega_\iota,\Omega_\iota,\rho_\iota}$$

$$\mathbf{d}^{\overline{\iota}} = \frac{1}{2}\left[\nabla\mathbf{v}^{\overline{\iota}} + \left(\nabla\mathbf{v}^{\overline{\iota}}\right)^{\mathrm{T}}\right]$$

$$\boldsymbol{\varphi}^{\overline{\overline{\iota}}} = \langle\boldsymbol{\varphi}_\iota\rangle_{\Omega_\iota,\Omega_\iota} - \left\langle\eta_\iota\left(\mathbf{v}_\iota - \mathbf{v}^{\overline{\iota}}\right)\right\rangle_{\Omega_\iota,\Omega_\iota}$$

$$b^{\iota} = \langle b_\iota\rangle_{\Omega_\iota,\Omega_\iota}$$

$$\Lambda^{\overline{\overline{\iota}}} = \langle\Lambda_\iota\rangle_{\Omega_\iota,\Omega}$$

$$\sum_{\iota\in\mathfrak{J}}\mathcal{S}^{\iota} = \sum_{\iota\in\mathfrak{J}}\left(\frac{\mathrm{D}^{\overline{\iota}}\eta^{\overline{\overline{\iota}}}}{\mathrm{D}t} + \eta^{\overline{\overline{\iota}}}\mathbf{l}{:}\mathbf{d}^{\overline{\iota}} - \nabla\cdot\left(\epsilon^{\iota}\boldsymbol{\varphi}^{\overline{\overline{\iota}}}\right) - \epsilon^{\iota}b^{\iota}\right) = \Lambda \geq 0$$

TCAT---Conservation Equations

$$\mathcal{M}^{\iota} = \frac{\mathrm{D}^{\overline{\iota}}\left(\epsilon^{\iota}\rho^{\iota}\right)}{\mathrm{D}t} + \epsilon^{\iota}\rho^{\iota}\mathsf{I}{:}\mathbf{d}^{\overline{\overline{\iota}}} - \sum_{\kappa\in\mathfrak{I}_{c\iota}} \overset{\kappa\to\iota}{M} = 0, \quad \text{for } \iota \in \mathfrak{I}$$

$$\boldsymbol{\mathcal{P}}^{\iota} = \frac{\mathrm{D}^{\overline{\iota}}\left(\epsilon^{\iota}\rho^{\iota}\mathbf{v}^{\overline{\iota}}\right)}{\mathrm{D}t} + \epsilon^{\iota}\rho^{\iota}\mathbf{v}^{\overline{\iota}}\mathsf{I}{:}\mathbf{d}^{\overline{\overline{\iota}}} - \nabla\cdot\left(\epsilon^{\iota}\mathbf{t}^{\overline{\overline{\iota}}}\right) - \epsilon^{\iota}\rho^{\iota}\mathbf{g}^{\overline{\iota}}$$
$$- \sum_{\kappa\in\mathfrak{I}_{c\iota}} \left(\overset{\kappa\to\iota}{\mathbf{M}_{v}} + \overset{\kappa\to\iota}{\mathbf{T}}\right) = 0, \quad \text{for } \iota \in \mathfrak{I}$$

$$\mathcal{E}^{\iota} = \frac{\mathrm{D}^{\overline{\iota}}\left[E^{\overline{\overline{\iota}}} + \epsilon^{\iota}\rho^{\iota}\left(\frac{1}{2}\mathbf{v}^{\overline{\iota}}\cdot\mathbf{v}^{\overline{\iota}} + K_{E}^{\overline{\overline{\iota}}} + \psi^{\overline{\iota}}\right)\right]}{\mathrm{D}t}$$
$$+ \left[E^{\overline{\overline{\iota}}} + \epsilon^{\iota}\rho^{\iota}\left(\frac{1}{2}\mathbf{v}^{\overline{\iota}}\cdot\mathbf{v}^{\overline{\iota}} + K_{E}^{\overline{\overline{\iota}}} + \psi^{\overline{\iota}}\right)\right]\mathsf{I}{:}\mathbf{d}^{\overline{\overline{\iota}}} - \nabla\cdot\left(\epsilon^{\iota}\mathbf{t}^{\overline{\overline{\iota}}}\cdot\mathbf{v}^{\overline{\iota}} + \epsilon^{\iota}\mathbf{q}^{\overline{\overline{\iota}}}\right)$$
$$-\epsilon^{\iota}h^{\iota} - \sum_{\kappa\in\mathfrak{I}_{c\iota}} \left(\overset{\kappa\to\iota}{M_{E}} + \overset{\kappa\to\iota}{T_{v}} + \overset{\kappa\to\iota}{Q}\right) = 0, \quad \text{for } \iota \in \mathfrak{I}$$

TCAT---Averaged Thermodynamics

$$\mathcal{V} = \left\{ \epsilon^{\iota}, \rho^{\iota}, \mathbf{v}^{\bar{\iota}}, \overset{ws\to\kappa}{M}, \mathbf{t}^{\bar{\bar{\iota}}}, \overset{ws\to\kappa}{\mathbf{T}}, E^{\bar{\bar{\iota}}}, K_E^{\bar{\bar{\iota}}}, \psi^{\bar{\iota}}, \mathbf{q}^{\bar{\bar{\iota}}}, h^{\iota}, \overset{ws\to\kappa}{Q} \right\}$$

$$\mathcal{T}^w = \frac{\mathrm{D}^{\overline{w}} E^{\overline{\overline{w}}}}{\mathrm{D}t} - \theta^{\overline{\overline{w}}} \frac{\mathrm{D}^{\overline{w}} \eta^{\overline{\overline{w}}}}{\mathrm{D}t} - \mu^{\overline{w}} \frac{\mathrm{D}^{\overline{w}} \left(\epsilon^w \rho^w\right)}{\mathrm{D}t} + p^w \frac{\mathrm{D}^{\overline{w}} \epsilon^w}{\mathrm{D}t}$$
$$+ \left\langle \eta_w \frac{\mathrm{D}^{\overline{w}} \left(\theta_w - \theta^{\overline{\overline{w}}}\right)}{\mathrm{D}t} + \rho_w \frac{\mathrm{D}^{\overline{w}} \left(\mu_w - \mu^{\overline{w}}\right)}{\mathrm{D}t} - \frac{\mathrm{D}^{\overline{w}} \left(p_w - p^w\right)}{\mathrm{D}t} \right\rangle_{\Omega_w, \Omega} = 0$$

$$\mathbf{v}^{\overline{w}} = \mathbf{v}^{\overline{s}} = \mathbf{v}^{\overline{ws}} = \text{constant}$$

$$\theta^{\overline{\overline{w}}} = \theta^{\overline{\overline{s}}} = \theta^{\overline{\overline{ws}}} = \text{constant}$$

$$\frac{\mathrm{D}^{\overline{w}} \epsilon^w}{\mathrm{D}t} = \frac{\mathrm{D}^{\overline{s}} \epsilon^s}{\mathrm{D}t} = \frac{\mathrm{D}^{\overline{ws}} \epsilon^{ws}}{\mathrm{D}t} = 0$$

$$\left\langle p_w + \mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s + \gamma_{ws} \nabla' \cdot \mathbf{n}_s - \rho_{ws} \mathbf{g}_{ws} \cdot \mathbf{n}_s \right\rangle_{\Omega_{ws}, \Omega_{ws}} = 0$$

$$\Lambda = \sum_i J_i F_i + \sum_j \mathbf{J}_j \cdot \mathbf{F}_j + \sum_k \mathbf{J}_k : \mathbf{F}_k$$

TCAT---Entropy Inequality Forms

$$\sum_{\iota\in\mathfrak{J}} \left(\mathcal{S}^{\iota} + \lambda^{\iota}_{\mathcal{M}}\mathcal{M}^{\iota} + \boldsymbol{\lambda}^{\iota}_{\boldsymbol{\mathcal{P}}}\cdot\boldsymbol{\mathcal{P}}^{\iota} + \lambda^{\iota}_{\mathcal{E}}\mathcal{E}^{\iota} + \lambda^{\iota}_{\mathcal{T}}\mathcal{T}^{\iota}\right) = \Lambda \geq 0$$

$$\sum_{\iota\in\mathfrak{J}} \left[\mathcal{S}^{\iota}_{D} + \frac{1}{\theta^{\overline{\overline{\iota}}}}\left(K_{E}^{\overline{\overline{\iota}}} + \mu^{\overline{\iota}} + \psi^{\overline{\iota}} - \frac{\left(\mathbf{v}^{\overline{\iota}}\cdot\mathbf{v}^{\overline{\iota}}\right)}{2}\right)\mathcal{M}^{\iota}_{D}\right]$$
$$+\sum_{\iota\in\mathfrak{J}} \left[\frac{\mathbf{v}^{\overline{\iota}}}{\theta^{\overline{\overline{\iota}}}}\cdot\boldsymbol{\mathcal{P}}^{\iota}_{D} - \frac{1}{\theta^{\overline{\overline{\iota}}}}\left(\epsilon^{\iota}\rho^{\iota}\frac{\mathrm{D}^{\overline{\iota}}\left(K_{E}^{\overline{\overline{\iota}}} + \psi^{\overline{\iota}}\right)}{\mathrm{D}t} + \mathcal{E}^{\iota}_{D}\right)\right]$$
$$+\frac{1}{\theta^{\overline{\overline{w}}}}\left(p^{w}\frac{\mathrm{D}^{\overline{w}}\epsilon^{w}}{\mathrm{D}t} + \mathcal{T}^{w}_{r}\right) + \frac{\mathcal{T}^{s}_{r}}{\theta^{\overline{\overline{s}}}} - \frac{1}{\theta^{\overline{\overline{ws}}}}\left(\gamma^{ws}\frac{\mathrm{D}^{\overline{ws}}\epsilon^{ws}}{\mathrm{D}t} - \mathcal{T}^{ws}_{r}\right) = \Lambda \geq 0$$

TCAT---Simplified Entropy Inequality

$$\frac{\epsilon^w}{\theta^{\overline{\overline{w}}}}\left(\mathbf{t}^{\overline{\overline{w}}}+p^w\mathbf{I}\right):\mathbf{d}^{\overline{\overline{w}}}+\frac{\epsilon^s}{\theta^{\overline{\overline{s}}}}\left(\mathbf{t}^{\overline{\overline{s}}}-\mathbf{t}^s\right):\mathbf{d}^{\overline{\overline{s}}}$$

$$+\frac{\epsilon^{ws}}{\theta^{\overline{\overline{ws}}}}\left[\mathbf{t}^{\overline{\overline{ws}}}-\gamma^{ws}\left(\mathbf{I}-\mathbf{G}^{ws}\right)\right]:\mathbf{d}^{\overline{\overline{ws}}}+\frac{\epsilon^w\mathbf{q}^{\overline{\overline{w}}}}{\left(\theta^{\overline{\overline{w}}}\right)^2}\cdot\nabla\theta^{\overline{\overline{w}}}+\frac{\epsilon^{ws}\mathbf{q}^{\overline{\overline{ws}}}}{\left(\theta^{\overline{\overline{ws}}}\right)^2}\cdot\nabla\theta^{\overline{\overline{ws}}}$$

$$+\frac{1}{\left(\theta^{\overline{\overline{s}}}\right)^2}\left[\epsilon^s\mathbf{q}^{\overline{\overline{s}}}-\left\langle\left(\mathbf{t}_s-\boldsymbol{\sigma}_s:\frac{\mathbf{C}_s}{j_s}\mathbf{I}\right)\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_s,\Omega}\right]\cdot\nabla\theta^{\overline{\overline{s}}}$$

$$-\overset{ws\to w}{M}\frac{1}{\theta^{\overline{\overline{ws}}}}\left[\left(\mu^{\overline{w}}+K_E^{\overline{\overline{w}}}+\psi^{\overline{w}}\right)-\left(\mu^{\overline{ws}}+K_E^{\overline{\overline{ws}}}+\psi^{\overline{ws}}\right)\right]$$

$$-\overset{ws\to s}{M}\frac{1}{\theta^{\overline{\overline{ws}}}}\Bigg\{\left(\mu^{\overline{s}}+K_E^{\overline{\overline{s}}}+\psi^{\overline{s}}\right)+\left\langle\frac{\boldsymbol{\sigma}_s}{\rho_s}:\frac{\mathbf{C}_s}{j_s}-\frac{1}{\rho_s}\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\right\rangle_{\Omega_{ws},\Omega_{ws}}$$

$$-\left(\mu^{\overline{ws}}+K_E^{\overline{\overline{ws}}}+\psi^{\overline{ws}}\right)\Bigg\}$$

$$-\frac{1}{\theta^{\overline{\overline{w}}}}\Bigg\{\overset{ws\to w}{\mathbf{T}}+\left(\frac{\mathbf{v}^{\overline{w},\overline{s}}-\mathbf{v}^{\overline{ws},\overline{s}}}{2}\right)\overset{ws\to w}{M}+\epsilon^w\rho^w\mathbf{g}^{\overline{w}}$$

$$+\epsilon^w\rho^w\nabla\left(\psi^{\overline{w}}+\mu^{\overline{w}}+K_E^{\overline{\overline{w}}}\right)-\nabla\left(\epsilon^w p^w\right)+\eta^{\overline{\overline{w}}}\nabla\theta^{\overline{\overline{w}}}\Bigg\}\cdot\mathbf{v}^{\overline{w},\overline{s}}$$

TCAT---Simplified Entropy Inequality

$$
\begin{aligned}
&+\frac{1}{\theta^{\overline{\overline{ws}}}}\Bigg\{\sum_{\iota\in\mathfrak{J}_p}\left[\overset{ws\to\iota}{\mathbf{T}}+\left(\frac{\mathbf{v}^{\overline{\iota},\overline{s}}-\mathbf{v}^{\overline{ws},\overline{s}}}{2}\right)\overset{ws\to\iota}{M}\right]-\epsilon^{ws}\rho^{ws}\mathbf{g}^{\overline{ws}} \\
&\quad-\epsilon^{ws}\rho^{ws}\left(\mathsf{I}-\mathsf{G}^{ws}\right)\cdot\nabla\left(\mu^{\overline{ws}}+K_E^{\overline{\overline{ws}}}+\psi^{\overline{ws}}\right) \\
&\quad-\eta^{\overline{\overline{ws}}}\left(\mathsf{I}-\mathsf{G}^{ws}\right)\cdot\nabla\theta^{\overline{\overline{ws}}}-\nabla\cdot\left[\epsilon^{ws}\gamma^{ws}\left(\mathsf{I}-\mathsf{G}^{ws}\right)\right]\Bigg\}\cdot\mathbf{v}^{\overline{ws},\overline{s}} \\
&-\frac{1}{\theta^{\overline{\overline{ws}}}}\langle p_w+\mathbf{n}_s\cdot\mathsf{t}_s\cdot\mathbf{n}_s+\gamma_{ws}\nabla'\cdot\mathbf{n}_s-\rho_{ws}\mathbf{g}_{ws}\cdot\mathbf{n}_s\rangle_{\Omega_{ws},\Omega_{ws}}\frac{\mathrm{D}^{\overline{s}}\epsilon^s}{\mathrm{D}t} \\
&+\Bigg\{\overset{ws\to w}{Q}+\left(\frac{E^{\overline{\overline{w}}}}{\epsilon^w\rho^w}-\mu^{\overline{w}}\right)\overset{ws\to w}{M}+\mathbf{v}^{\overline{w},\overline{s}}\cdot\left[\overset{ws\to w}{\mathbf{T}}+\left(\frac{\mathbf{v}^{\overline{w},\overline{s}}-\mathbf{v}^{\overline{ws},\overline{s}}}{2}\right)\overset{ws\to w}{M}\right] \\
&\quad-\langle p_w\rangle_{\Omega_{ws},\Omega_{ws}}\frac{\mathrm{D}^{\overline{s}}\epsilon^s}{\mathrm{D}t}\Bigg\}\left(\frac{1}{\theta^{\overline{\overline{w}}}}-\frac{1}{\theta^{\overline{\overline{ws}}}}\right) \\
&+\Bigg\{\overset{ws\to s}{Q}+\left(\frac{E^{\overline{\overline{s}}}}{\epsilon^s\rho^s}-\mu^{\overline{s}}\right)\overset{ws\to s}{M}-\langle\mathbf{n}_s\cdot\mathsf{t}_s\cdot\mathbf{n}_s\rangle_{\Omega_{ws},\Omega_{ws}}\frac{\mathrm{D}^{\overline{s}}\epsilon^s}{\mathrm{D}t} \\
&\quad-\left\langle\frac{\boldsymbol{\sigma}_s}{\rho_s}:\frac{\mathsf{C}_s}{j_s}-\frac{1}{\rho_s}\mathbf{n}_s\cdot\mathsf{t}_s\cdot\mathbf{n}_s\right\rangle_{\Omega_{ws},\Omega_{ws}}\overset{ws\to s}{M}\Bigg\}\left(\frac{1}{\theta^{\overline{\overline{s}}}}-\frac{1}{\theta^{\overline{\overline{ws}}}}\right)=\Lambda\geq 0
\end{aligned}
$$

TCAT---Model Closure

$$\frac{\mathrm{D}^{\overline{\iota}}\left(\epsilon^{\iota}\rho^{\iota}\right)}{\mathrm{D}t} = -\epsilon^{\iota}\rho^{\iota}\nabla\cdot\mathbf{v}^{\overline{\iota}}, \quad \text{for } \iota \in \mathcal{J}_p$$

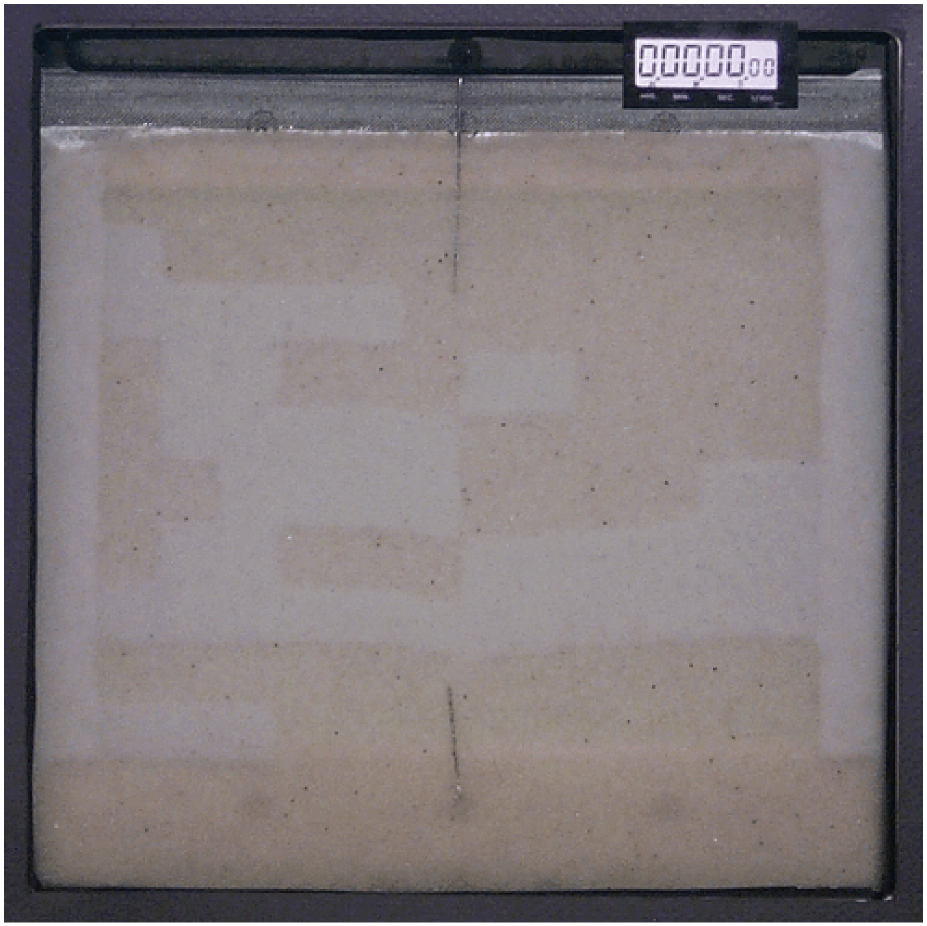
$$\frac{\mathrm{D}^{\overline{\iota}}\left(\epsilon^{w}\rho^{w}\mathbf{v}^{\overline{w}}\right)}{\mathrm{D}t} = -\epsilon^{w}\rho^{w}\mathbf{v}^{\overline{w}}\nabla\cdot\mathbf{v}^{\overline{w}} - \hat{\mathsf{R}}^{w}\cdot\mathbf{v}^{\overline{w},\overline{s}} - \epsilon^{w}\rho^{w}\nabla\left(\psi^{\overline{w}} + \mu^{\overline{w}}\right)$$

$$\frac{\mathrm{D}^{\overline{\iota}}\left(\epsilon^{s}\rho^{s}\mathbf{v}^{\overline{s}}\right)}{\mathrm{D}t} = -\epsilon^{s}\rho^{s}\mathbf{v}^{\overline{s}}\nabla\cdot\mathbf{v}^{\overline{s}} + \nabla\cdot\left(\epsilon^{s}\mathbf{t}^{\overline{\overline{s}}}\right) + \epsilon^{s}\rho^{s}\mathbf{g}^{\overline{s}} + \epsilon^{w}\rho^{w}\mathbf{g}^{\overline{w}}$$
$$+\epsilon^{w}\rho^{w}\nabla\left(\psi^{\overline{w}} + \mu^{\overline{w}}\right) - \nabla\left(\epsilon^{w}p^{w}\right) + \hat{\mathsf{R}}^{w}\cdot\mathbf{v}^{\overline{w},\overline{s}}$$

Characteristics of Behavior

- NAPLs leave a state of residual saturation in media through which they pass
- NAPLs follow a complex pattern of flow, which is importantly influenced by media heterogeneity
- LNAPLs accumulate on the top of the water table
- DNAPLs can sink below the water
- NAPLs often reach stable configurations of locally high saturations known as pools
- NAPLs are usually sparingly soluble and DNAPL contaminants usually degrade slowly---thus are long lived in the environment

Two-Dimensional Unsaturated Downward Vertical Displacement of TCE



- 21-cm x 21-cm two-dimensional cell
- Pooled TCE established
- TCE dyed with Oil Red O for visualization
- Established bottom brine layer
- Drained to unsaturated conditions
- 0.3 pore-volume downward flush with mixture of sulfosuccinate surfantants
- Measured 80.0% TCE removal, no visible pools
- Reference: Hill et. al. [ES&T, 35(14), 2001]