

# Prediction of Air–Water Interfacial Area in Wet Unsaturated Porous Media

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A numerical model is developed to predict the air–water interfacial area of water-wetted unsaturated porous media. A model space is first designed consisting of elements capable of containing a single material. Water, air, and quartz are considered in this work. The elements are square in two dimensions and cubic in three dimensions. The contents of elements containing quartz are considered immobile, while the contents of elements containing fluid (air and water) are treated as mobile. The fluid elements are then arranged in a manner to minimize the total interfacial energy of the system by the simulated annealing optimization technique. Air–water interfacial area predictions are compared to experimental data for two systems of glass beads. Predictions are excellent at high water contents, but fail at low water contents. The failure of this and other thermodynamic models at low water contents is explained by low hydraulic conductivity, which prevents low water content systems from reaching thermodynamic equilibrium.

## Introduction

An assembly of particles that is wet but not filled with a liquid may be termed “unsaturated.” The interparticle spaces in such a system contain air as well as the liquid, and an air–liquid interface exists whose extent approaches the area of the dry particle surfaces as liquid saturation approaches 0% and disappears as liquid saturation approaches 100%. The air–liquid interfacial area at intermediate saturations is generally not known.

Because this air–liquid interfacial area influences important system properties, such as the rate at which mass transfer through the pores may occur, many attempts have been made to estimate it. In most cases, the liquid of interest has been water. The estimated air–water interfacial areas have been based on general area models that could not be verified experimentally.

This situation changed in 1996 when the first experimental method to measure air–water interfacial area in water-wetted unsaturated systems was published by Karkare and Fort.<sup>1</sup> The measurements they made, and subsequent measurements by Silverstein and Fort,<sup>2</sup> showed that the previous model predictions for air–water interfacial area as a function of saturation were flawed. The models fail to predict rapid, nonlinear increases in air–water interfacial area as the system saturation decreases below about 60% and also often fail to predict the correct area values as the system saturation approaches zero.

Karkare suggested that the final configuration of water in a wet unsaturated system was a configuration that minimized the air–water interfacial area (energy) and presented data<sup>3</sup> which supported this idea. Silverstein and Fort<sup>2</sup> then proposed that the relatively large changes

in interfacial area observed over relatively small changes in water content were caused by a rearrangement of the water to minimize system interfacial energy. This hypothesis was supported by a geometric model of water in a simple three-pore system. The model showed that very small increases in water content could lead to relatively large decreases in air–water interfacial area through spontaneous filling of small pores by movement of liquid previously held in capillary spaces around the contact points of particles.

In this paper we present a numerical model for predicting the air–water interfacial area in water-wetted porous media systems. The model is based on the assumption that the fluid in a porous matrix can reach an equilibrium configuration that minimizes system interfacial energy. It is realized that in real systems true equilibrium is seldom if ever attained. However, the energy minimization tendency is real and the assumption provides a useful baseline condition for model development. A detailed map of fluid configuration is predicted by the model and is the subject of a companion manuscript.

## Background

**Measuring Interfacial Area.** Karkare and Fort developed a method of measuring the total air–water interfacial area of a system by conducting a series of simple water movement experiments. Inside a glass column of 2.5-cm inner diameter, they packed 10 cm of particulate material, either glass spheres or sand. The particulate material had been wetted to a uniform water content, but material added to half of the column was also mixed with a metered amount of 1-tetradecanol, a long-chain water-insoluble alcohol. When the surfactant was present in sufficient quantity to form a condensed monolayer at the air–water interface in the section of column where it was deposited, the surface tension of the air–water interface decreased in that column section. A capillary pressure gradient between the two sides of the column was generated. Water was then displaced from the surfactant-containing region to the surfactant-free region because of this gradient. When insufficient surfactant was present to form a condensed monolayer at the air–water interface, the surface tension was not reduced and no water movement occurred. When a series of these water move-

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ment experiments were conducted at the same initial water content but with different quantities of surfactant, the critical surfactant concentration for inducing water movement was determined. Because the area occupied by a single molecule of 1-tetradecanol in a condensed monolayer is known, the area occupied by a condensed monolayer of the quantity of surfactant added to the system at the critical concentration corresponds to the total air–water interfacial area of the region to which surfactant was added.

Another method of measuring interfacial areas has recently been published. Annable et al.<sup>4</sup> describe a method of estimating air–water interfacial areas for systems in which unsaturated flow is occurring. A known amount of surfactant is added to the source reservoir, and the concentration of the surfactant in the effluent is monitored. The initial retention of the surfactant, which is adsorbed preferentially at the air–water interface, is used to determine the “effective” interfacial area. This effective interfacial area should correspond to the interfacial area of the portion of the total water interface under which unsaturated flow is occurring. Hence, the air–water interface of stagnant water is not included in the predicted values. Consequently, the interfacial areas reported by Annable et al. tend to be lower than those measured by Karkare and Fort for similar systems.

Karkare and Fort’s method for measuring area was used in the work reported here because our model is designed to predict the total air–water interfacial area in equilibrium systems.

#### Previous Models for Air–Water Interfacial Area.

Leverett<sup>5</sup> developed the earliest model for predicting air–water interfacial areas. His model was based on fundamental thermodynamic principles. He gave the relationship between interfacial areas at two saturation states as

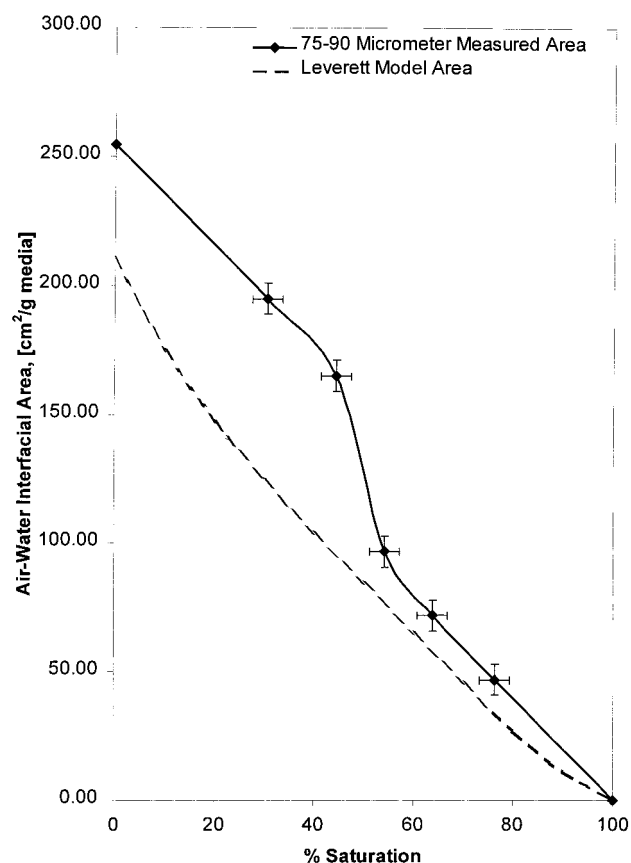
$$A_{v2} - A_{v1} = \frac{G_2 - G_1}{\gamma} = -\frac{1}{\gamma} \int_{S_{w1}}^{S_{w2}} P_c dS_w \quad (1)$$

where  $A_v$  is the interfacial area per unit volume,  $G$  is the Gibbs free energy,  $\gamma$  is the surface tension,  $P_c$  is the capillary pressure, and  $S_w$  is the fractional saturation. Figure 1 compares experimental air–water interfacial areas we determined for a system of glass beads with areas we calculated for this same system using Leverett’s model. Bead diameters ranged from 75 to 90  $\mu\text{m}$ . The model predictions are based on measured capillary pressures, not correlations. The model does a reasonable job of matching the predicted areas at high water contents (>50%) but fails at low water contents. Additionally, it fails to approach the known zero water content end point of the air–water interfacial area versus water content curve.

Rose and Bruce<sup>6</sup> combined Leverett’s derivation with the Kozeny equation for flow in porous media to form an expression for capillary pressures based on interfacial areas. Miller<sup>7</sup> rearranged their expression to

$$A_v = \frac{P_c \epsilon S_w}{\gamma} \quad (2)$$

where  $\epsilon$  is the porosity of the medium. As Figure 2 shows, areas calculated from this equation at high water contents



**Figure 1.** Predicted air–water interfacial areas for Leverett’s model and experimentally measured areas for a system of 75–90- $\mu\text{m}$  diameter glass beads. Leverett’s model predictions are based on measured capillary pressures.

are closer to the areas determined from experiments than are areas calculated from Leverett’s model. However, good agreement between experiment and model predictions is not achieved at low water contents. Additionally, areas predicted by the model for low water contents do not approach the known surface area of the dry system.

Skopp<sup>8</sup> developed a statistical model based on a simplified pore geometry for predicting the air–water interfacial area. Cary<sup>9</sup> modified the model somewhat to make his model yield the known correct areas at 0% and 100% water saturation. However, neither model improves upon the predictions of the other models for the air–water interfacial areas at low water contents.

With measured areas available for verification of model predictions, it became clear that the existing models are inadequate for some applications and are certainly unsuitable for understanding the configuration of fluid in porous media. Hence, the model proposed here was developed.

**Original Model.** A numerical model developed for a two-dimensional porous medium by Knight, Chapman, and Knoll<sup>10</sup> appeared to be well-suited for the determination of water configuration and interfacial area modeling in particulate media. They used this numerical model to predict the water configuration for a two-dimensional sandstone model space. The work involved creating a digital representation of the model system and assigning each element in the system a value associated with a particular substance: in their case, either quartz, water,

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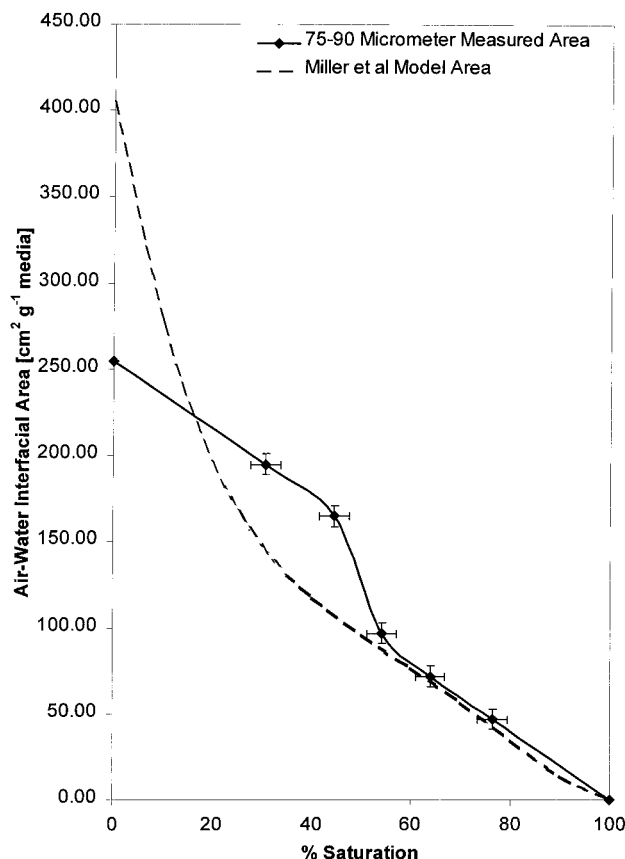
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**Figure 2.** Predicted air–water interfacial areas for Miller's model and experimentally measured areas for a system of 75–90- $\mu\text{m}$  diameter glass beads. Miller's model predictions are based on measured capillary pressures.

or air. Each possible interface was assigned a value of interfacial energy. For two adjacent identical elements, no interface exists. For the air–water interface, the energy was taken as  $72 \text{ mJ m}^{-2}$ .<sup>11</sup> For the quartz-saturated air interface the energy was taken as  $422 \text{ mJ m}^{-2}$  and for the quartz–water interface the energy was taken as  $350 \text{ mJ m}^{-2}$ .<sup>12</sup>

To calculate the global value of interfacial energy, the interfacial energy of each element was evaluated with respect to its nearest neighbors, which for central elements number 8 in two dimensions and 26 in three dimensions. The sum of the interfacial energies of these local elements yields the global interfacial energy.

To obtain a realistic fluid configuration, Knight, Chapman, and Knoll optimized the arrangement of fluid by minimizing the overall interfacial energy according to

$$G_t^s = \sum_i A_i \gamma_i \quad (3)$$

Here  $i$  represents the interface,  $G_t^s$  is the total interfacial free energy of the system,  $A_i$  is the length (in two dimensions) or area (in three dimensions) of the interface, and  $\gamma_i$  is the interfacial free energy of the interface. They used three optimization methods in their work, minimizing the interfacial free energy of the system as calculated by eq 3. The most effective method for finding the apparent optimal configuration of water was simulated annealing. Typical iterative improvement optimization techniques

frequently lead to solutions resulting in metastable states. Simulating annealing resolves the difficulty with metastable states and yields a solution that either reaches or is near the global optimum solution.

Simulated annealing was developed in the 1940s by Metropolis<sup>13</sup> and evolves from statistical dynamic calculations involving the cooling of a substance on a molecular level. If a nonhomogeneous substance is cooled rapidly from a liquid to a solid state, the substance does not reach its lowest energy state in the solid—pockets of high energy will be present. If the substance is cooled sufficiently slowly, however, the molecules have sufficient opportunity to “find” an arrangement of minimal total energy. Kirkpatrick et al.<sup>14</sup> formally applied simulated annealing to combinatorial optimization problems in the 1980s.

The simulated annealing technique used in this model randomly swaps water and air “elements” and evaluates each swap's effect on interfacial energy. If the swap results in a decrease in energy, the move is accepted. If there is an increase or no change in energy, a random number is chosen and compared against a threshold value determined by a Boltzman distribution at the current simulation “temperature”. If the random number lies above the threshold, the move is accepted; otherwise, it is rejected. A large number of such swaps are evaluated at each temperature before the temperature is dropped according to the “cooling schedule”. At some point the temperature becomes low enough that only swaps resulting in a decrease in overall interfacial energy are accepted. In theory, if enough trials are made at each temperature and the temperature drops very slowly, the method will converge on the global minimum.<sup>15</sup> The possibility of “uphill” moves makes this technique well-suited to optimization problems where metastable states are possible. Given sufficient swaps at a temperature high enough that some uphill moves can be accepted, the simulation usually avoids entrapment in nonoptimal solutions.

Knight, Chapman, and Knoll followed the criterion suggested by Kirkpatrick that an initial temperature be chosen such that at least 80% of all attempted moves be accepted. They also stated that reducing the temperature by a factor between 0.5 and 0.98 after each simulation iteration “consistently” provided minimum energy results. They gave no indication of the number of trials attempted at each temperature, nor of how elements at the edge of the model space were handled.

Knight was contacted<sup>16</sup> regarding further development of this model early in the present study. She stated that her work on this project had ceased.

### Further Development of Numerical Model

The modeling work presented here is based upon the work of Knight, Chapman, and Knoll. However, the assumptions made in their model have been modified to better correspond to the targeted model system. The model has been given the capacity to handle three dimensions and is readily modified to handle additional cost functions. The fundamental assumptions upon which the model is based are now discussed.

**Model Space Representation.** A significant strength of the model lies in the manner in which the system is

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represented. It does not require an analytical description of the model system, so regular geometries are not required. Similarly, it is not limited to representing a matrix of spheres, or even a particulate medium. Any system that can be adequately represented digitally in the model space allocated may be simulated.

The model space may be visualized as an array of squares (in two dimensions) or cubes (in three dimensions) laid out in a Cartesian coordinate system. Each square or cube is referred to as an element of the model space. Each element has a single property—in the current version of the model, the identity of the material, whether quartz, water, or air. Additional materials may be readily added.

The solid elements are assumed to be static and define the solid portion of the model space. A collection of solid elements may be arranged to represent a particular geometry of a particle or other body. The number of elements used to represent a particular geometric dimension is referred to as the resolution of the model space. It is clear that a model system at a low resolution, or having few elements represent a unit of real geometric dimension, will give poor representation of spherical and other particles which have curved surfaces. A high-resolution model will give an excellent representation of such particles, but at a high computational cost because more elements will be required to represent the same model system. The resolution of a model space is ultimately determined by a trade-off between computational and geometric constraints.

**Energy Evaluation.** The fundamental principle behind the model is that the real system being considered tends to minimize its free energy as it approaches thermodynamic equilibrium. As described earlier, the model optimizes the arrangement of fluid elements such that the total interfacial energy of the system is minimized. Naturally, the interfacial energy must be evaluated to quantify the success of the optimization.

The model assumes that only first-order interactions between elements are significant. The interfacial energy values given by Parks<sup>12</sup> and Adamson<sup>11</sup> were used in these model simulations. These values ( $\gamma_{lv} = 72 \text{ mJ/m}^2$ ,  $\gamma_{sl} = 350 \text{ mJ/m}^2$ , and  $\gamma_{sv} = 422 \text{ mJ/m}^2$ ) are based on the assumptions that “the liquid phase is pure water, the vapor phase is saturated with water vapor, and the solid surface is quartz at equilibrium with water vapor and thus includes an adsorbed water layer, probably several monolayers thick.”<sup>10</sup> Because the energy evaluations only consider the interface between two pure substances at a constant temperature and pressure, entropy effects are not considered by the model. Numerous approaches are available for handling the edges of the model space for energy evaluations. One may assume a single component exists beyond the edges of the model space, as though it were surrounded by air, for example. One may assume no interface exists at the edge, which is equivalent to assuming the element beyond the edge is the same as the edge element. Or one may assume periodic boundary conditions, where the model space is assumed to “wrap around”. Then, as one exits the top of the model space, one immediately enters the bottom of the model space. This approach is best suited to modeling unit cells and model spaces intended to represent much larger systems, but may be used to handle smaller structures if care is given to the layout of the model space. For example, with a small structure, a large air space should be established around the structure to eliminate bridging of water across the edges of the model space. This handling of edge effects was adopted for all simulations after basic model development was complete.

Air–water interfacial areas were calculated by assuming that the solid phase is hydrophilic and is entirely covered with a thin film of water. The thin film is much smaller than the dimension a single model element represents in the model simulations performed here, in which a single element may be considered to represent a space with a characteristic length measured in microns. The presence of this film is accounted for by the choice of interfacial energy values.

**Simulated Annealing Model.** The only optimization technique employed in the model is simulated annealing. As described earlier, simulated annealing is a heuristic technique designed to find a global optimal condition without being entrapped by local minima. The model simulation involves two major steps: adjusting saturation and optimizing the system configuration.

Saturation adjustment involves adjusting the ratio of water to air elements so that a desired water saturation of fluid pore space is achieved. Water elements are assigned or de-assigned to random fluid elements until the desired saturation is achieved. The simulation technique effectively scrambles the fluid arrangement during its initial iteration, so the final configuration predicted by the model is independent of the initial water configuration.

To achieve system optimization through simulated annealing, three parameters must be considered. The first is the “temperature”, or the control parameter. The control parameter affects the probability that a “move”, or a swap of air and water elements, that increases the interfacial energy of the system will be accepted. A randomly generated number is compared to the number calculated from the Boltzman distribution:

$$e^{-k\Delta E/RT} \quad (4)$$

For the purpose of the simulation,  $k/RT$  is assumed to have a value of unity. The initial value of  $T$  is assigned such that 80% of the moves proposed are accepted, as suggested by Kirkpatrick. The control parameter stays constant for a single iteration during which a large number of moves are proposed and evaluated.

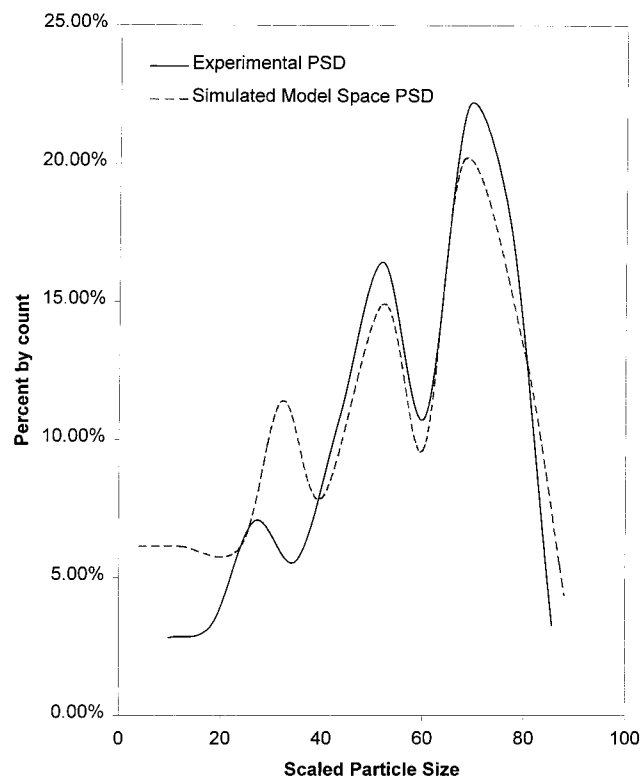
The second parameter is the number of proposed moves. This number should be dependent on the size of the model space. For these simulations, the number of moves proposed was at least 2 orders of magnitude greater than the total number of elements in the model space.

The third parameter involves the method by which the control parameter is decreased after each iteration and is known as the “annealing schedule”. The simplest annealing schedule was chosen for the model, whereby the control parameter is decreased by a fixed ratio after each iteration. Examination of the effect of the annealing schedule on the progress of the simulation indicated that a value of 0.7 for the ratio was suitable.

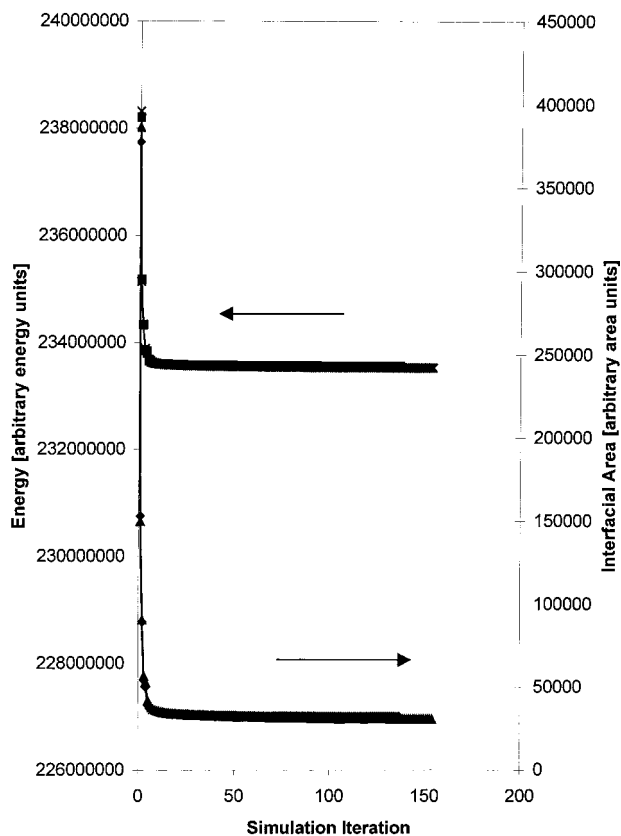
The model was first tested with simple two- and three-dimensional structures. The model space used by Knight, Chapman, and Knoll was initially examined. Model spaces representing ordered packings of circles and spheres in simple cubic and hexagonal close-packed structures were then simulated. Finally, randomly packed assemblages of monodisperse and polydisperse collections of circles and spheres were simulated. The resolution of each model was selected such that an increase in the number of elements used to represent the model space resulted in no significant change in the magnitude of the simulation results.

## Model Results

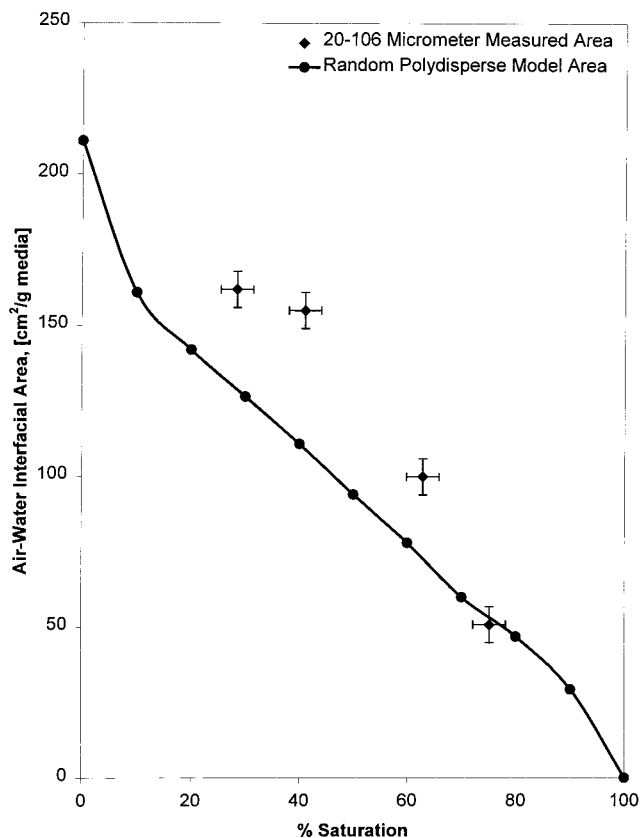
A model space composed of randomly packed differently sized spheres was used to predict the air–water interfacial



**Figure 3.** Particle size distribution of 20–106- $\mu\text{m}$  diameter beads and the model space used to represent it. The line representing the real system was obtained by examining electron micrographs of the sample and counting particle sizes.



**Figure 4.** Typical simulation convergence for model simulations. Shown are the progression of energy and interfacial area as a function of iteration. The simulation temperature was reduced by a factor of 0.7 after each iteration. More than 5 million swaps were attempted during each iteration. Reported results are two independent simulations for a system designed to represent 75–90- $\mu\text{m}$  diameter glass beads at 50% saturation.



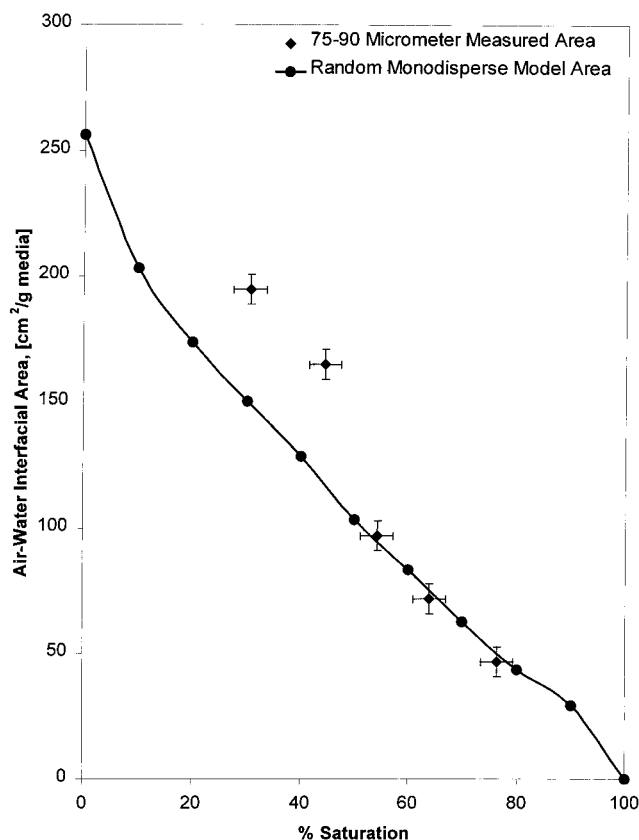
**Figure 5.** Predicted air–water interfacial areas for the annealing model and experimentally measured areas for a system of 20–106 micrometer diameter glass beads. The model space used for the annealing model was a randomly packed array of spheres with the particle size distribution indicated in Figure 3. The model space consisted of 80 elements in each direction with a mean sphere diameter of 15 elements.

area of a collection of quartz beads with a particle size distribution ranging from 20 to 106  $\mu\text{m}$ .<sup>2</sup> The particle size distribution of the model space corresponded to the particle size distribution of the real system as illustrated in Figure 3. The porosity of the model systems was 0.68, which is somewhat high because of the nature of the digital implementation of the sphere-packing algorithm.

The model reports the number of air–water and quartz–air interfaces that exist between nearest neighbor elements in the model. The count of air–water and quartz–air interfaces of a dry model space is scaled to match the surface area of the dry system of interest. The same scaling factor is used to convert other model-predicted values of air–water interfacial area to the real system interfacial areas. Figure 4 illustrates the convergence of several independent simulations runs for this system at a single saturation. Figure 5 illustrates the model predictions of air–water interfacial area for this system. Experimental data are provided for comparison.

The model predicts area values that match experimental data only at high-percentage saturations for this wide particle size distribution system. The remainder of the model predictions falls below the actual area values, failing in the same manner as do other thermodynamics-based models.

A model space consisting of randomly packed identically sized spheres was used to predict air–water interfacial areas for a narrow particle size distribution system of glass spheres whose actual diameter was 75–90  $\mu\text{m}$ . The porosities of these systems were 0.72. The predicted areas are given in Figure 6. Again, only the high-percentage



**Figure 6.** Predicted air–water interfacial areas for the annealing model and experimentally measured areas for a system of 75–90 micrometer diameter glass beads. The model space used for the annealing model was a randomly packed array of spheres of a single diameter. The model space consisted of 80 elements in each direction with a sphere diameter of 15 elements.

saturation areas are predicted accurately. The dependence of air–water interfacial area on saturation resembles that predicted by Leverett's model and does not show the rapid decrease in interfacial area with increasing water content between 40% and 60% saturation, which is shown by the experimental data.

### Discussion

The simulated annealing model predicts air–water interfacial areas at least as accurately as previous thermodynamic models, succeeding in high-percentage water saturation systems but failing in low-percentage water saturation systems. Thermodynamic models should work at all percentage saturations if it were always possible for the system to reach a global minimum energy. The failure of such models at low-percentage water

saturations, even when they are adjusted so that interfacial areas fit known end points, implies the presence of a factor that prevents the system from reaching a water configuration which achieves this energy minimum at low-percentage saturations.

The factor may be associated with limited hydraulic conductivity. Hydraulic conductivities of systems such as those modeled here are high at high-percentage saturations where the fluid is mostly continuous and highly mobile, but very low at low water contents where these conditions are not met. This fact suggests an energy barrier that must be overcome for water to move into its lowest energy configuration at low percentage saturations. Mechanisms for establishing such a condition are discussed by Larson.<sup>17</sup> It is useful here to compare the model algorithm with the real system behavior. Implementation of the model involves making swaps of elements containing air or water from random locations in the model space. No consideration is given to the relative positions of these elements, so a single move may take an element from one extreme of the model space and swap it with an element at another extreme of the model space. This is appropriate for an optimization routine like simulated annealing, which is not actually simulating fluid behavior. However, in the real system fluid elements must move across real distances. Modifying the annealing swaps to consider the relative separations of the involved elements should provide a means of incorporating the real mobility of fluid into the model. An approach is addressed in a forthcoming manuscript.

### Conclusions

The model as presented in this paper appears to be a reasonable means of predicting air–water interfacial areas for water-wetted unsaturated porous media systems at high water contents. The only experimentally measured quantities required to implement this model are the particle size distribution and packing density of the porous medium. Other models require measuring capillary pressures or the use of empirical correlations for capillary pressure and may require additional parameters. For reasons of simplicity of the method alone, the new model shows significant promise. The potential of the model is restricted only by the creativity put into writing additional cost functions for the optimization routines to account for other physical phenomena associated with water-wetted unsaturated particulate porous media.

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