FINAL REPORT

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On the Inclusion of the Interfacial Area Between Phases in the Physical and Mathematical Description of Subsurface Multiphase Flow

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EXECUTIVE SUMMARY

A distinguishing feature of multiphase subsurface flow in comparison to single phase flow is the existence of fluid-fluid interfaces. These interfaces define phase boundaries at the pore scale and influence overall system behavior in many important ways. For example, fluid-fluid interfaces support non-zero stresses, allowing for different fluid phase pressures across each interface. In problems of inter-phase mass transfer, such as evaporation in vadose zone (e.g., air-water) systems or dissolution in NAPL- or hydrocarbon--water systems, all mass is exchanged across the interfaces. While interfaces are central to multiphase flow physics and associated contaminant transport, their treatment in traditional porous-media theories has been given little attention. Theoretical work developed in this project provides a general framework within which interfacial area is incorporated explicitly into volume-averaged equations for conservation of mass, momentum, and energy. This has led to an expanded set of continuum-scale equations that carry the overhead burden of an associated set of expanded constitutive relationships. To make these equations a scientifically useful tool for the study of fluid flows in vadose zone or NAPL-contaminated environments, parameterization of these constitutive relationships must occur. This parameterization requires that the equations be studied in light of the actual behavior of porous media systems. To perform the early stages of this work effectively, the porous media must be controlled, well-understood systems that lend themselves to careful scientific analysis. This project has contributed to the improved understanding and precise physical description of multiphase subsurface flow by combining theoretical derivation of equations, lattice Boltzmann modeling of hydrodynamics to identify characteristics and parameters, and simplification to field-scale equations to assess the advantages and disadvantages of the complete theory. This approach includes both fundamental scientific inquiry and a path for inclusion of the scientific results in a technical tool that will improve assessment

capabilities and predictability for multiphase flow situations (e.g., vadose zone contamination or due to spills of organic materials in the natural environment).

RESEARCH OBJECTIVES

The mathematical study of flow in porous media is typically based on the 1856 empirical result of Henri Darcy. This result, known as Darcy's Law, states that the velocity of a single phase flow through a porous medium is proportional to the hydraulic gradient. The publication of Darcy's work has been referred to as "the birth of groundwater hydrology as a quantitative science" [*Freeze and Cherry*, 1979]. Although Darcy's original equation was found to be valid for slow, steady, one-dimensional, single-phase flow through a homogeneous and isotropic sand, it has been applied in the succeeding twelve dozen years to complex transient flows involving multiple phases in heterogeneous media. To attain this generality, a modification has been made to the original formula such that the constant of proportionality between flow and hydraulic gradient is allowed to be a spatially varying function of the system properties. The extended version of Darcy's Law is expressed in the form:

$$\mathbf{q}^{\alpha} = -\mathbf{K}^{\alpha} \bullet \mathbf{J}^{\alpha} \tag{1}$$

where $\mathbf{q}^{\alpha}$ is the vector volumetric flow rate per unit area of the α-phase fluid, $\mathbf{K}^{\alpha}$ is the hydraulic conductivity tensor of the α-phase and is a function of the viscosity and saturation of the α-phase, and $\mathbf{J}^{\alpha}$ is the vector hydraulic gradient that accounts for pressure, gravitational, and interphase effects. Although this generalization is occasionally criticized for its shortcomings, equation (1) is considered today to be a fundamental principle in analysis of porous media flows [e.g. *McWhorter and Sunada*, 1977].

If, indeed, Darcy's experimental result is the birth of quantitative hydrology, a need still remains for quantitative analysis of porous media flow to progress toward maturity on a strong theoretical foundation. The problem of unsaturated flow of water has been attacked using experimental and theoretical tools since the early part of the twentieth century. *Sposito* [1986] attributes the beginnings of the study of soil water flow as a subdiscipline of physics to the fundamental work of *Buckingham* [1907] which uses a saturation-dependent hydraulic conductivity and a capillary potential for the hydraulic gradient. *Scheidegger* [1974], however, notes that extension of Darcy's law to multiple phase flow is only theoretical speculation. *Hillel* [1971] warns against overlooking the limitations of present multiphase theories in considering soil physics problems:

> In applying to the soil oversimplified concepts and theories borrowed from simpler or "purer" systems, we must be careful not to take our models too seriously or literally. Present-day theories of soil physics should therefore be taken with a grain or two of salt, as they were developed by entirely fallible (though courageous) soil physicists desperately attempting to make their system manageable by simplifying it. As the science develops, however, its tools are becoming more sophisticated and capable of handling some of the complexities which previous soil physicists disregarded.

Indeed, it has been the goal of this project to continue to make use of sophisticated theoretical and computational tools to handle some of those disregarded complexities of multiphase flows.

Placement of the quantitative understanding of unsaturated and multiphase porous media flow on firm footing requires that the problem be attacked from a variety of complementary

perspectives. The conservation principles of mass, momentum, and energy must be obtained at a macroscale, a scale consistent with the scale of analysis of the problem, i.e. much greater than the scale of a single pore. These principles must consider phases, interfaces between phases, and common lines where interfaces come together. Fundamental tools to derive macroscale equations include averaging theorems that relate the average of a derivative to the derivative of the average thus allowing a rigorous change in scale from microscopic to macroscopic. Appropriate theorems for phases, interfaces, and contact lines have been collected in *Gray et al.* [1993]. This technique does indeed produce equations for the water, soil, air, and organic phases; but it also leads to complications in that constitutive relations are needed for the variables that arise due to averaging.

A theoretical tool exists for developing constitutive functions in a systematic manner that is based on the second law of thermodynamics. This method follows the procedure of *Coleman* and *Noll* [1963] and assures that the second law of thermodynamics is not violated by constitutive approximations. To use this method, the dependence of energy on independent variables (e.g. density, temperature, etc.) must first be hypothesized. Based on these hypotheses, various thermodynamic properties of the system may be determined and inter-related. These relations must then be subjected to experimental scrutiny to determine if they are appropriate for the particular system of interest. If found to be inappropriate or lacking in generality, the hypotheses must be modified and the constitutive relations reformulated. Thus a framework is provided in which assumptions can be consistently employed to simplify the problem description and to help identify areas where parameters must be determined from experimental or computational considerations.

Babcock and Overstreet [1955, 1957] succinctly describe two guidelines for a correct application of thermodynamics to a heterogeneous system:

> First, the number of properties that must be fixed in order to define the state of a given system must be established experimentally. … Thus, the number of differential terms required to specify the total differential in some given property can be known only from experimental observation of the system. … Second, … it is essential that all thermodynamic formulations be written only in terms of macroscopic properties of the system, that is, in terms of state variables.

Thus to develop a thermodynamic theory for multiphase flow, it is important to provide a correct dependence of the macroscale energy on macroscale variables only. Point quantities such as contact angle and interface curvature that can be observed at the pore scale cannot be state variables for a macroscopic theory, yet their effects must be accounted for. On the other hand, saturation and interfacial area per unit volume are macroscale variables that should contribute to the proper description of the thermodynamic state of a multiphase system. Insights gained from applying microscale-based thermodynamics to multiphase systems [e.g. *Edlefsen and Anderson*, 1943; *Morrow*, 1970; *Moeckel*, 1975; *Miller and Neogi*, 1985] are extremely valuable in formulating a macroscale theory, but do not replace the need for that theory.

In recent years, a systematic averaging procedure has been developed that transforms the conservation equations and the thermodynamic equations from the microscale to the macroscale [*Hassanizadeh and Gray*, 1979a, 1979b, 1980]. This procedure provides a consistent framework for the study of multiphase flows. Subsequent enhancements of that theory include the theorems

for averaging of interfacial conservation equations [*Gray and Hassanizadeh*, 1989]. The use of these theorems in a general framework allowing for dependence of free energy on saturations and areas leads to a complete, but complex set of equations that require knowledge of a huge number of parameters [*Hassanizadeh and Gray*, 1990; *Gray and Hassanizadeh*, 1991a, 1998]. DOE support for the present project has led to a theoretical description that provides an adequate description of the phenomena of interest while requiring a minimum of new parameters [*Gray*, 1999, 2000; *Gray et al.*, 1999, 2000].

Besides conservation equations and a thermodynamic framework, experimental studies are needed to ensure that real multiphase systems behave according to the theory and to provide a basis for measuring physical parameters or coefficients. These experiments can be laboratory studies, computer studies, field studies, or some mix of these, and can encompass different spatial or temporal scales. Physical experiments at both the laboratory and the field scale provide fundamental data to which any theory must conform. Traditional physical experiments usually provide measured values for individual phase pressures and for phase saturations. Combination of these data lead to standard relationships such as that between capillary pressure and saturation.

If new theories are to be tested, and these theories introduce additional macroscopic variables that include measures of interfacial areas and perhaps contact-line lengths, then new experimental techniques must be developed to measure these quantities and assess their relationship to macroscopic state variables like pressure, saturation, and velocity. Some progress on these issues has been recently made [*Soll et al.*, 1997]. *Montemagno and Gray* [1995] have developed a method to experimentally measure the interfacial areas between two immiscible fluids in a porous medium, although the approach was complex and limited to a static, non-flowing system. *Rashidi et al.* [1996] were able to analyze dynamic pore scale velocity and tracer concentrations in an experimental medium, although their approach was limited to single-phase flow. *Saripalli et al.* [1996] have pursued methods to measure fluid interfacial areas in larger field scale systems, but have met with limited success. *Coles et al.* [1998] applied Computed Micro-Tomography (CMT) to investigate fluid distributions and permeabilities. Using this technique it was possible to obtain the pore geometry, porosity, absolute permeability, and an end-state relative permeability, plus the multiphase fluid distribution in the pore space at this end state. However, this approach is expensive, and limited to a small sample size. Absent more general technologies to measure changing variables such as interfacial area per unit volume, some alternative technique must be developed to serve as an independent test of the proposed theory. One such alternative is numerical simulation.

Numerical simulators can be implemented at different scales to provide support and verification of the developed theory. First a microscale or pore scale model can be employed to solve the continuum conservation equations. The solutions obtained can then be averaged and compared with solutions of the macroscopic equations in order to determine, or gain further insight into the validity of macroscale parameters. For example, *Celia et al.* [1995] and *Reeves and Celia* [1996] have successfully employed idealized capillary network models to study the interdependence of capillary pressure, saturation, and interfacial area at different equilibrium (non-flowing) configurations of the pore fluids. Although network models are powerful for studying static, equilibrium systems, they are limited by their use of idealized pore space configurations, and the inability to directly distinguish sub-pore phenomena, such as interfaces and contact lines. In this project, we utilized lattice Boltzmann techniques to model the pore scale flows of two immiscible fluids. This

approach is ideal for transient, non-equilibrium flow problems while also affording us the opportunity to measure new macroscopic variables such as interfacial areas, saturations, and capillary pressures for comparison with the new macroscale equations. These macroscale equations will then be used in a discrete numerical model to simulate field scale phenomena. The synergistic combination of theory, microscale modeling, and field scale modeling will thus advance capabilities for understanding, simulation, and assessment of multiphase subsurface contamination problems.

Lattice Boltzmann models provide the opportunity to interrogate a transient pore scale simulation to determine the geometric configuration of moving fluids and extract the values of important microscopic variables (e.g., velocity, pressure). In this sense, the physics that influence microscopic fluid behavior during a simulation will be appropriately accounted for in the averaged measurements of the system behavior. Lattice Boltzmann algorithms have been developed and applied to simulating a variety of pore-scale flow phenomena. These methods provide a computational capability to study the details of multiphase flow in pores [*Gunstensen et al*., 1991; *Succi et al*., 1993; *Chen et al*., 1992]. Recent simulations of two-phase fluid flows have favorably represented observed fluid flow patterns visually and have provided encouraging qualitative agreement with observed experimental results [*Grunau*, 1993; *Hazlett et al.*, 1998]. The simulations from that two-phase model have concentrated on representations of displacement experiments where one fluid is used to sweep out another that originally occupies the pore space. Thus the procedure is ideal for examination of the evolution of interfaces and regions of fluid occupation that can be averaged for identification of macroscale parameters and functions. Recent increases in computing capability now make it possible to simulate a variety of physical phenomena in pores using pore-scale data from samples that are sufficiently large to provide meaningful results [*Chen et al*., 1991; *Soll et al*., 1994; *Hazlett, 1995; Hazlett et al.*, 1998, *Zhang et al.*, 2000].

The lattice Boltzmann approach is an ideal surrogate experimental platform from which macroscale parameters, equations of state, and invariance relationships associated with the derived multiphase flow equations and a particular porous medium geometry can be identified. For example, *Ladd* [1994] has applied the lattice Boltzmann approach to study single phase flow in a periodic array of spheres. Averages of his solutions have been used to estimate the permeability of the macroscopic system and, more importantly, demonstrate that permeability is a constant property of the system under a range of different flow configurations. *Tompson and Gray* [1986b] have used a similar pore scale modeling technique to measure parameters associated with a macroscopic constitutive model of momentum dispersion in porous media, and demonstrate that these terms are invariant with respect to changes in the average flows as postulated by theory. During this project, *Soll et al.* [1998a] have begun to examine the correlated variations of saturation and interfacial areas in a capillary displacement problem using a lattice Boltzmann model. *Zhang et al.* [2000] have applied the lattice Boltzmann model to demonstrate the validity of the Representative Elementary Volume scaling relationship that is used in macroscopic averaging theories.

In addition to being able to represent a particular porous medium geometry, the lattice Boltzmann approach provides a means of generalizing our understanding in ways that are often not possible with physical experiments. Using the LB model we can run the exact same experiment in the exact same physical domain with very carefully controlled variations. For example, we can modify only the solid surface wettability to assess exactly how wettability affects permeability or

interfacial area - time relationships. Furthermore, we can control the spatial distribution of wettability, to gain insight into how variable wetting affects fluid movement [*Soll et al.*, 1998]

Once parameters and invariance relationships are identified for a particular medium, they may be used within the macroscopic model equations to analyze practical multiphase flow problems, much in the same way hydrologists do now. This project will take steps to solve the parameterized macroscopic equations for a simplified laboratory-scale system in order to demonstrate their applicability, identify “choke” points in the application process, and understand more fully the importance of the new formulation with respect to more traditional methods. This process is expected to lead to simplifications or modifications in the theory and pore scale modeling activities by distinguishing between important and less important features of the equations, as determined from their contribution to the macroscale solutions. The result is an increased ability to make predictions and improve effectiveness of remediation.

METHODS

The goal of improving the understanding, physical description, and numerical simulation of multiphase flows depends on successful integration of three study techniques [*Soll et al.*, 1997]:

1. *An averaging procedure* coupled with application of the macroscale second law of thermodynamics;

2. *Use of the lattice Boltzmann methods* to simulate pore scale phenomena; and

3. *Implementation of a discrete numerical model* that solves the averaged equations making use of parameters gleaned from the lattice Boltzmann study.

Each of these three techniques will be outlined here.

The Averaging Procedure and Resultant Equations

The direct solution of the microscale mass, momentum, and energy transport equations in the void space of a multi-phase porous system is theoretically possible but practically impossible for any real system. The solution of the equations requires boundary conditions that cannot be specified without detailed knowledge of the pore geometry. Thus, an averaging procedure is employed to affect a change of scale at which governing (pore scale) equations are considered. This averaging provides equations for essentially overlapping continua. For example, at the microscale, a wetting phase occupies particular portions of space. To describe this phase at the microscale, the boundaries between the phase and all other phases must be well-defined. At the macroscale, however, the wetting phase is described in terms of its average properties within a small volume. Thus, at each point, a macroscale phase is characterized as occupying a fraction of the available volume and, perhaps, to have a certain amount of interface per volume with other phases. Each phase in the system is described in a similar fashion. At the microscale, the interfaces serve as particular locations where boundary or flux conditions must be applied. At the macroscale, the surfaces are within the volume and must be accounted for as source terms. Precise definition of the interface shape is neither required nor possible to obtain at the macroscale.

Although the macroscale equations remove the tremendous burden of having to specify the internal geometry of the multi-phase system, they do provide a number of challenges that must be overcome if they are to be useful. Constitutive theory, at the macroscale, is required to close the equations so that the number of unknowns is equal to the number of equations obtained. Effort has been expended to find appropriate parameterization of the source terms that arise in various situations [e.g. *Whitaker*, 1967; *Tompson and Gray*, 1986a; *Rose*, 1988]; nevertheless, the matching of the approximations to field data remains a challenge. Heterogeneities observable at various scales require that the constitutive laws adapt to account for these non-uniformities at different regions in the domain. An even more fundamental challenge is to select the macroscale equations that are needed to provide a consistent theoretical description of the system under study. In particular, it must be determined if adequate system description requires mass, momentum, and energy balance equations for the phases and species in the phases or if corresponding equations for the interfaces, contact lines, and even common points are also necessary. When modeling is done at the microscale, these locations of interaction are explicitly accounted for and described by jump conditions that are treated as auxiliary conditions. However, when the phase equations are averaged, the jump conditions tend to be incorporated into the source terms such that the full dynamics of interactions are not accounted for. For flow of a single fluid in a porous medium, neglect of interface dynamics is warranted. However, for multiple fluid flow, where the interfaces between the fluid play an extremely important role in the system behavior, the interface equations may be necessary for providing a consistent system description [*Drew*, 1971; *Marle*, 1982; *Hassanizadeh and Gray*, 1990; *Gray and Hassanizadeh*, 1991].

One of the more interesting side effects of averaging governing equations is that new geometric parameters appear that were not present in the original microscale system. For example, porosity, the volume of space available for fluid flow per unit volume of the system, is a key quantity at the macroscale. At the microscale, the concept of porosity is not employed; a particular point is considered to be in one phase or another or on an interface. Saturation, the fraction of the void space occupied by each fluid, is another parameter that is important at the macroscale but does not exist at the microscale. Because these new parameters are important to the description of the state of the porous media system, it is also important to ensure that the complete and correct thermodynamic description of the system incorporates these variables as needed. The description employed at the microscale, the standard dependence of energy on microscale independent variables, may not still be valid or complete at the macroscale. The entropy inequality, the mathematical statement of the second law of thermodynamics, is an important and essential tool in determining what quantities need be included as independent variables. This equation may be obtained by averaging the microscale statement of the entropy equation. Then by hypothesizing dependence of free energy on independent variables, particular thermodynamic restrictions are obtained.

In light of these considerations, the approach to be adopted here is to obtain a minimum set of governing equations and thermodynamic relations that is consistent with experimental observation of multiphase flow in porous media. Besides serving to provide a framework for the mathematical description of multiphase flow, this set of equations should relate to the known microscale dependence of free energy, observed equilibrium states in multiphase systems, and information that can be obtained from idealized models of porous media. The following procedure for developing usable equations for the simulation of multiphase subsurface flow will be used:

1. *Derivation of conservation equations for phases, interfaces, and common lines at the porous media scale, the macroscale, and of the entropy inequality for the system*. Work to do this has been ongoing for many years, including the work supported in the first three years of DOE funding. Initially, the work considered only phases; and balance laws studied were restricted to conservation of mass and momentum [e.g. *Whitaker*, 1967]. The papers by *Hassanizadeh and Gray* [1979a, 1979b, 1980] employed an averaging theory that extended this approach to inclusion of the energy equation and entropy inequality. Subsequent to this, *Gray and Hassanizadeh* [1989] developed averaging theorems for interfaces and developed conservation relations for the interface properties as well. Finally, theorems for averaging over common lines were developed by *Gray et al.* [1993] and have been employed in papers by *Gray and Hassanizadeh* [1998] and *Gray* [1999a]. The latter references, in fact, present sets of averaged equations of mass, momentum, and energy conservation for phases, interfaces, and common lines that form the basis for a general study of multiphase flow. At present, we have developed a complete set of equations for phases, interfaces, and common lines. However, film effects need to be accounted for.

2. *Postulation of thermodynamic dependences of the energy on independent variables for phases, interfaces, and common lines and incorporation of these postulates into the entropy inequality.* This task was addressed thoroughly in a consistent manner for macroscale thermodynamic systems for the first time under this project. There is a need to ensure that the fundamental ideas of thermodynamics are not neglected when making use of the principles of continuum mechanics. Note that classical thermodynamics deals with equilibrium systems only, while continuum mechanics deals with both equilibrium states and the transitions when a system is not at equilibrium. Nevertheless, it is important that the continuum mechanical description reduce to the classical thermodynamic one at steady state. Thermodynamics requires that consistent and systematic postulates be made concerning the dependence of internal energy on independent variables. The presence of interfaces adds the complication of excess surface properties such as mass per unit area and interfacial tension that must be accounted for in a conceptually and quantitatively consistent manner (surface excess properties from a microscale Gibbsian perspective are discussed, for example, in *Miller and Neogi* [1985] and *Gaydos et al.* [1996]). Then, from the postulated forms, relations among variables and insights into system behavior can be obtained. One of the most useful approaches for postulating the thermodynamic dependence of internal energy is the approach advocated in *Callen* [1985] and used to advantage by *Gaydos et al.* [1996] in a study of microscopic capillarity, whereby the extensive energy is considered to be a function of the extensive variables of the system. With this approach, confusion about differences among Helmholtz potential, Gibbs potential, grand canonical potential, and enthalpy are diminished as they are simply mathematical rearrangements of the original postulated form for internal energy. Insights gained from applying microscale-based thermodynamic postulates to multiphase systems [e.g. *Edlefsen and Anderson*, 1943; *Morrow*, 1970; *Moeckel*, 1975; *Miller and Neogi*, 1985; *Alts and Hutter*, 1988a, 1988b, 1988c, 1989] are extremely valuable in formulating a macroscale theory, but do not replace the need for formulation of that theory in terms of macroscale variables. To develop the macroscale thermodynamics, the postulative approach of *Callen* [1985] has been employed after extension to the macroscale perspective *Gray* [1999a, 2000]. This same approach will be employed here to obtain thermodynamic relations that are appro-

priate for a macroscale description of a porous media system that includes films and wetting fluids at very low saturation. One important point is that from the perspective of the macroscale, the system is composed of coexisting phases at a point and not juxtaposed phases, interfaces, and common lines. Thus, in fact, the energy postulate should be made in terms of all components. Decomposition of the internal energy for the total system to the component parts describing each phase, interface, and common line must be undertaken with caution.

3. *Determination of mechanical equilibrium constraints and their incorporation into the entropy inequality.* Although the geometric variables including porosity, saturation, areas per volume, and common line length per volume are independent variables, their deviations around an equilibrium state are not (e.g., a change in saturation of one fluid would be expected to cause a change in the amount of area bounding that fluid). These considerations give rise to employment of mechanical equilibrium concepts in conjunction with averaging theorems to obtain relations among changes in geometric variables. These closure relations are useful in deriving both thermodynamic equilibrium conditions and dynamic relations between changes in geometric variables the thermodynamic state of the system [*Gray*, 2000; *Gray et al.*, 2000], but they present challenges for parameterization that can be addressed through the lattice Boltzmann simulation.

4. *Exploitation of the entropy inequality to obtain equations that describe equilibrium system behavior.* The entropy inequality provides a condition that requires a system to be at its minimum energy state when at equilibrium. It also provides some guidance on allowable dependences of functions on independent variables. Furthermore, it provides guidance on the positivity or negativity of some coefficients by forbidding, for example, transfer of heat from a cold body to a warmer one or flow in a direction opposite to a gradient in potential. A theoretical tool exists for developing constitutive functions in a systematic manner that is based on the second law of thermodynamics. The procedure of *Coleman* and *Noll* [1963] was applied to single phase systems to assure that the second law of thermodynamics is not violated by constitutive assumptions. Complementing this work are extensions and variations that consider multiphase mixtures and interfaces [e.g., *Hassanizadeh and Gray*, 1980; *Gray and Hassanizadeh*, 1991a; *Müller*, 1993; and *Svendsen and Hutter*, 1995]. In the first years of the present DOE funding, the correct procedure for postulating macroscopic dependence of energy on system independent variables has been determined *Gray* [1999a] and *Gray et al.* [2000]. This procedure will also be used in considering film effects to ensure that the thermodynamic formulation is consistent, both physically and mathematically.

5. *Linearization of some of the constitutive functions to obtain conservation equations with their coefficients capable of modeling dynamic systems.* Although the localization theory for a three phase system provides 35 balance equations of mass, momentum, and energy for the phases, interfaces, and common lines, it also contains 150 constitutive functions that must be specified. The dependence of these functions on other system parameters are obtained under some assumptions. Also, the functional forms of the dependences of the stress tensors are obtained. However, in general, the actual functional relations between the constitutive functions and their independent variables are not known except at equilibrium. For example, at equilibrium the heat conduction vector is zero; but the general functional representation of

this vector in terms of independent variables is not known at an arbitrary state of disequilibrium. Thus a compromise must be employed whereby functional forms are obtained "near" equilibrium. Experimental and computational studies must subsequently be undertaken to determine the definition of "nearness." By this approach, which is similar to taking a Taylor series expansion of a function and ignoring higher order terms, results such as the heat conduction vector being proportional to the temperature gradient and a velocity proportional to a potential gradient are obtained. Because multiphase porous media flows are typically slow, they also satisfy the conditions of being "near enough" to equilibrium that this linearization procedure provides relations appropriate for many physical situations. It is important to note, however, that although the equations are linearized, the coefficients that arise still may have complex dependence on system parameters (e.g., relative permeability, which is traditionally simplified to be a function of saturation). Identification of those coefficients remains a challenging task. Additionally, the inclusion of films will add to the numbers of equations, variables, and constitutive parameters. It is essential that these be examined with the intention of obtaining physically meaningful values and not simply curve fitting values. The analysis procedures used in conjunction with the theoretical developments serve as stiff tests for the theory and guide the work toward a minimally sufficient formulation.

6. *Determination of the physical interpretation of the coefficients, as possible, using geometric approximations that provide insight into required laboratory measurements.* It is important that the theoretical procedure not simply be a propagator of unknown coefficients that have no chance of being measured or even understood. Therefore, effort must be made to allow insightful study of the new coefficients through laboratory and computer experimentation. Thus, although a general formulation is employed, it is simplified to a manageable, yet still challenging and relevant, set of equations that can be effectively studied. As progress is made in parameterizing these systems, the approximations employed can be relaxed so that more complex systems may be studied. Indeed, in the first three years of the study, the correct formulation of the balance of forces at a common line has forced an alteration in the theory so that the variables will be meaningful [*Gray et al.*, 2000].

Elements of these steps, representing progress made this project, have already been reported in *Hassanizadeh and Gray* [1997]; *Gray and Hassanizadeh* [1998], *Muccino et al.* [1998]; *Gray* [1999a,;, Gray and Schrefler, 1999; Gray, 2000], *Gray and Miller* [2000], *Gray et al.* [2000], and *Tompson et al.* [2000]. Additional considerations to be addressed in future work the investigators would like to undertake are discussed below.

Subjecting the theoretical results from the averaging theory to the scrutiny of the lattice Boltzmann and field-scale simulations will allow for determination of important constitutive parameters, the importance of the additional dependence of capillary pressure on interfacial area, and whether a simpler form of the relative permeability function is appropriate. Note that the explicit inclusion of interfacial area per volume in the formulation may be of particularly significant value in simulating biodegradation reactions, surfactant or steam injection techniques, where the amount of area between phases is important for mass transfer.

Fundamentals of the Lattice Boltzmann Approach

Pore scale simulations are based on a lattice Boltzmann (LB) model for the numerical solution of the Navier-Stokes equations. In this approach, the fluid is conceptualized as an infinite distribution of "particles" that are moved across a lattice and "collided" at lattice junctions over discrete time steps. The method is a generalization of a simpler lattice gas automata method in which a finite number particles are explicitly considered. In the lattice gas approach, particles are assigned to lattice nodes and moved to neighboring nodes in a two-step process during each time step. Each particle is assigned a unit mass and a unit momentum in the direction of one of the lattice links. In the first part of a time step, particles move to their next lattice location ("streaming") according to their assigned direction of movement. In the second part of the time step, they interact with other particles that arrive at the same location ("collision") such that their directions (momentum) for the next time step are reassigned. Because particles are not created or destroyed in this process, mass is conserved. The collision step at each lattice junction is designed to preserve the ensemble momentum of the incoming particles. Although it is conceptually simple, care must be taken in choosing the numbers of particles, lattice geometry, collision operators, and time scaling factors in order to realize an ensemble "fluid" behavior that satisfies the Navier Stokes equations, especially when incompressible conditions are of interest.

The LBM approach is more general in that explicit consideration of discrete particles at lattice points is replaced by the use of average or *expected* particle populations. Particle distribution functions (PDF's) are used to represent the expected particle mass moving in discrete lattice directions. They are updated in time using analogous "streaming" and "collision" steps that conserve PDF mass, momentum and energy. The PDF conservation equations are applied to the Boltzmann equation and the correct choice of coefficients ensures that the ensemble "fluid" behavior again satisfies the Navier-Stokes equations. Using purely local particle interactions on the lattice, this technique is second order accurate in space and time.

The LBM approach is particularly attractive for the current application because

- *It can efficiently be adapted to treat immiscible two-fluid (or multiphase) systems* [*Gunstensen et al.* 1991; *Grunau,* 1993; *Grunau et al*. 1993]. In this sense, moving interfacial regions are generated from a local "particle-to-particle" repulsion effect which, in turn, generates appropriate drops in pressure that are consistent with interfacial surface tensions. Competitive techniques based upon the full Navier Stokes equations have difficulty tracking the interface and rapidly become computationally intractable.
- *It naturally incorporates arbitrary flow domain geometries.* Any space can be modeled equally efficiently, from totally open (no walls) to nearly all solid. The ease in handling complex geometries comes from the ease in handling no-slip (or controlled slip) conditions on irregular boundaries. Another advantage is its ability to finely discretize the pore space and the flow therein, while still incorporating tens to hundreds of pores. It therefore provides a tool to study the influence of many microscale system variables on resulting bulk scale flow behavior.
- *It offers high resolution that can accurately capture sub-pore scale phenomena.* The finer-than-pore scale discretization means that the LB method can resolve

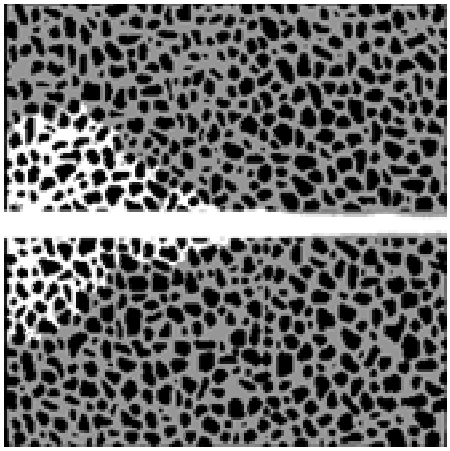

Figure 1. Lattice Boltzmann simulation of 2D immiscible displacement in a "fractured" synthetic pore space. White fluid is displacing grey fluid. The solid is shown as black. The total system size is 128×128 [*Soll et al.,* 1998b]

and quantify sub-pore scale features, such as interfaces moving through pores, films, and individual interface velocities. Other microscale methods that discretize only to the level of an individual pore must still use empirical relations to describe sub-single pore phenomena.

- *It has a number of inherent computational advantages* [*Chen*, 1996]. In the LBM the convection operator is linear, where it is non-linear in traditional methods. The pressure is described by an equation of state, and therefore does not require solving a Poisson equation. Thus, solution for the pressure distribution is non-iterative, and has better numerical stability. The transformation from the microscopic particle distribution functions to the macroscopic quantities is simple, requiring only local communication and arithmetic calculations. Therefore, no matrix inversion is required. The simple local operations make this method extremely parallelizable, and result in a fast efficient technique on parallel computer systems.

The LB approach is mature enough that extensive reviews and derivations are available in the literature [for example, see *Chen et al*., 1995; *Rothman and Zaleski*, 1994; *Succi et al*., 1993]. The derivation of *Grunau et al*. [1993] provides good background for understanding and extending the LBM.

Lattice Boltzmann models have been developed and applied to simulate a variety of pore-scale flow phenomena associated with groundwater remediation problems and enhanced oil recovery. Simulations of two-phase fluid flows have favorably represented observed fluid flow patterns visually, and have provided very encouraging qualitative agreement with observed experimental results [*Eggert et al*.; 1991; *Grunau*, 1993; *Grunau et al*., 1993b; *Soll et al*., 1994; *Ferreol and Rothman*, 1995; *Hazlett et al*., 1995; *Coles et al*., 1998; and *Soll et al.,* 1998b]. As an example, Figure 1 shows a snapshot of an immiscible fluid displacement in a "fractured" synthetic pore space. A two-dimensional system is used for ease in demonstration in black and white. The system is 128×128 pixels and the resulting fluid and solid locations and interfaces are highly resolved.

As Figure 1 helps to demonstrate, it is an easy task to quantify the interfaces between the different phases. The sub-pore scale resolution results in highly accurate measurements of the contacts between phases. The temporally discrete nature of this model also makes it simple to compute changes in contact areas over time. Similarly, the pressure on either side of an interface can be calculated from the local lattice pressures, and related to the apparent curvature of the interface, on a pore by pore basis.

The lattice Boltzmann work utilized the Los Alamos-developed LB multiphase flow code (LBMFC) which is based on the 3-D, 2 speed, 14-neighbor lattice of *Chen et a*l. [1992]. Multiple fluids are implemented based on *Gunstensen et al.* [1991] with modifications described by *Grunau et al*. [1993a] to more efficiently model fluid interfaces and fluid segregation. The LBMFC has the following capabilities:

- Three-dimensional
- Arbitrarily complex flow domains (pore space geometries)
- More than 16.7 million lattice sites (equivalent to 256^3)
- Spatially variable rock surface properties (such as wettability)
- One or two fluids plus the solid
- Arbitrary fluid characteristics (density, viscosity, interfacial tension)
- No-flow or periodic boundary conditions on the domain sides
- Fixed pressure drop, fixed flow rate, or Dirichlet conditions for the inlet and outlet sides
- Film flow

It is currently coded to provide the following information:

- Exact fluid distributions
- Average fluid saturation
- Local and averaged velocities
- Local and averaged pressures
- Interfacial area (fluid-fluid and fluid-solid)
- Momenta
- Bulk quantities such as permeability and relative permeability
- Temporal tracking of all parameters / variables (time derivatives)

Purpose of the lattice Boltzmann simulations

The purpose of the lattice Boltzmann simulations is to provide a computational experimental platform from which further insights into the improved representation of multiphase flow can be investigated. From this perspective, for example, we can investigate the validity of the geometric closure relationships more carefully [e.g., eq. 78 of *Gray*, 1999a], especially in cases where complex geometries exist and more substantial fluid movements are of interest. We are also in a position to eval-

uate, or investigate the existence of, proposed constitutive relationships that relate, for example, the mean (macroscopic) interfacial curvature in a multiphase system to the saturation and interfacial area(s) [e.g., eq. 80 of *Gray,* 1999a]. LB simulations also provide the ability to look at the differences among the mean curvature and mean pressures and mean interfacial pressure drops in equilibrium (static) and nonequilibrium flow configurations.

It is important to recognize that this approach is fundamentally computational in nature and offers a slightly different perspective than would a corresponding physical experiment. Much of the desired information at the pore scale would be hard to obtain or measure in a physical sense in a real apparatus. Theoretically, the lattice Boltzmann approach offers greater possibilities for interrogating flow solutions at the pore scale for meaningful variables. Nevertheless, this does not mean the required manipulations are trivial. Indeed, we invested a considerable amount of effort over the four years of this project in developing new tools for the lattice Boltzmann study, especially as needed for calculating relative permeabilities, saturations, interfacial areas, and interfacial curvatures over the course of a transient simulation [*Hou et al.* 1997; *Hazlett et al.,* 1998; *Soll et al.,* 1998a, 2000; and the *Research Accomplishments* section]. We are continuing to develop and verify new tools for measuring contact line lengths, interfacial pressure drops, and interfacial velocities that will be needed for experimental problems focused on the new multiphase flow equations.

Discrete Numerical Simulation

As defined here, “discrete numerical simulation” involves the development of a field-scale numerical model for flow based on a set of simplified and parameterized equations [such as eqs. 76-83 of *Gray,* 1999a]. Medium properties (e.g., the porosity or saturated hydraulic conductivity) and parametric relationships (e.g., for the capillary pressure equation-of-state as in *Gray,* [1999a], equation (80) or for relative permeability) can be determined from LB simulations or other *a-priori* specification. Discrete numerical simulators developed using traditional finite difference or finite element techniques [e.g., *Celia and Gray,* 1992] and applied to one or more multiphase flow test problems characterized by specific auxiliary conditions, geometrical features, fluid types, and porous medium properties are important tools for verification of the theoretical advances. Simulations to be investigated should be chosen to be compatible with the applicable range of the simplified equations [such as eqs. 76-83 of *Gray,* 1999a], medium, geometrical, and process restrictions associated with the lattice Boltzmann model, and other comparative or “canonical” experiments analyzed using more traditional theoretical approaches. Based on eqs. 76-83 of *Gray* [1999a] as an example, such an activity will require the solution of a set of nonlinear coupled equations and a focused, well-planned approach to maintain solution accuracy and consistency [e.g., *Celia et al.,* 1990, *Celia and Binning,* 1992, *Tompson and Gray,* 1986b]. Under the funding provided by this project we have developed the background and insights necessary to integrate discrete numerical simulation into the development of improved descriptions of multiphase flow in porous media.

RESULTS

During the years of this grant, we addressed all the research tasks identified in our original proposal. We have made progress, in varying degrees, on all fronts. We have gained insight into important processes and expanded our thoughts on the modeling of these processes. The results of our analysis have provided some new understanding of the physical mechanisms driving multiphase flow. These mechanisms are theoretically more complex but physically more simple than we had anticipated. As a result of this, we need to continue our work in order to enhance the theory, better demonstrate its utility through applications, and move this work to a more applicable state for the research and assessment community. Our proposal was to perform basic research, and we used the funding to support basic research. During this first part of the study, we encountered several obstacles in the theory that were greater than we had originally anticipated. The effort required in overcoming those obstacles distracted from our implementation of the computational verifications and macroscale model development. However, the theory developed is the first thermodynamically consistent approach to the macroscale description of the physics of multiphase flow in porous media. We are poised to extend our computational capability with a clear understanding of the pitfalls we face and of the robustness of the theory developed.

The following sections indicate the breadth of issues addressed and the progress made on the main points of activity.

Development of general macroscale equations based on the averaging framework and thermodynamics

This task has led to several significant findings. First, in the averaging of the equations, questions existed as to the presence of energy per mass for the interface and common lines. The obvious issue relates to the meaning of such quantities in light of the possibility of massless interfaces. The need existed to formulate the energy in such a fashion that a re-derivation is not required for the case of massless interfaces. This was accomplished by formulating all energy on a per-unit-averaging-volume basis. Because the equations apply at the macroscale, the interfacial energy per unit volume of the system is a meaningful parameter. Thus by this rather simple (in hindsight, obvious) definition of parameters, it was possible to obtain a set of governing equations that was both easy to work with and intuitively satisfying. We were thus able to successfully obtain general macroscale equations from the averaging framework for phases, interfaces, and common lines.

Once these equations are obtained, the problem exists as to how to exploit them. In the past, continuum mechanics formulations have led to some paradoxes in that, for example, results obtained working with energy per unit mass were not consistent with those obtained based on energy per unit volume. Additionally, the reduction of the thermodynamic relations obtained at the macroscale to microscale thermodynamics was not possible. This problem has been overcome by borrowing the classical microscale approach of positing the dependence of extensive energy on extensive variables and extending this to the macroscale. This approach has allowed for a completely consistent set of thermodynamic relations that account for subscale processes in an appropriate manner. One very useful outcome of the analysis performed was the recognition that the grand canonical potential plays a key role in describing the physics of multiphase flow (It should be emphasized that introduction of this function is a convenience, not a necessity, as the set

of equations remain consistent as long as the thermodynamic potentials are defined correctly in terms of the energy.). In fact, by formulating the entropy inequality in terms of this function, it is possible to gain a correct understanding of the "pressure" in multiphase flow. It is ironic that the definition of a "pressure" at the macroscale has been presented as a variety of thermodynamic forms in the continuum mechanics and multiphase flow literature. However, these theoretical efforts have not been concerned with how these pressures might be measured. We have discovered what is, in fact, being measured (the grand canonical potential) and how this can be related to the phase movement, the interfacial areas, and the common line dynamics. Thus, a connection has been made between the theory and the field measurements of properties.

One long-standing and persistently under-appreciated problem has been the fact that in transforming the governing equations from the microscale to the macroscale, geometric parameters are introduced. These parameters are the volume fractions of each of the phases, the interfacial areas per unit volume, and the common line length per unit volume. For example, in a system composed of two fluids and a solid, seven such parameters will be introduced (three volume fractions, three interfacial areas per volume, and the common line length per volume). One of these parameters may be eliminated through the constraint that the volume fractions must sum to 1, but six parameters remain such that six additional (dynamic) equations are needed to close the system. In the more traditional approaches of soil physics, this need is unrecognized altogether, and is "accounted" for by imposing hysteresis and non-uniqueness in the capillary pressure and relative permeability relationships. In the more recent past, this need was articulated, but has essentially been buried in the complex manipulations of the entropy inequality with the result that, again, inconsistencies existed. In this context, two approaches seem to have been prevalent. The first was to ignore the issue. This results in a system where the interfacial tension and capillary pressure must be identically zero. This is equivalent to requiring that the dynamics of the interfacial quantities be unimportant. The second approach was to add complex functional dependence to the energy function and assume that the terms that are obtained account for the missing equations. In fact, this approach is also faulty because the added terms can be shown to be zero or very small based on physical grounds such that they cannot possibly account for the actual phenomena observed. Instead, we have performed a variational analysis of the macroscale energy function so that mechanical, as well as thermodynamic, equilibrium conditions can be formally established. Then the results of this equilibrium analysis have been extended using the entropy inequality to include the "near equilibrium" equations. These six additional equation provide, for the first time, reasonable conditions on the dynamics of the geometric quantities such that a closure scheme for the equations is obtained.

Thus, we have obtained a theoretical approach that is i) internally consistent; ii) consistent with microscale dynamics; iii) thermodynamically consistent; iv) able to yield reasonable closure relations; v) capable of describing the movement and distribution of phases, interfaces, and common lines in multiphase subsurface flow; and vi) subject to verification by experimental and computational analyses.

Equation Simplification

We have worked to ensure that we are doing more than generating equations and coefficients. It is our conviction that understanding of the dynamics of phase interfaces is particularly important for

the modeling of multiphase flow. To demonstrate this, we have been developing a series of idealized problems that involve the study of fluid movements in idealized porous media constructed from repeated arrays of simple geometric pore spaces. The fluid movements are limited to small displacements that allow infinitesimal changes in the fluid saturations, interfacial areas, interfacial curvatures, contact line lengths, and solid wall contact angles to be evaluated analytically and compared with the dynamic geometry equations cited above. We are thus able to demonstrate that our formulation describes these situations and that our geometric closure relations are, in fact, meaningful. These simple problems have also provided important insights into the nature of force balances along contact lines and their role in determining interfacial contact angles along solid boundaries in the pore spaces.

Inherent in this process is an equation simplification procedure in which the most simple aspects of the balance equations (e.g., one-dimensional macroscopic behavior, fixed porosity, rigid solid) are preserved for the analysis. We are using these equations as a means to identify the most pertinent aspects of the new theory to be tested in the lattice Boltzmann simulations, as well as to guide our initial macroscopic model development.

Lattice Boltzmann Parameterizations

The purpose of the lattice Boltzmann method (LBM) simulations is to provide a computational experimental platform from which to test, validate, and, if necessary, refine the improved macroscopic equations of multiphase flow. From this perspective, for example, we can investigate the validity of new geometric balance relationships that arise in these equations [e.g., eq. 78 of *Gray*, 1999a], evaluate or investigate the validity of proposed constitutive relationships [e.g., eq. 80 of *Gray*, 1999a] in physically realistic media with complex pore geometries, or even estimate the magnitude of parameters that are part of these relationships. To date, the LBM effort has largely been focussed on

- The completion of several multi-phase LBM simulations in porous media [*Hou et al.*, 1997; *Hazlett et al.*, 1998].
- The development of new “interrogation” tools within the LBM framework to calculate new geometric parameters called for in the new macroscopic equations [*Soll et al.*, 2000].
- The development of several preliminary test problems for the application and validation of the interrogation tools [*Soll et al.*, 1998; *Zhang et al.*, 2000].

The overall progress in the LBM effort is less than anticipated, largely because of difficulties in developing the new interrogation tools. Although several simple problems have been studied for testing purposes, we still need to focus additional attention on verifying the measurement tools and applying them to experimental simulations as described earlier.

In order to design experimental simulations for testing or assessing the validity of the macroscale flow formulation, it was necessary to add capabilities in the LBM to track interfaces and common lines in the pore spaces of the medium, measure their areas and lengths per unit volume of the medium, and calculate interfacial curvatures, interfacial velocities, and pressure differences across these interfaces. These are in addition to existing capabilities that measure bulk

phase saturations, pressures, and velocities from LBM simulation results. There are two steps to obtaining values for these terms: deriving the theoretical definitions at the microscale, and computationally implementing these definitions within the LBM. For example:

Interfacial area. Interfacial area per unit volume is an important new variable that appears in the new macroscopic formulation [e.g., eqs. 78-81 of *Gray,* 1999a], and is, as it turns out, one of the easiest parameters to calculate within the LBM. The information can be derived directly from the fundamental solutions of the LBM in terms of the distribution of particle "color" or phase mass. Image analysis techniques allow these solutions to be directly interrogated for measurement of the interfacial areas between any pair of materials (fluid-fluid or fluid-solid) at any snapshot in time. Multiphase fluid displacement in a sinusoidal tube was used as a test case for looking at the influence of wettability on interfacial area [*Soll et al.*, 1998]. This seemingly simple but mathematically complex problem illustrated the strong role that surface wetting and large variations in the pore and throat configurations in actual porous materials have on fluid movements. Interfacial areas varied significantly, depending on the wettability of the pore walls and the constrictions in the tube, reinforcing our belief that interfacial area is a critical aspect of the system that must be explicitly incorporated at the macroscale.

Common line length. Common line length per unit volume [appearing, for example, in eq. 79 of *Gray,* 1999a], on the other hand, is much more difficult to implement. Conceptually it is similar to interfacial area, but computationally it would require extensive calculations and tests. Due to the computational difficulty and potential second order influence (behind interfacial area), we have delayed attempting to implement common line length calculations in favor of other, more important terms like interfacial curvature.

Interfacial curvature. The mean interfacial curvature per unit volume [appearing, for example, in eqs. 78 and 80 of *Gray,* 1999a] is another important new macroscopic variable. Eq. 80 [of *Gray,* 1999a] suggests that the product of mean curvature (of the interfaces separating two immiscible fluids) and the surface tension along that interface is related to the difference in mean fluid pressures, or "capillary pressure," and a term proportional to the rate of change of fluid saturation. There are two important implications of this result:

- *At equilibrium,* the product of mean curvature and interfacial tension is exactly balanced by the "traditional" capillary pressure. Since the mean curvature is postulated to be a function of both saturation *and* interfacial area [e.g., eq. 83a of *Gray,* 1999a], the usual assumption that capillary pressure (at equilibrium) is only dependent on saturation would appear to be incomplete.
- *Away from equilibrium,* under transient, flowing conditions, there appears to be a dynamic "capillary pressure" that differs from the mean curvature by the term proportional to the rate of change of saturation. This has also been suggested by *Kalaydjian* [1992], who was able to measure a coefficient of proportionality in a simple experiment.

Thus, measurement of the curvature has important implications in verifying various geometric balances as well as providing further insight into the dynamic capillary pressure relationship. However, its computational evaluation within the LBM framework is turning out to be a significant challenge, equal in many respects to the development of the theory itself. At the microscale, along an interface, the *local* interfacial curvature is defined to be the divergence of the normal vector on the interface. The corresponding macroscopic value is the mean curvature existing within a unit volume of porous medium, which can be a transient and spatially variable quantity. Interfacial curvature can be extracted from the basic LBM information, but it is somewhat more complex than calculating interfacial area. It is first necessary to locate and operate on the interface between fluids. Within the LBM, the interface is defined to be the locus of lattice points where the magnitude of the gradient in fluid "color" is maximized. Although the "color gradient" vector can be calculated everywhere in terms of fluid densities, it is only nonzero at interfaces where different fluids – in LBM terminology "fluids of different color" – come together. Hence, when its magnitude is maximal, the color gradient vector (i) lies on an interface, (ii) is *normal* to the interface, and (iii) when normalized by its magnitude, is equivalent to the normal vector on the interface. Thus, we have defined how to get the curvature, but are still engrossed in its implementation within the LBM.

Mean pressure drop across the interface. Once the interface between fluids is located, determining the local pressure drop across the interface is relatively straightforward. Calculating the pressure drop requires calculating the average pressure drop across all interface nodes. The challenge arises in determining if this quantity can be computed directly as a domain average or whether it needs to be averaged over individual interfaces existing in discrete pores. Because computing pressure drops depends on the color gradient, which is a signed value, it is possible that a given system state may have positive and negative local quantities, which would result in an incorrect system average. This is a condition that must be addressed in the work proposed in the next three year term.

Derivation of extraction methods for other parameters and terms called for in the macroscale equations, such as interfacial velocity and common line length are thus far incomplete. They remain at the stage of ideas and discussion. These, too, are important to the validation of the macroscale approach, and must be addressed in future extensions of this work.

Macroscopic Model Development

The purpose of the macroscopic model development phase was to build a "field scale" model of multiphase flow that is based upon the new balance equations and constitutive approximations developed in this project. Our initial approach has been to focus on a one-dimensional model, similar to the simplified versions cited previously, and to develop the iterative solution process that would be followed in a computational solution procedure. Important in this process is a careful consideration of initial and boundary conditions that will be encountered, from both the mathematical and field measurement perspectives. Progress on this topic is strongly dependent on the completion of the previous topics. Issues relating to boundary condition formulation, particularly for the interfacial area properties and the geometric quantities, cannot be addressed until the equations being solved have been finalized. Based on the results obtained and the understanding gained

from our analyses of the equations, we believe we are in a strong position to pursue this topic aggressively in the extended funding period. We view the application of our theoretical results in computational models to be an extremely important aspect of this overall study that ties our work together and establishes that this fundamental research will impact simulation and study of multiphase flow problems in the field.

Iterative Activities

Our experience in the years of this study has confirmed the crucial importance of iteration among equation development, lattice Boltzmann information, and the discrete numerical model. By subjecting the equations developed to scrutiny based on what the parameters in the model mean, how the equations model idealized problems, how to extract information from the lattice Boltzmann form, and how field scale models should be constructed, we have been able to improve our theoretical development and recognize phenomena (such as film flow and contact angle dynamics) that must be adequately captured. This particular form of iterative scientific inquiry for studying pore scale processes was the focus of a workshop entitled "Porous Media Processes— Linking the Pore and Continuum Scales through Theory, Direct Modeling, and Direct Experimentation", held at Los Alamos National Laboratory in 1997. This meeting was co-sponsored by the PIs on this project as was summarized in a recently published meeting report [*Soll et al.*, 1997].

RELEVANCE AND IMPACT

The relevance and impact of the work is identified as follows:

(a) The current work addresses the very real and fundamental problem of how we quantitatively describe multiphase flow phenomena (including unsaturated flow) in porous media. Specifically, it addresses a number of acknowledged shortcomings of the traditional models that have been used for decades to forecast these flows, This is central to the myriad of existing and potential contamination problems across the DOE complex, and has specific relevance to contamination problems in the vadose zone.

(b) The current work has illuminated the complexity of multiphase flow processes in porous media and has sought to better describe the more important features of the physics. These improvements ultimately should serve to improve the viability of analyses of fluid and contaminant movement in porous media which are central to he effectiveness of many, if not all in-situ cleanup technologies and programs.

(c) This work is fundamental research in its entirety, and is not directly central to "applied technology development". This work was proposed as such to the original EMSP program announcement (1996) under which such fundamental research was sought.

(d) The results are of interest to many scientists and engineers in DOE laboratory system, academia, and in foreign institutions who study and do experimental and theoretical investigations in the areas of multiphase flow in porous media. The relevant applications not only include subsurface contaminant migration and remediation problems, but are also germane to

the fields of petroleum reservoir engineering, agricultural engineering, and water resources engineering.

(e) The originally proposed research envisioned several practical applications which, as described elsewhere, were never completed due to time constraints.

(f) The scientific capabilities of the three collaborators have improved, as each brought individual specialties to the project. The project afforded the three collaborators the opportunity to become more knowledgeable of these specialties and appreciative of the interdisciplinary interactions this project requires.

(g) As mentioned in (a), the work has led to a number of new insights that address shortcomings in the present-day models of multiphase flow in porous media.

(h) As has been mentioned in Future Work section, additional advances need to be made in representation of geometric dynamics, selection thermodynamic variables for inclusion of film processes, and assurance that macroscale representations are consistent with microscopic and field observations.

PRODUCTIVITY

During the four years of this grant, several of the proposed research tasks identified have been addressed with success. We have gained insight into important processes and expanded our thoughts on the modeling of these processes. The results of our analysis have provided some new understanding of the physical mechanisms driving multiphase flow. These mechanisms are both theoretically more complex but physically more simple than we had anticipated. As a result of this, we are in search of sources of funding to continue our work that will allow us to enhance the theory, better demonstrate its utility through applications, and move this work to a more applicable state for the research and assessment community. During the current study, we encountered several obstacles in the theory that were greater than we had originally anticipated. The effort required in overcoming those obstacles distracted from our implementation of the computational verifications and macroscale model development. Our progress was also hampered by one-year delays in funding the national laboratory collaborators by DOE. However, the theory developed is the first thermodynamically consistent approach to the macroscale description of the physics of multiphase flow in porous media. We are poised to extend our computational capability with a clear understanding of the pitfalls we face and of the robustness of the theory developed.

PERSONNEL SUPPORTED

Dr. William G. Gray, University of Notre Dame (PI)
Dr. Julia Muccino, University of Notre Dame (postdoctoral associate)
Dr. Anton Leijnse, University of Notre Dame (postdoctoral associate)
Dr. Wendy E. Soll, Los Alamos National Laboratory (co-PI, collaborator)
Dr. Andrew F. B. Tompson, Lawrence Livermore National Laboratory (co-PI, collaborator)

PUBLICATIONS

Gray, W. G., "Thermodynamics and Constitutive Theory for Multiphase Porous-media Flow Considering Internal Geometric Constraints," Advances in Water Resources, Vol. 22, No. 5 (January, 1999) pp. 521-547.

Gray, W. G., "Macroscale Equilibrium Conditions for Two-Phase Flow in Porous Media," *International Journal of Multiphase Flow*, Vol. 26, No. 3 (March, 2000) pp. 467-501.

Gray, W. G., "Elements of a Systematic Procedure for the Derivation of Macroscale Conservation Equations for Multiphase Flow in Porous Media," in *Kinetic and Continuum Thermodynamical Approaches to Granular and Porous Media*, edited by K. Hutter and K. Wilmanski, CISM Courses and Lectures No. 400, International Centre for Mechanical Sciences, Springer-Verlag, Vienna (April, 1999), pp. 67-129.

Gray, W. G., and S. M. Hassanizadeh, "Macroscale Continuum Mechanics for Multiphase Porous-media Flow Including Phases, Interfaces, Common Lines, and Common Points," *Advances in Water Resources*, Vol. 21, No. 4 (July, 1998) pp. 261-281.

Gray, W. G., and C. T. Miller, "Comment on 'Dynamics of Wetting Fronts in Porous Media' by I. Mitkov, D. M. Tartakovsky, and C. L. Winter," *Physical Review E* Vol. 61, No. 2 (February, 2000) pp. 2150-2151.

Gray, W. G., and B. A. Schrefler, "Thermodynamic Approach to Effective Stress in Partially Saturated Porous Media", *European Journal of Mechanics A/Solids* (in press).

Gray, W. G., A. F. B. Tompson, and W. E. Soll, "Closure Conditions for Two-Fluid Flow in Porous Media" (submitted, March, 2000).

Hassanizadeh, S. M., and W. G. Gray, "Basic Equations of Flow and Transport in Porous Media," in *Bioremediation: Principles and Practice, Volume I, Fundamentals and Applications*, edited by S. K. Sikdar and R. L. Irvine, Technomic Publishing Company, Inc., (October, 1997), pp. 19-57.

Hazlett, R. D., S. Y. Chen, and W. E. Soll. Wettability and Rate Effects on Immiscible Displacement: Lattice Boltzmann Simulation in Microtomographic Images of Reservoir Rocks. *J. of Petroleum Science and Engineering*, 20(3-4), (Jun 1998), pp. 167-175.

Hou, S., X. Shan, Q. Zou, G. D. Doolen, and W. E. Soll. Evaluation of Two Lattice Boltzmann Models for Multiphase Flow. *J. of Computational Physics*, 138 1997. pp. 695-713.

Muccino, J. C., W. G. Gray, and L. A. Ferrand, "Toward an Improved Understanding of Multiphase Flow in Porous Media," *Reviews of Geophysics*, Vol. 36, No. 3 (August, 1998) pp. 401-422.

Soll, W. E., W. G. Gray, D. R. Janecky, and A. F. B. Tompson. Meeting Report: Linking the Pore and Continuum Scales Through Theory, Modeling, and Experimentation. *EOS, Transactions, American Geophysical Union*, 78(44), Nov 4, 1997, p. 495

Soll, W. E., W. G. Gray, and A. F. B. Tompson, "Influence of Wettability on Constitutive Relations and its Role in Upscaling," in *Computational Methods in Water Resources XII, Vol. 1* (edited by V. N. Burganos, G. P. Karatzas, A. C. Payatakes, C. A. Brebbia, W. G. Gray, and G. F. Pinder), Computational Mechanics Publications, Southampton (1998), pp. 413-420.

Soll, W. E., A. F. B. Tompson, and W. G. Gray. Lattice Boltzmann Used to Determine Constitutive Relations for Multiphase Flow Equations. (in preparation, March 2000).

Tompson, A. F. B., W. E. Soll, and W. G. Gray, "An Assessment of Closure Conditions for Two-Fluid Flow in Porous Media Based on Idealized Models" (submitted, August, 2000).

Zhang, D., R. Zhang, S. Chen, and W.E. Soll, Pore scale study of flow in porous media: Scale dependency, REV, and statistical REV, *Geophysical Research Letters* (in press, 2000).

INTERACTIONS

Workshop

A workshop entitled, “Porous Media Processes— Linking the Pore and Continuum Scales through Theory, Direct Modeling, and Direct Experimentation”, was held at Los Alamos National Laboratory in 1997. This meeting was co-sponsored by the PIs on this project as was summarized in a recently published meeting report [*Soll et al.*, 1997].

Presentations and Lectures

Gray, W. G., “A Systematic Approach to Modeling Multiphase Flow in Porous Media,” Department of Environmental Sciences, University of Virginia (November, 1996) 1 hr. lecture.

Gray, W. G., “The Challenges of Incorporating Internal Structure into Models of Subsurface Flow and Transport,” Symposium on Advanced Simulation of Subsurface Flow and Contaminant Transport, sponsored by Cray Computing at the North Carolina Supercomputing Center (December, 1996) 30 minute lecture.

Gray, W. G., “Theoretical Considerations in the Development of Models of Multiphase Flow in Porous Media,” First Ever Workshop on Porous Media Processes - Linking the Pore and Continuum Scales Through Theory, Direct Modeling, and Direct Experimentation, Los Alamos (April, 1997) 1 hr. lecture.

Gray, W. G., “Thermodynamic Considerations in Multiphase Flow,” Fourth SIAM Conference on Mathematical and Computational Issues in the Geosciences, Albuquerque (June, 1997) 30 minute lecture.

Gray, W. G., “After Dinner (Fluid) Film Festival,” Dunwalke International Workshop on Multiphase Flow in Porous Media, Princeton University (October, 1997) 1.5 hr. lecture.

Soll, W.E. Integrating Important Microscale Characteristics into Field Scale Prediction Through Upscaling. International Workshop on Characterization and Measurement of the Hydraulic Properties of Unsaturated Porous Media, Riverside, CA (October 22-24, 1997).

Gray, W. G., “Framework for Systematic Description of Multiphase Flow Physics,” Department of Geography and Environmental Engineering, The Johns Hopkins University (November, 1997) 1 hr. lecture.

Gray, W. G., “Framework for the Systematic Description of the Physics of Multiphase Flow in Porous Media,” Department of Mathematics, University of North Carolina (February, 1998) 2 hr. lecture.

Gray, W. G., “Theoretical Aspects for Consideration of Multiphase Flow in Porous Media,” Geoanalysis Group, Los Alamos National Laboratory (May, 1998) 1.5 hr. lecture.

Soll, W. E., W. G. Gray, and A. F. B. Tompson, “Influence of Wettability on Constitutive Relations and its Role in Upscaling,” XII International Conference on Computational Methods in Water Resources, Crete, Greece (June 15-19, 1998).

Gray, W. G., “Macroscopic and Microscopic Description of Porous Material Flow and Transport,” Centre International des Sciences Mécaniques (CISM), Udine, Italy (July, 1998) 6 hrs. of lectures.

Gray, W. G.,“On the Derivation of Equations for Single Phase Flow in Porous Media,” Workshop on Nonlinear Flow and Transport Processes in Porous Media, Delft University of Technology, Delft, The Netherlands (November, 1998) 2 hr. lecture.

Gray, W. G., “On the Geometric Closure Conditions for Multiphase Flow in Porous Media,” Tutorial Lectures on Nonlinear Flow and Transport Processes in Porous Media, Delft University of Technology, Faculty of Civil Engineering and Geosciences, Delft, The Netherlands (November, 1998) 1 hr. lecture.

Gray, W. G., “Incorporation of Interfacial Areas in Models of Two-phase Flow in Porous Media,” Department of Civil Engineering and Structures, Hong Kong University of Science and Technology, Hong Kong (December, 1998) 2.5 hrs. of lectures.

Gray, W. G., “The Importance of Interfacial Areas to Multiphase Flows,” Centre for Water Research, University of Western Australia, Nedlands, Australia (February, 1999) 1 hour lecture.

Gray, W. G., “On the Incorporation of Interface Physics into the Analysis of Multiphase Flow in Porous Media,” CSIRO Land and Water Seminar Series, Perth Laboratory, Australia (March, 1999) 1 hr. lecture.

Gray, W. G., “A Continuum Approach to Multiphase Flow in Porous Media,” Tutorial Lecture Series, Centre for Water Research, University of Western Australia, Nedlands, Australia (February - March, 1999) 5 hrs. of lectures.

Gray, W. G., “On Closure of the Flow Equations for Two-Phase Flow in Porous Media,” Workshop on FLow and Transport in Porous Media, organized by Department of Mathematics, University of Bergen, held in Lindas, Norway (June, 1999) 1 hr. lecture.

Gray, W. G.,“On the Need for a Consistent Approach to Modeling Multiphase Flow in Porous Media,” Matematisk Institutt, Universitetet I Bergen, Norway (June, 1999) 1 hr. lecture.

Gray, W. G., “An Extended Description of Two-Phase Flow in Porous Media,” Norsk Hydro, Bergen, Norway (June, 1999) 1 hr. lecture.

Tompson, A. F. B., W. E. Soll, and W. G. Gray, “Lattice Boltzmann simulation of multiphase flow at the pore scale -- Implications for improving macroscale flow theories”, User's Meeting, Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA, July 21--24, 1999

Gray, W. G., “Elements of Multiphase Flow Dynamics,” Computational and Applied Mathematics Department, Rice University, Houston, TX (April, 2000), 1 hr. lecture.

Gray, W. G., “Scaling Issues in Multiphase Flow Modeling,” Department of Mathematics, Texas A&M University, College Station, TX (April, 2000) 1 hr. lecture.

Tompson, A. F. B., W. E. Soll, and W. G. Gray, ``Lattice Boltzmann simulation of multiphase flow at the pore scale: Implications for improving macro-scale flow theories", U. S. Department of Energy, Environmental Management Science Program, Annual Meeting, Atlanta, GA, April, 2000.

FUTURE WORK

Although we believe that we have exceeded the goals outlined in our proposal for the development of the averaging framework as, we also have identified some issues that require further attention and clarification. First among these is the definition of capillary pressure in the multiphase system. Experimental studies designed to generate curves of capillary pressure vs. saturation typically specify capillary pressure as a pressure difference between two external fluid reservoirs. We believe that a more consistent approach defines the capillary pressure at a point within the system as an average pressure jump across the interfaces within an averaging volume. Our intent would be to demonstrate this hypothesis. To do this will require some additional analysis and the specific inclusion of fluid films in our formulation. Films are extremely important in multiphase flow, and the interfaces between films and bulk fluids must be captured in a complete thermodynamic analysis. We are confident that the film effects can be captured within the framework we have developed, but several tasks must be performed including evaluation of coefficients that arise in the expanded dependence of energy on independent variables. This task involves the inclusion of disjoining pressure in the formulation. We have some preliminary results relating to the solid phase involving the disjoining pressure and the expectation is that an extended formulation including the fluids can be obtained.

Although the three basic scientific procedures that we are pursuing - thermodynamically consistent averaging, LB simulation, and field scale model development - have merit in their own right, it is the integration of these approaches that offers the potential for significant strides in the development of the next generation of physics-based simulation models. The principal investigators have worked together on and discussed these approaches among themselves for over fifteen

years. We also bring the perspectives of our experience in academia and in the national laboratories to this project. These perspectives have convinced us of the need to integrate sound scientific description of multiphase flow processes with robust simulation models at multiple scales if the important problems involving DNAPL and the vadose zone are to be attacked effectively.

LITERATURE CITED

Alts, T., and K. Hutter, Continuum description of the dynamics and thermodynamics of phase boundaries between ice and water. Part I: Surface balance laws and their interpretation in terms of three dimensional balance laws averaged over the phase change boundary layer, *J. Non-equilibrium Thermodynamics*, **13**, 221-257 (1988a).

Alts, T., and K. Hutter, Continuum description of the dynamics and thermodynamics of phase boundaries between ice and water. Part II: Thermodynamics, *J. Non-equilibrium Thermodynamics*, **13**, 259-280 (1988b).

Alts, T., and K. Hutter, Continuum description of the dynamics and thermodynamics of phase boundaries between ice and water. Part III: Thermostatics and its consequences, *J. Non-equilibrium Thermodynamics*, **13**, 301-329 (1988c).

Alts, T., and K. Hutter, Continuum description of the dynamics and thermodynamics of phase boundaries between ice and water. Part IV: On thermostatic stability and well posedness, *J. Non-equilibrium Thermodynamics*, **14**, 1-22 (1989).

Babcock, K. L., and R. Overstreet, Thermodynamics of soil moisture: a new application, *Soil Science*, **80**, 257-263 (1955).

Babcock, K. L., and R. Overstreet, The extra-thermodynamics of soil moisture, *Soil Science*, **83**, 455-464 (1957).

Buckingham, E., Studies on the movement of soil moisture, *Bureau of Soils Bull. 38*, USDA, Washington, D. C. (1907).

Callen, H. B., *Thermodynamics and an Introduction to Thermostatistics*, 2nd Edition, John Wiley and Sons, New York (1985).

Celia, M. A., E. T. Bouloutas, and R. L. Zarba, A general mass-conservative numerical solution for the unsaturated flow equation, *Water Resources Research*, **26**(7), 1483-1496 (1990).

Celia, M. A. and P. Binning, A mass-conservative numerical solution for two-phase flow in porous media with application to unsaturated flow, *Water Resources Research*, **28**(10), 2819-2828 (1992).

Celia, M. A., and W. G. Gray, *Numerical methods for differential equations: fundamental concepts for scientific and engineering applications*, Prentice Hall, (1992).

Celia, M. A., P. C. Reeves, and L. A. Ferrand, Recent advances in pore scale models for multiphase flow in porous media, *Reviews in Geophysics*, Supplement, **00**, 1049-1057 (1995)

Chen, S. Y, H. D. Chen, D. O. Martinez, and W. H. Matthaeus, Lattice Boltzmann model for simulation of magnetohydrodynamics. *Phys. Rev. Let.*, **67**(27), 3776-3779 (1991).

Chen, S. Y., H. D. Chen, G. D. Doolen, S. Gutman, and M. X. Lee, A lattice gas model for thermohydrodynamics. *J. Stat. Phys*., **62**(5/6), 1121-1151 (1991).

Chen, S. Y., S. P. Dawson, G. D. Doolen, D. R. Janecky, and A. Lawniczak. Lattice methods and their applications to reacting systems. *Computers & Chemical Engineering*, **19**(6-7), 617-646 (1995).

Chen, S. Y., D. O. Martinez, and R. Mei, On boundary conditions in lattice Boltzmann methods. *Physics of Fluids*, **8**(9) 2527-2536 (1996).

Chen, S. Y., Z. Wang, X. W. Shan, and G. D. Doolen, Lattice Boltzmann computational fluid-dynamics in three dimensions. *J. Stat. Phys*., **68**(3/4), 379-400 (1992).

Coleman, B. D., and W. Noll, The thermodynamics of elastic materials with heat conduction and viscosity, *Archive for Rational Mechanics and Analysis*, **13**, 168-178 (1963).

Coles, M. E., R. D. Hazlett, P. Spanne, W. E. Soll, E. L. Muegge, and K. W. Jones, Pore level imaging of fluid transport using synchrotron x-ray microtomography, *J. of Petroleum Science and Engineering*, **19**(1-2) 55-63 (1998).

Drew, D. A., Averaged field equations for two-phase media, *Studies in Applied Mathematics*, **50**(2), 133-166 (1971).

Edlefsen, N. E., and A. B. C. Anderson, Thermodynamics of soil moisture, *Hilgardia*, **15**, 31-298 (1943).

Eggert, K. G., S. Y. Chen, B. J. Travis, D. W. Grunau, E. Loh, and F. Kovarik. Simulation of pore scale porous media flow using lattice gas methods, *Proceedings of SPE/UH Emerging Technologies Conference*, 269-279 (1990).

Ferreol, B, and D. H. Rothman, Lattice-Boltzmann simulations of flow through Fontainebleau sandstone, *Transport in Porous Media*, **20**(1-2), 3-20 (1995).

Freeze, R. A., and J. A. Cherry, *Groundwater*, Prentice-Hall, Englewood Cliffs (1979).

Gaydos, J., Y. Rotenberg, L. Boruvka, P. Chen, and A. W. Neumann, The generalized theory of capillarity, in *Applied Surface Thermodynamics*, (edited by A. W. Neumann and J. K. Spelt), Surfactant Science Series, **63**, Marcel Dekker, New York, 1-51 (1996).

Gray, W. G., and S. M. Hassanizadeh, Averaging theorems and averaged equations for transport of interface properties in multiphase systems, *International Journal of Multiphase Flow*, **15**(1), 81-95 (1989).

Gray, W. G., and S. M. Hassanizadeh, Unsaturated flow theory including interfacial phenomena, *Water Resources Research*, **27**(8), 1855-1863 (1991a).

Gray, W. G., and S. M. Hassanizadeh, Paradoxes and realities in unsaturated flow theory, *Water Resources Research*, **27**(8), 1847 (1991b).

Gray, W. G., A. Leijnse, R. L. Kolar, C. A. Blain, *Mathematical Tools for Changing Spatial Scales in the Analysis of Physical Systems*, CRC Press, Boca Raton, FL (1993).

Gray, W. G., M. A. Celia, and P. C. Reeves, Incorporation of interfacial areas in models of two-phase flow, Vadose Zone Hydrology: Cutting Across Disciplines, M. B. Parlange and J. W. Hopmans, eds., Refereed volume in honor of D. R. Nielsen and J. W. Biggar, Oxford University Press, 58-85 (1999).

Gray, W. G., and S. M. Hassanizadeh, Macroscale Continuum Mechanics for Multiphase Porous-media Flow Including Phases, Interfaces, Common Lines, and Common Points, *Advances in Water Resources*, **21**(4), 261-281 (1998)

Gray, W. G., and C. T. Miller, Comment on 'Dynamics of Wetting Fronts in Porous Media' by I. Mitkov, D. M. Tartakovsky, and C. L. Winter, *Physical Review E*, **61**(2) 2150-2151 (2000)

Gray, W. G., Thermodynamics and Constitutive Theory for Multiphase Porous-media Flow Considering Internal Geometric Constraints, *Advances in Water Resources*, **22**(5) 521-547 (1999a)

Gray, W. G., Elements of a Systematic Procedure for the Derivation of Macroscale Conservation Equations for Multiphase Flow in Porous Media, in *Kinetic and Continuum Thermodynamical Approaches to Granular and Porous Media*, edited by K. Hutter and K. Wilmanski, CISM Courses and Lectures No. 400, International Centre for Mechanical Sciences, Springer-Verlag, Vienna, 67-129 (1999b)

Gray, W. G., and B. A. Schrefler, "Thermodynamic Approach to Effective Stress in Partially Saturated Porous Media" (submitted, 1999c).

Gray, W. G., Macroscale Equilibrium Conditions for Two-Phase Flow in Porous Media, *International Journal of Multiphase Flow*, **26**(3), 467-501, (2000).

Gray, W. G., A. F. B. Tompson, and W. E. Soll, Closure Conditions for Two-Fluid Flow in Porous Media, *Transport in Porous Media*, (submitted, April, 2000).

Grunau, D. W. *Lattice Methods for Modeling Hydrodynamics*, Ph.D. Dissertation, Colorado State University, Dept. of Mathematics, (1993).

Grunau, D. W., S. Y. Chen, and K. G. Eggert. A lattice Boltzmann model for multi-phase fluid flows, *Phys. of Fluids A*, **5**(10), 2557-2562 (1993a).

Grunau, D. W., T. Lookman, S. Y. Chen, and A. S. Lapedes. Domain growth, wetting, and scaling in porous-media, *Physical Review Letters*, **71**(25), 4198-4201 (1993b).

Gunstensen, A. K., D. H. Rothman, S. Zaleski, and G. Zanetti. Lattice Boltzmann model of immiscible fluids, *Phys. Rev. A*, **43**(8), 4320-4327 (1991).

Hassanizadeh, S. M., and W. G. Gray, General conservation equations for multi-phase systems: 1. averaging procedure, *Advances in Water Resources*, **2**(3), 131 (1979a).

Hassanizadeh, S. M., and W. G. Gray, General conservation equations for multi-phase systems: 2. mass, momenta, energy, and entropy equations, *Advances in Water Resources*, **2**(4), 191 (1979b).

Hassanizadeh, S. M., and W. G. Gray, General conservation equations for multi-phase systems: 3. constitutive theory for porous media flow, *Advances in Water Resources*, **3**(1), 25 (1980).

Hassanizadeh, S. M., and W. G. Gray, Mechanics and thermodynamics of multiphase flow in porous media including interface boundaries, *Advances in Water Resources*, **13**(4), 169-186 (1990).

Hazlett, R.D. Simulation of capillary-dominated displacements in microtomographic images of reservoir rocks, *Transport in Porous Media*, **20**(1-2), 21-35 (1995).

Hazlett, R. D., S. Y. Chen, and W. E. Soll. Wettability and Rate Effects on Immiscible Displacement: Lattice Boltzmann Simulation in Microtomographic Images of Reservoir Rocks. *J. of Petroleum Science and Engineering*, **20**(3-4), 67-175 (1998).

Hillel, D., *Soil and Water*, Academic Press, New York (1971).

Hou, S., X. Shan, Q. Zou, G. D. Doolen, and W. E. Soll. Evaluation of Two Lattice Boltzmann Models for Multiphase Flow, *J. of Computational Physics*, **138,** 695-713. (1997).

Kalaydjian, F. J.-M., Dynamic capillary pressure curve for water/oil displacement in porous media: theory vs. experiment, Professional paper SPE 24813, Society of Petroleum Engineers, Richardson, TX (1992).

Ladd, A. J., Numerical simulation of particulate suspensions via a discretized Boltzmann equation, part 2. Numerical results, *Journal of Fluid Mechanics*, **271**, 311-339 (1994)

Marle, C. M., On the macroscopic equations governing multiphase flow with diffusion and chemical reaction in porous media, *International Journal of Engineering Science*, **20**(5), 643-662 (1982).

McWhorter, D., and D. K. Sunada, *Ground-water Hydrology and Hydraulics*, Water Resources Publications, Fort Collins (1977).

Miller, C. A., and P. Neogi, *Interfacial Phenomena*, Marcel Dekker, New York, 1985.

Moeckel, G. P., Thermodynamics of an interface, *Archive for Rational Mechanics and Analysis*, **57**, 255-280 (1975).

Montemagno, C. D., and W. G. Gray, Photoluminescent volumetric imaging: A technique for the exploration of multiphase flow and transport in porous media, *" Geophysical Research Letters*, **22**(4), 425-428 (1995).

Morrow, N. R., Physics and thermodynamics of capillary action in porous media, in *Flow Through Porous Media*, American Chemical Society, Washington, D. C., 103-128 (1970).

Muccino, J. C., W. G. Gray, and L. A. Ferrand, Toward an Improved Understanding of Multiphase Flow in Porous Media, *Reviews of Geophysics*, 36(3), 401-422. (1998)

Müller, I., *Extended Thermodynamics*, Springer-Verlag, New York (1993).

Rashidi, M., L. Peurrung, A. F. B. Tompson, and T. J. Kulp, Experimental analysis of pore-scale flow and transport in porous media, *Advances in Water Resources*, **19**(3), 163-180 (1996).

Reeves, P. C., and M. A. Celia, A functional relationship between capillary pressure, saturation, and interfacial area as revealed by a pore scale network model, Water Resources Research, **32**(8), 2345-2358 (1996).

Rose, W., Measuring transport coefficients necessary for the description of coupled two-phase flow of immiscible fluids in porous media, *Transport in Porous Media*, **3**(2), 163-171, 1988.

Rothman, D. H., and S. A. Zaleski. Lattice-gas models of phase-separation - interfaces, phase-transitions, and multiphase flow, *Rev. of Modern Phys*, **66**(4), 1417-1479 (1994).

Saripalli, K. P., H. Kim, P. S. C. Rao, and M. D. Annable, Use of interfacial tracers to measure immiscible fluid interfacial areas in porous media, Environmental Science and Technology, **31**(3), 932-936 (1996).

Scheidegger, A. E., *The Physics of Flow through Porous Media*, Third Edition, University of Toronto Press, Toronto (1974).

Soll, W. E., S. Y. Chen, K. G. Eggert, D. W. Grunau, and D. R. Janecky. Application of the lattice Boltzmann / lattice gas technique to multi-fluid flow in porous media, in *Proceedings of the 10th International Conference on Computational Methods in Water Resources*, Heidelberg, Germany, (1994).

Soll, W. E., W. G. Gray, D. R. Janecky, and A. F. B. Tompson. Meeting Report: Linking the Pore and Continuum Scales Through Theory, Modeling, and Experimentation. *EOS, Transactions, American Geophysical Union*, **78**(44), 495 (Nov. 4, 1997).

Soll, W. E., W. G. Gray, and A. F. B. Tompson, Influence of Wettability on Constitutive Relations and its Role in Upscaling, in *Computational Methods in Water Resources XII, Vol. 1* (V. N. Burganos, G. P. Karatzas, A. C. Payatakes, C. A. Brebbia, W. G. Gray, and G. F. Pinder, eds.), Computational Mechanics Publications, Southampton, 413-420 (1998a).

Soll, W. E., and K. H. Birdsell The Influence of Coatings and Fills on Flow in Fractured Unsaturated Tuff Porous Media Systems, *Water Resources Research*, **34**(2),193-202 (1998b).

Soll, W. E., A. F. B. Tompson, and W. G. Gray. Lattice Boltzmann Used to Determine Constitutive Relations for Multiphase Flow Equations. (in preparation, 2000).

Sposito, G., The “physics” of soil water physics, *Water Resources Research*, **22**, 9, 83s - 88s, (1986).

Succi S., R. Benzi, and F. Massaioli, A review of the lattice boltzmann method. *International Journal of Modern Physics C-Physics and Computers*, **4**(2), 409-415 (1993).

Svendsen, B., and K. Hutter, On the thermodynamics of a mixture of isotropic viscous materials with kinematic constraints, *International Journal of Engineering Science*, **33**, 2021-2054 (1995).

Tompson, A. F. B., and W. G. Gray, A second order approach for the modeling of dispersion transport in porous media: 1. Theoretical development, *Water Resources Research*, **22**(5), 591-600 (1986a).

Tompson, A. F. B. and W. G. Gray, A second order approach for the modeling of dispersive transport in porous media, 3: Application to two porous media problems, *Water Resources Research*, **22**(13), 1959--1971 (1986b)

Tompson, A. F. B., W. E. Soll, and W. G. Gray, An Assessment of Closure Conditions for Two-Fluid Flow in Porous Media Based on Idealized Models (submitted, 2000).

Whitaker, S., Diffusion and dispersion in porous media, *American Institute of Chemical Engineers, Journal*, **13**, 420-427 (1967).

Zhang, D., R. Zhang, S. Chen, and W.E. Soll, Pore scale study of flow in porous media: Scale dependency, REV, and statistical REV, *Geophysical Research Letters* (in press, 2000).

FEEDBACK

We encountered several problems associated with the DOE management of this project.

- This project was developed in response to the original DOE program notice 96-10 and was approved for funding beginning in October, 1996. Unfortunately, the DOE funding for the national laboratory collaborators was not put into the laboratory FIN plans, and they had to wait a full year before beginning their portions of the project. Ultimately, the project was extended by one year to accommodate this mistake.
- DOE sponsored two gatherings of PIs under the EMSP program. These gatherings involved poster presentation of work done with DOE funding. The organizers of the workshop required that the posters be submitted for posting on the DOE website. This is consistent with a desire to make the program visible, but it is absolutely inconsistent with good science. Results of research should be made available to the community through appropriate peer review in scientific journals. Work “in progress” or less well developed is certainly suitable for conference presentations, workshops, and posters. This generates discussion that helps the researchers with their work. However, taking such informal presentations and documenting them on the web inhibits scientific advances by forcing researchers to present only what they have already put into the literature.
- In the Fall of 1999, the PI oft his project was notified of the opportunity to submit a renewal proposal for funding in the FY 2001 time frame. The PI and the collaborators undertook preparation of a proposal with the expectation that based on the excellent progress had been made in our basic research (as described in this report), sufficient arguments could be made to continue the work. As with most proposals, a significant amount of effort was expended in writing the renewal proposal, and all knew that the review process would, indeed, be competitive. Nevertheless, the renewal was submitted in April 2000 without any acknowledgment of its being “received” at DOE. The PI and collaborators basically waited until mid October 2000 to be notified that the project would not be renewed for reasons that “it was too fundamental” and not central to the “applied focus of the EMSP program”. This reason for non-renewal was surprising in that the project was obviously consistent with the program’s focus in the 1996 call, and, ironically, seemingly consistent with the “Science advancing solutions” slogan on the EMSP web page. We agree that the project involves very fundamental science, but if, indeed, the basic research focus of the program has been abandoned since 1996, this should have been made explicitly clear in the announcement of opportunity for renewal. We believe that in failing to provide the criteria on which renewals would be based, the DOE wasted our time in suggesting a new proposal. In delaying a response to our renewal proposal to a date months after notifying those renewed, the DOE further compromised our opportunities to seek appropriate funding and showed a lack of concern for those attempting to make its mission successful.