

# Prediction of Water Configuration in Wet Unsaturated Porous Media

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A numerical model for predicting the air–water interfacial area of fluid in wet unsaturated particulate media is utilized to predict the pore-scale configuration of the fluid in the porous matrix. The model is based on simulating annealing and random swapping of air and water elements in the system to achieve a global energy minimum. Predictions of water configuration are consistent with descriptions found in the literature. Explanations for phenomena observed for surfactant-induced capillary pressure gradient-driven flow of fluid in porous media are suggested and supported by model predictions of fluid configuration. The shape of the experimental air–water interfacial area versus water content curve is explained in terms of hydraulic conductivity and its inhibiting role in achieving thermodynamic equilibrium.

## Introduction

One question asked by people who work with porous materials involving water is “Where is the water?”. While many properties and characteristics of porous materials may be determined without knowing the detailed location of water in a porous matrix, the ability to examine the configuration of water in such systems will enable more effective design of processes in which the fluid configuration is important. Some examples of processes where this information is important include agglomeration, oil recovery, and environmental remediation.

A model which was originally proposed by Knight, Chapman, and Knoll<sup>1</sup> and later developed by Silverstein and Fort<sup>2,3</sup> for prediction of air–water interfacial area has the desirable benefit of generating a detailed map of water configuration in the model space. This paper examines the predictions of water configurations made by the model and demonstrates that the predicted configurations correspond to the fundamental structures expected in water-wetted particulate porous media. It demonstrates an application of the predicted configurations, enabling understanding of some phenomena encountered in experiments used to measure air–water interfacial area. It also proposes an explanation for the shape of the air–water interfacial area versus water content curve, which has consistently evidenced a sharp change in area over a small change in water content in all experimental measurements.

## Background

**Simulated Annealing Model.** The model has been described.<sup>2</sup> Implementation involves establishing a digital model space composed of square or cubic “elements” which serve as placeholders for one of three materials, either

quartz, air, or water. In the simulations reported here, a single element translates to an edge length of about 5  $\mu\text{m}$ . Multiple quartz elements are arranged to form spheres in an ordered packing or a random arrangement. Elements containing quartz remain unchanged during the course of the simulation. The remaining elements, which contain either air or water, are rearranged to minimize the total interfacial energy of the system. The resulting arrangement yields configurations that give good predictions of air–water interfacial area. The rearrangement is accomplished through use of the simulated annealing optimization technique. Simulated annealing is a method that is less easily entrapped in local minima than iterative improvement methods and allows near-optimal configurations to be found while exploring a very small fraction of all possible configurations.

**Water Movement Experiments and Measurement of Air–Water Interfacial Area.** Karkare and Fort<sup>4</sup> investigated surfactant-induced capillary pressure gradient-driven flow 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 saturation, but material added to half of the column was 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 in which it was deposited, the interfacial tension was lowered. The reduced interfacial tension generated a capillary pressure gradient between the two sides of the column. Water was 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, no water movement occurred.

By conducting a series of these water movement experiments 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 known concentration of surfactant at the interface at the critical concentration corresponds to the total air–water interfacial area.

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(1) Knight, R.; Chapman, A.; Knoll, M. *J. Appl. Phys.* **1990**, *68*, 994.

(2) Silverstein, D. L.; Fort, T. Prediction of Air–Water Interfacial Area in Wet Unsaturated Porous Media. *Langmuir* **2000**, *16*, 829.

(3) Silverstein, D. L.; Fort, T. Incorporating Low Hydraulic Conductivity into a Numerical Model for Predicting Air–Water Interfacial Area in Wet Unsaturated Particulate Porous Media. *Langmuir* **2000**, *16*, 835.

(4) Karkare, M. V.; Fort, T. *Langmuir* **1993**, *9*, 2398.

All of the reported experimental air–water interfacial area versus water content curves indicate some sort of transitional region at intermediate water contents.<sup>2,3,5,6</sup> The transition appears as a steep drop in interfacial area as the water content increases. Silverstein and Fort<sup>5</sup> proposed that a shift in fluid structures over a small increase in water content caused the drop in area. They demonstrated with a simple geometric model that, for a simple system containing two dissimilar pore sizes, water initially fills the capillary regions around the contact points of particles. When water was added to the system, the system's tendency to minimize its interfacial energy caused water from the capillary regions associated with larger pores to move into the smaller pores to completely fill the smaller pores. This fluid shift caused a significant drop in interfacial area because the air–water interface in the smaller pores was completely eliminated.

Silverstein and Fort<sup>3</sup> later proposed that the drop in area occurred around a water content representing a critical hydraulic conductivity, above which water was sufficiently mobile to reach thermodynamic equilibrium and below which it was unable to reach equilibrium in a timely manner.

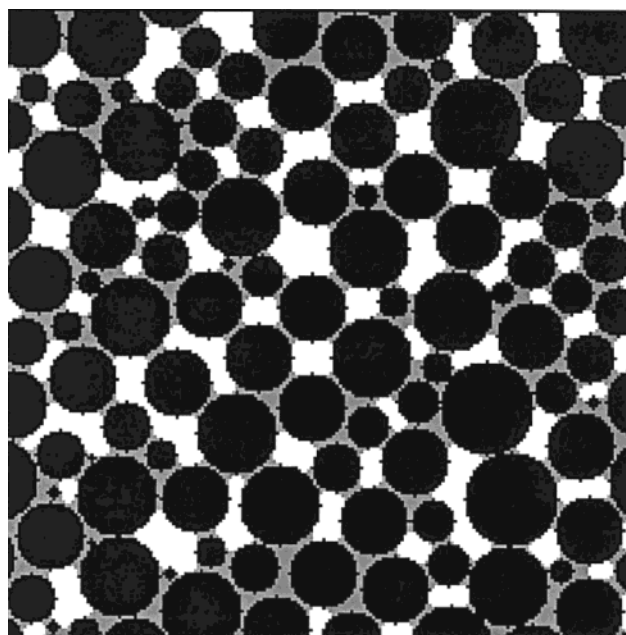
**Lack of Surfactant Drift in Water Movement Experiments.** Karkare and Fort<sup>7</sup> reported that the displacement of water in these experiments was stable over a period of months. Radiotracer experiments indicated that the surfactant did not drift substantially from its original position in half of the packed column. The surfactant was water-insoluble; therefore, it would presumably remain at the air–water interface and only spread if the air–water interface were continuous.

**Limits of Capillary-Driven Flow.** Karkare and Fort<sup>4</sup> also reported that the limits of water displacement coincided with limits established by the capillary pressures of the two segments of the column. The maximum water drainage possible corresponded to the nearly vertical portion of the capillary pressure curve of the porous material at low water contents. Morrow<sup>8</sup> called the remaining water in the system “undrainable” through pressure gradients.

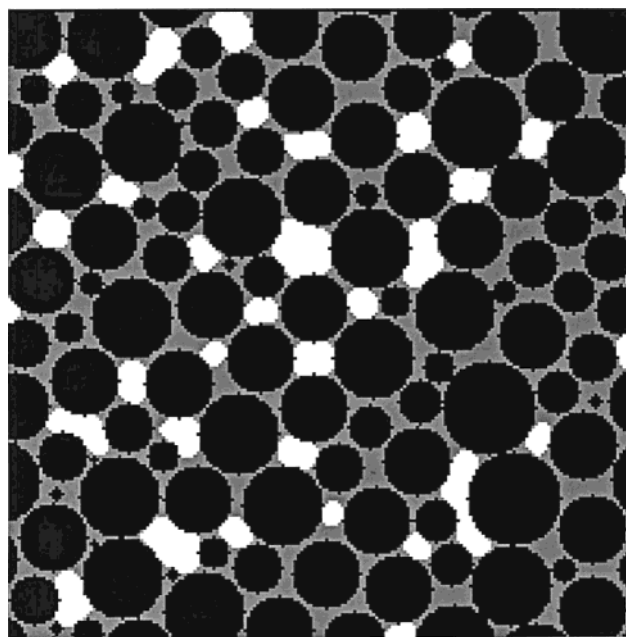
**General Characteristics of Water Configuration.** Soil scientists<sup>8,9</sup> have a simple model to characterize the filling of pores in particulate media. Filling begins with capillary spaces near contact points of particles. The fluid forms pendular rings around these contact points. As the quantity of fluid in the system continues to increase, smaller pores are filled preferentially to the larger pores. Smaller pores continue to fill until the system is saturated. Hysteresis effects may affect the order in which pores are filled.<sup>10</sup>

### Model Predictions for Real Systems

If the model is realistic, then the predicted fluid configurations should be consistent with the previously mentioned observations. At low water contents, water should be found in the capillary regions around contact points of particles. At higher water contents, small pores should fill preferentially to large pores. At water contents corresponding to the maximum drainage achievable through pressure gradients, the water configuration should be discontinuous and isolated so that flow will not easily occur. Finally, at water contents at which surfactant



**Figure 1.** Portion of a two-dimensional polydisperse randomly packed model space simulated at 40% saturation. The solid black elements represent quartz, the shaded elements represent water, and the white elements represent air.



**Figure 2.** Portion of a two-dimensional polydisperse randomly packed model space simulated at 70% saturation. The solid black elements represent quartz, the shaded elements represent water, and the white elements represent air.

drift does not occur, there should be no continuous air–water interface over which the surfactant may spread across the model space.

The first two observations may be confirmed most easily through use of two-dimensional model spaces. Figure 1 is a representation of such a space at 40% fluid saturation. It shows that the model predicts water is indeed preferentially located at capillary spaces near contact points of particles. Figure 2 shows that, at the higher water content of 70% fluid saturation, the smaller pores are filled. The remaining water continues to be held in capillary regions. This same behavior is observed in three-dimensional model spaces.

(5) Silverstein, D. L.; Fort, T. *Langmuir* **1997**, *13*, 4798.

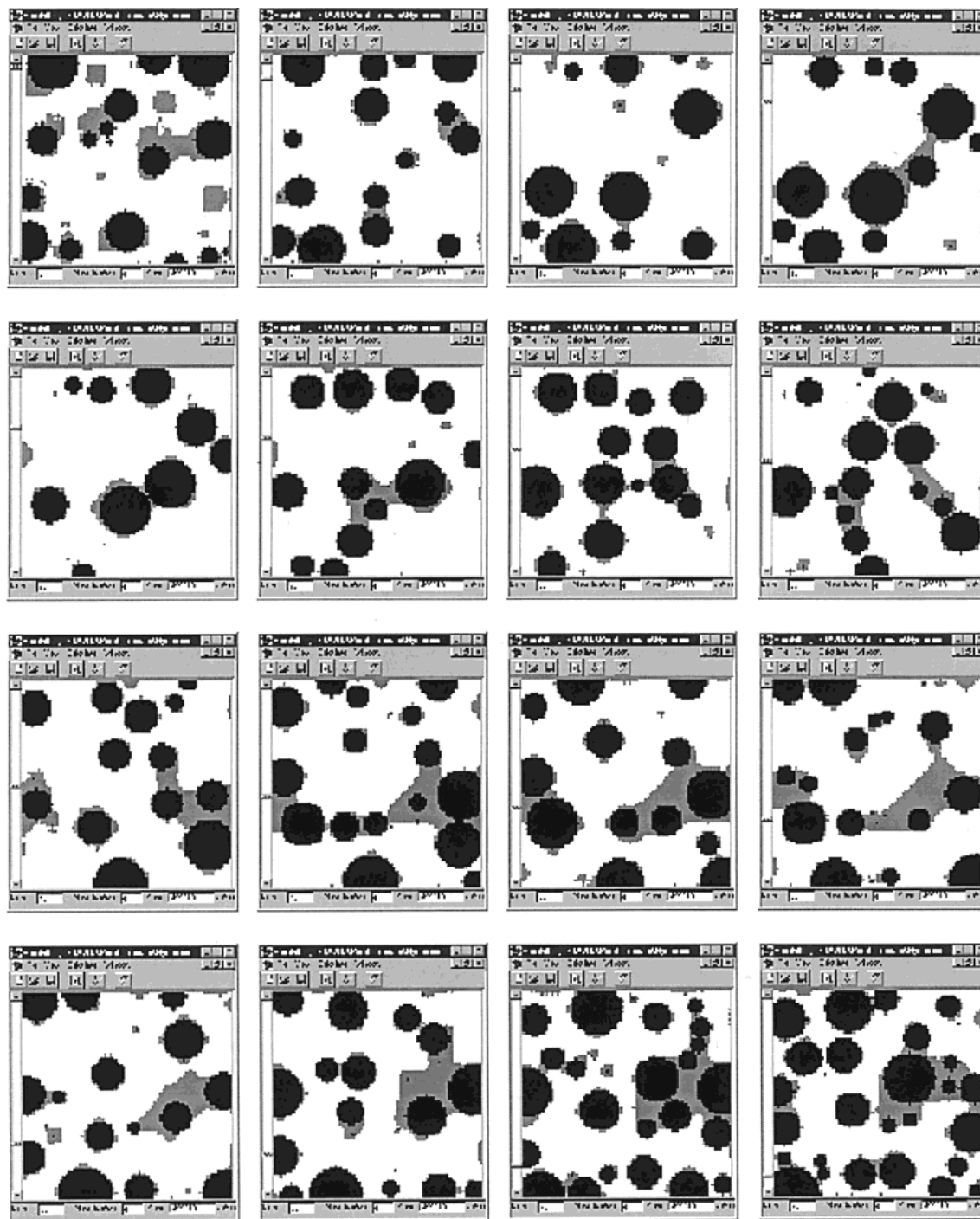
(6) Karkare, M. V.; Fort, T. *Langmuir* **1996**, *12*, 2041.

(7) Karkare, M. V.; La, H. T.; Fort, T. *Langmuir* **1993**, *9*, 1684.

(8) Morrow, N. *Chem. Eng. Sci.* **1970**, *25*, 1799.

(9) Versluys, J. *Int. Mitt. Boden.* **1917**, *7*, 117.

(10) Larson, R. G.; David, H. T.; Scriven, L. E. *Chem. Eng. Sci.* **1981**, *36*, 57.



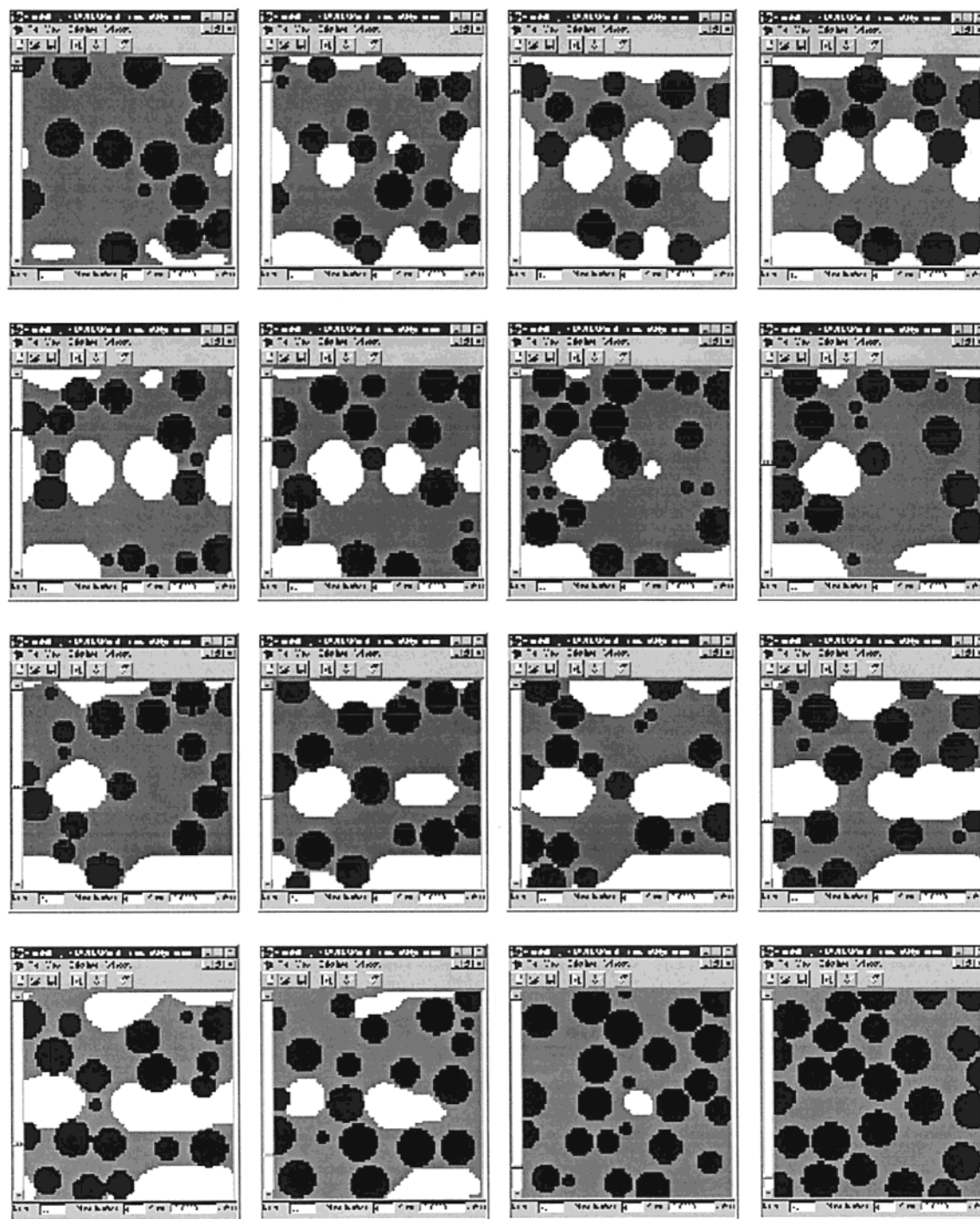
**Figure 3.** Water configurations at selected levels for the polydisperse randomly packed model system at 10% water content. Level 0 is at the upper left. The level increases by 5 with each subsequent image. The solid black elements represent quartz, the shaded elements represent water, and the white elements represent air. No continuous film exists from one face of the model space cube to the opposite face.

Relating surfactant drift to water content requires consideration of three-dimensional systems. Such systems are not easily displayed in two dimensions. To aid visualization, in the figures that follow the model space is divided into layers, only one of which is visible at any time. A layer represents an opaque view one element deep. For example, if the model space were a single sphere, the first layer would show only a single element in the center of the space. In successive layers the diameter of the visible circle would increase until the layer passed through the center of the sphere. Then, successive layers would show a visible circle of diminishing size until only a single point

was visible again. Contact points between spheres are present throughout the model space, although they may not always be visible in the images presented here.

Figure 3 contains a collection of layers of a randomly packed collection of spheres with a particle size distribution similar to that of an experimental system (glass beads with particle sizes ranging from 20 to 106  $\mu\text{m}$ ) for which the maximum drainage of fluid by capillary pressure gradients reduced the fluid content to about 10% saturation. It is clear that the water present in the system is mostly collected into a single region and is discontinuous. If the water was continuous across the model space, it





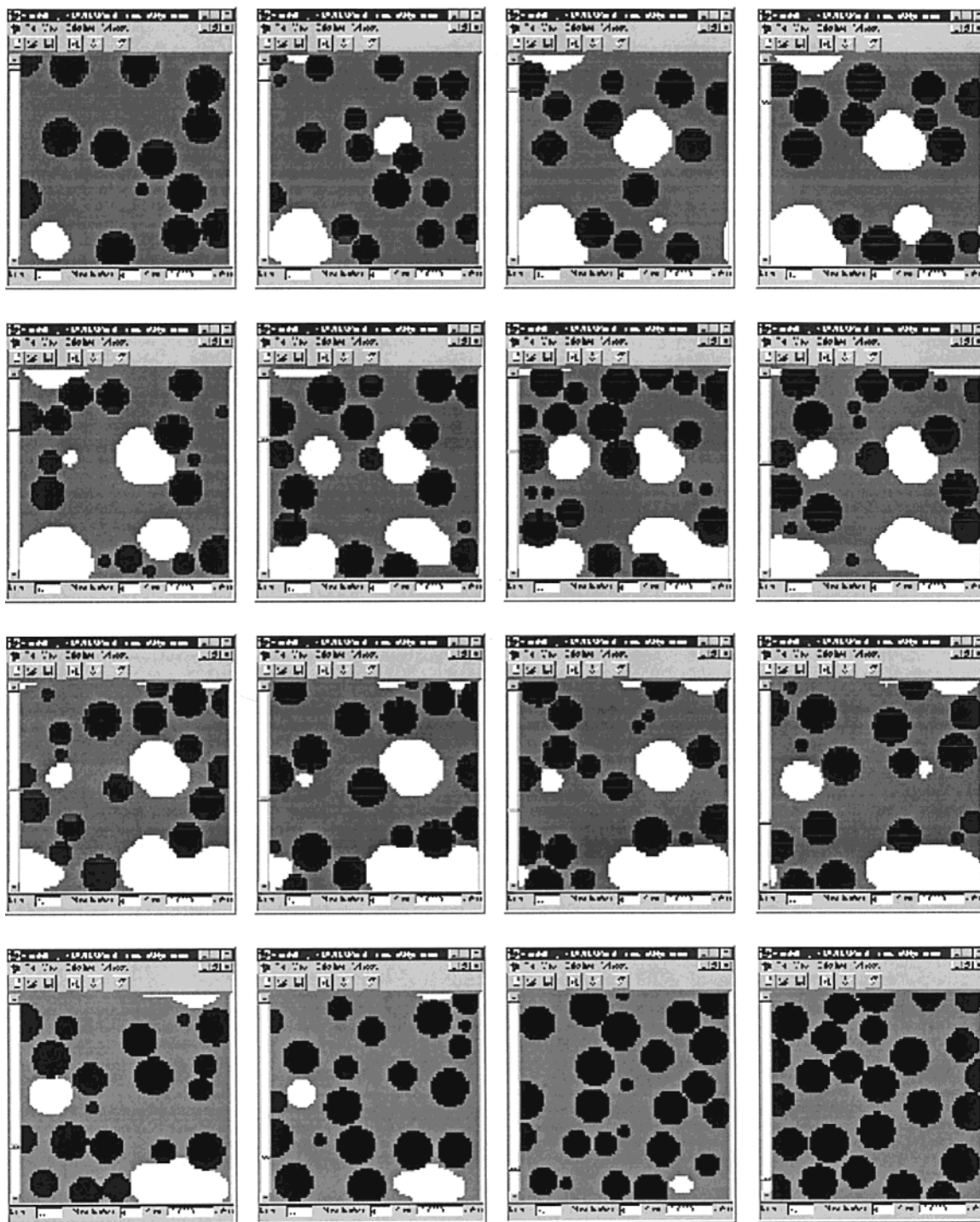
**Figure 4.** Water configurations at selected levels of a monodisperse randomly packed system at 70% water content. Level 0 is at the upper left. The level increases by 5 with each subsequent image. The solid black elements represent quartz, the shaded elements represent water, and the white elements represent air. Numerous paths across a continuous film of water exist from one face of the model space to the opposite face.

would be reasonable to expect that increased pressure gradients would result in flow. The discontinuity prevents flow, even when capillary pressure gradients are extreme.

Figures 4 and 5 contain collections of layers from monodisperse randomly packed collections of spheres which were designed to model a system of glass spheres of narrow particle size distribution (75–90- $\mu\text{m}$  diameter). The system shown in Figure 4 is filled with water to 70% saturation. The system shown in Figure 5 is filled to 80% saturation. At equilibrium in the water movement radiotracer experiments, the region of the column

without surfactant was saturated to about 75%. In the model system at 70% saturation, there is clearly a path for surfactant to drift over a continuous air–water interface. At 80% saturation, no such path exists, as the air–water interface exists exclusively in isolated pore spaces.

As noted in our previous papers,<sup>2,3</sup> the porosities of the three-dimensional model spaces we used were somewhat higher than those we would expect for the real systems they were intended to represent. This would reduce the number of contact points between spheres and therefore alter the configuration of water in the system. Work is



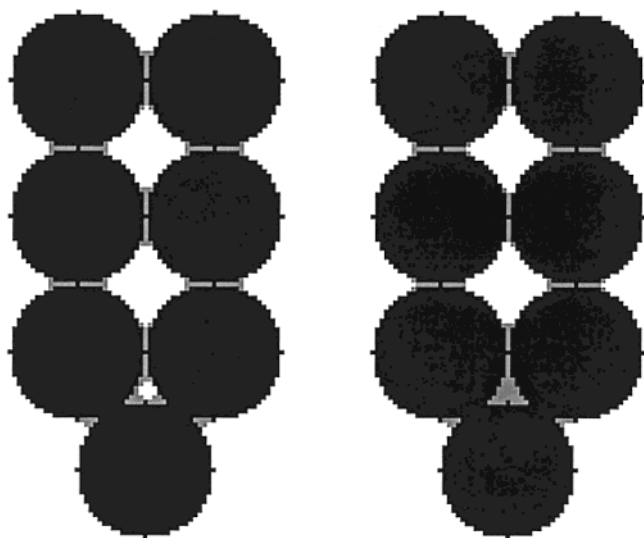
**Figure 5.** Water configurations at selected levels of a monodisperse randomly packed system at 80% water content. Level 0 is at the upper left. The level increases by 5 with each subsequent image. The solid black elements represent quartz, the shaded elements represent water, and the white elements represent air. No paths across a continuous film of water exist from one face of the model space to the opposite face.

underway to improve the packing of the spheres in the model space to better represent the real systems.

#### The Shape of the Air–Water Interfacial Area versus Water Content Curve

A simple two-dimensional model space similar to that used for the geometric model of Silverstein and Fort<sup>5</sup> was developed for application of the annealing model of Silverstein and Fort.<sup>2,3</sup> It consisted of five circular particles arranged to form two large pores and a single small pore.

Water initially added to the system collected in the capillary spaces around the contact points of the particles, as expected. At some higher water content, the transition illustrated in Figure 6 occurred. While the net increase in elements containing water from Figure 6a to Figure 6b is only one element, water in 11 elements in the capillary regions move to elements in the center of the smaller pore to completely saturate the pore. The impact of this transition on the air–water interfacial area is shown in Figure 7. A large number of transitions of this sort that

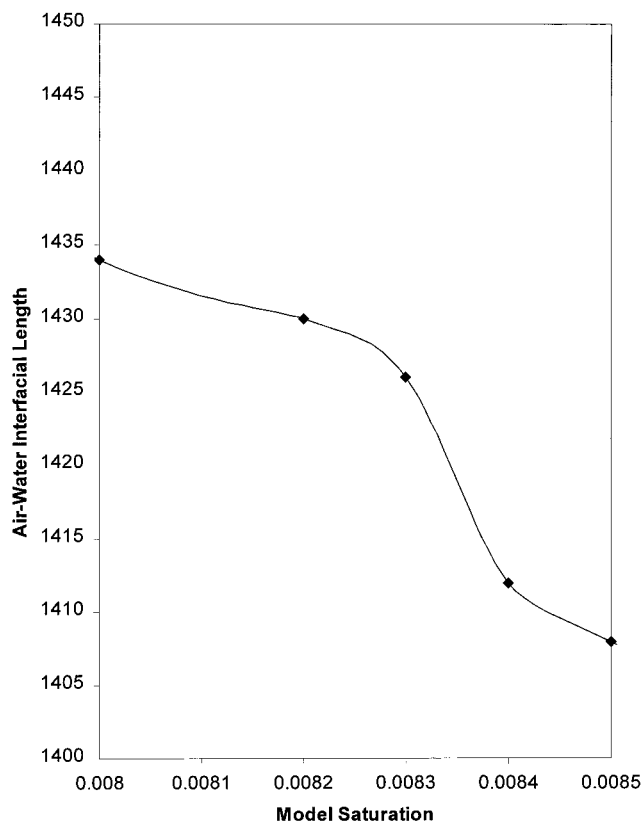


**Figure 6.** Water configuration predicted by a simulated annealing method for a system of seven contacting circles arranged to form two large pores and one small pore. The saturation in the figure on the right is higher than that in the figure on the left by one element. However, addition of this one element causes 11 elements to move from capillary spaces around contact points of circles to complete the filling of the smaller pores. The solid black elements represent quartz, the shaded elements represent water, and the white elements represent air.

occur over a small range of water contents could be responsible for the sharp change in the air–water interfacial area seen in experimental systems.

Our model simulations determine the minimum interfacial energy configuration of fluid in the system. Simulations on larger model spaces, such as those shown in Figure 2, indicate that the minimum energy configuration requires that water shift to fill smaller pores continually as water contents increase, rather than over a small range of saturations. Because the predicted configurations do not indicate a sudden transition over a small range of saturations, we look to other evidence from our modeling work to explain the shape of the curves.

Silverstein and Fort<sup>3</sup> discussed a critical water content above which water moved freely and reached thermodynamic equilibrium quickly and below which could not do so because of limited water mobility. This limited mobility would prevent transitions from capillary-held water to filled pores from occurring in a globally optimal manner. Therefore, we propose that the shape of the air–water interfacial area curve depends on the ability of the water elements to take thermodynamically favored arrangements of fluid in the system. Limited hydraulic conductivity represents an “activation energy” barrier for water element motion. When water contents are sufficiently low that water cannot move freely, water rearranges to form structures which are only locally at their thermodynamic minima. When hydraulic conductivity increases beyond some critical value or values, water is free to rearrange into a globally thermodynamically favored structure, a rearrangement that causes a significant drop in air–water interfacial area. This rearrangement does involve pore structure transitions of the type originally proposed as the cause of the shape of the experimental curves, but these transitions are a mechanism of the change, not the cause.



**Figure 7.** Change in interfacial area (length) as a function of fluid content for the seven-circle system in Figure 6. The shift in pore structure causes a significant drop in interfacial area on the pore scale.

## Conclusions

The simulated annealing model provides a method for generating detailed maps of water configuration in water-wetted porous media. The predicted configurations correspond to the general expectations of fluid behavior in such systems, filling capillary regions first and then filling smaller pores preferentially to larger pores. Other phenomena including maximum drainage through capillary pressure gradients and lack of surfactant drift in surfactant-induced capillary pressure gradient-driven flow are explainable by fluid configurations predicted by the model.

The model also shows a mechanism by which the air–water interfacial area may drop sharply over a small increase in water content. The mechanism is a shift in water from capillary regions to fill smaller pores. No intermediate structures are observed in the model. At water contents below the critical water content for hydraulic conductivity proposed in an earlier paper, this rearrangement of water results in local interfacial energy minima. Above the critical water content a global optimum is achieved, resulting in a significant drop in interfacial area over a small increase in water content.

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