A Monte Carlo paradigm for capillarity in porous media

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Received 27 September 2010; accepted 26 October 2010; published 7 December 2010.

[1] Wet porous media are ubiquitous in nature as soils, rocks, plants, and bones, and in engineering settings such as oil production, ground stability, filtration and composites. Their physical and chemical behavior is governed by the distribution of liquid and interfaces between phases. Characterization of the interfacial distribution is mostly based on macroscopic experiments, aided by empirical formulae. We present an alternative computational paradigm utilizing a Monte Carlo algorithm to simulate interfaces in complex realistic pore geometries. The method agrees with analytical solutions available only for idealized pore geometries, and is in quantitative agreement with Micro X-ray Computed Tomography (microXCT), capillary pressure, and interfacial area measurements for natural soils. We demonstrate that this methodology predicts macroscopic properties such as the capillary pressure and air-liquid interface area versus liquid saturation based only on the pore size information from microXCT images and interfacial interaction energies. The generality of this method should allow simulation of capillarity in many porous materials. Citation: Lu, N., B. D. Zeidman, M. T. Lusk, C. S. Willson, and D. T. Wu (2010), A Monte Carlo paradigm for capillarity in porous media, Geophys. Res. Lett., 37, L23402, doi:10.1029/2010GL045599.

1. Introduction

[2] Capillary phenomena in porous media involve an intricate interplay of liquid, solid, and gas [e.g., de Gennes et al., 2004]. The interfacial geometries that separate phases are often complicated and are dictated by intermolecular forces, pore structure, pressure and temperature [e.g., Israelachvili, 1992]. At the pore scale, analytical techniques are generally confined to solutions of the Laplace-Young equation for idealized particle geometries such as spheres or disks [e.g., Fisher, 1926; Mason and Clark, 1965; Orr et al., 1975; Pierrat and Caram, 1997; Richefeu et al., 2006; Grof et al., 2008; Lechman and Lu, 2008]. While such solutions give important physical insights, the need remains for a methodology to address more complicated pore geometries such as in soils [e.g., Hornbaker et al., 1997]. Yet, to date, few existing methodologies are capable of simulating capillarity in complex geometries at pore-scales in porous media like soils. Monte Carlo (MC) simulation, and the related lattice-gas and lattice-Boltzmann techniques that account for coarse-grained transport, can in principle incorporate the fundamental physical interactions in more complex geometries. Several recent studies have carried out MC simulations of capillarity at the molecular and nanometer scale in pores. However, these systems are strongly influenced by thermal fluctuations and have also focused on simple pore geometries such as slits and cylinders [e.g., Albano et al., 1997; Reszko-Zygmunt et al., 2001; Cao and Wang, 2001; Gelb, 2002; Coasne and Pellenq, 2004; Paul and Rieger, 2005]. Furthermore, such microscopic approaches must be scaled-up to predict macroscopic properties of a composite like soils. Along another path, computational fluid dynamics and lattice gas automata methods have been used to compute the pore-scale geometrical evolution of liquid bodies in porous media with complex pore geometries, but with the computational overhead of capturing the transport behaviour [Rothman and Zaleski, 1994]. There has also recently been a coarse-grained approach based on direct discretized simulation of the liquid-vapor interface, although this introduces complications associated with the merging and breakup of liquid domains [Grof et al., 2008]. To address the need for an efficient pore-scale simulation methodology and overcome some of the aforementioned deficiencies in the previous simulation methods, we developed a coarse-grained Monte Carlo lattice gas approach.

2. Methodology

[3] This simulation methodology is capable of efficiently ascertaining the phase distribution and interface equilibria found in porous materials with complex arrangements. To illustrate these abilities we chose several granular pore systems with increasing geometric complexity: Two spherical grains in contact (for which exact solutions to the Young-Laplace equation are possible), spherical grains of differing sizes arranged randomly, and the grain configuration for a real-world Ottawa sand sample. The multiphase nature of these systems is thus treated as a three-spin Ising model where the spins correspond to the different phases: solid, liquid, and gas. Initial simulation conditions were set by discretizing the granular and pore-space domains onto the lattice. These solid phase domains remain fixed. Next, a liquid phase is introduced in the pore space at random lattice points corresponding to the amount of liquid saturation we wish to simulate. An interfacial free energy of contact between the lattice points, $J_{\alpha\beta}$, is determined between cells of differing types $\alpha$ and $\beta$ [Landau and Binder, 2000]. The (free) energy of the system can be written as

$$E = \sum_{ij} \sum_{\alpha=\beta} J_{\alpha\beta} \delta_{\alpha} n_i \delta_{\beta} n_j$$  

where $n_i$ and $n_j$ denote the number of neighbors in the lattice for each site.
where the first sum is over all nearest neighbor cells \( i \) and \( j \), the second sum is over all phases, and \( n_{i\alpha} = 1 \) if cell \( i \) is in phase \( \alpha \) and 0 otherwise. The liquid and gas phases are then evolved according to the standard Metropolis algorithm where the probability of a given configuration is proportional to the Boltzmann factor, \( \exp(-E/kT) \), with \( k \) being Boltzmann’s constant and \( T \) the temperature. Due to the coarse-grained nature of the simulations, the interfacial energy is much greater than \( kT \) and configurations are dominated by local energy minima separated by energy barriers. To allow for efficient sampling, we chose a fictitious higher value for the temperature that allows exploration of possible configurations while still being low enough to be dominated by the (free) energy minima. We assume that the distribution of stable and metastable energy minima sampled is representative of that in a macroscopic sample. In this limit, the interfacial free energies per unit area were assigned as follows: \(-1\) for liquid/liquid, \(1\) for liquid/gas, and \(-2\) for liquid/solid interaction. Zero was assigned to all other interaction values. These otherwise arbitrary values were chosen to favor adsorption and wetting of liquid onto the solid phase. The unit of energy is taken to be \( kT \) throughout.

### 3. Validation

A simple geometry consisting of two disks of radius \( R \) in contact, shown in Figure 1, was used to compare the MC approach with the classical solution based on the Laplace-Young equation for different liquid contents. Figure 1i shows typical equilibrations of the energy for a range of liquid saturations. Systems with higher liquid content require more MC steps to reach equilibrium (though all simulations were carried out for much longer than shown in these plots). The two-dimensional Laplace-Young equation predicts that the liquid–vapor interface in the region between the disks is a circular arc, which is well-captured by the MC simulation. For the present case of zero contact angle, the theoretical radius of curvature is \( r = R(\cos \theta - 1) \), where the filling angle \( \theta \) depicts the liquid fraction. Simulated interface configurations are for (a) \( \theta = 22.5^\circ \), (b) \( \theta = 28.1^\circ \), (c) \( \theta = 36.6^\circ \), (d) \( \theta = 42.0^\circ \), (e) \( \theta = 45.0^\circ \), (f) \( \theta = 51.9^\circ \), (g) \( \theta = 61.9^\circ \), and (h) \( \theta = 65.1^\circ \).

**Figure 1.** Configurations of capillary condensation between two disks (brown) for varying liquid fractions. Simulations were run in a 250 × 150 lattice grid for \( \sim 11,000 \) MC steps with periodic boundary conditions. (i) Equilibrium was assumed when the standard deviation normalized with respect to the total system energy (equation (1)) was less than 1%. After equilibration, \( \sim 200 \) frames taken every 32 MC steps were averaged to create a density profile for the liquid. The air-liquid interface was chosen to be the 50% density contour. (j) least-squares circular fits of this contour permitted calculation of various interfacial properties that were compared with theory. The circular disks are 125 lattice units in diameter. The filling angle \( \theta \), depicted in Figure 1a, describes the liquid fraction. Simulated interface configurations are for (a) \( \theta = 22.5^\circ \), (b) \( \theta = 28.1^\circ \), (c) \( \theta = 36.6^\circ \), (d) \( \theta = 42.0^\circ \), (e) \( \theta = 45.0^\circ \), (f) \( \theta = 51.9^\circ \), (g) \( \theta = 61.9^\circ \), and (h) \( \theta = 65.1^\circ \).
angle $\theta$, depicted in Figure 1a, is defined to be the angle between the contact point between the disks and the three-phase contact point [e.g., Fisher, 1926; Lu and Likos, 2004]. A least-squares circular fit was performed on the averaged equilibrated profiles to extract a radius of curvature and filling angle for the simulation results shown in Figures 1a–1h. Figure 1j compares the theoretical and simulated radii of curvature. In general, the MC results accord well with analytical predictions but systematically estimate a smaller radius of curvature. This difference, which is less than 4%, can be attributed to the neglect in the analytical model of surface hydration on the solid, an effect known to play a role in surface adsorption phenomena. The disparity increases slightly with liquid content (Figure 1j), a trend seen in the thickness of the layer of liquid condensation (Figures 1a–1h).

Further validation of the MC methodology on a more complex geometry was obtained through comparisons with microXCT images for assemblies of randomly sized and distributed hydrophilic glass beads of size 400–600 microns. This system was imaged at the Swiss Light Source TOMCAT beamline with a constant suction head boundary condition. Figure 2 compares a representative 2D microXCT image showing water distributions (Figure 2a), with simulations of the same system (Figures 2b–2f) under different water saturations. For much of the sample, the simulated menisci shown in Figure 2c (at 25% saturation) match the bridging patterns seen in the microXCT image in Figure 2a. The few differences are mainly between particles farther apart and may reflect hysteresis between metastable water distributions associated with complex granular packings. In fact, multiple simulations and experiments on the same initial grain configurations yield slightly different equilibrated capillary bridging; nevertheless, interstitial pore spaces contain similar amounts and shapes of water.

4. Application to Capillarity in Soils

The MC methodology was next used to model the distribution of water in a more realistic sample of soil, one of the most abundant and complex porous materials. Small columns filled with Ottawa sand were prepared with each containing a different liquid saturation. Subvolumes from all of the columns were imaged at the Advanced Photon Source 13-BMD tomography beamline at Argonne National Laboratory. Representative two-dimensional (2D) cross-sectional images (Figures 3a–3d) of the grain and pore structure were extracted from the 3D image and then used in the MC analyses. We conducted simulations for each of these 2D configurations by varying liquid saturation from dry to completely wet. The results for each configuration at the same saturations as the experimental data (Figures 3a–3d), are shown in Figures 3e–3h. The distributions of liquid water are remarkably similar between the X-Ray images and MC predictions.

Having validated the MC approach, we now turn to its application in developing macroscopic constitutive relations. In particular, we focus on the relation between liquid saturation and capillary pressure, $\Delta P$, an important material property governing liquid retention, inter-granular forces, and fluid flow in porous materials. For porous media such as soil, the relation is often referred to as the adsorption isotherm or soil-water retention curve (SWRC) [e.g., van Genuchten, 1980; Lu and Likos, 2004]. The SWRC is typically constructed by fitting macroscopic experiments to an empirical equation. Here we offer a theoretical way to compute the SWRC employing the Laplace-Young equation,
\[ \Delta P = T_s \left( \frac{1}{r_1} + \frac{1}{r_2} \right) \]

where \( r_1 \) and \( r_2 \) are the principal radii of curvature obtained from the local liquid-vapor interfaces [e.g., Lu and Likos, 2004]. \( T_s \) is the surface tension of water: 71.79 dyn/cm at 25°C. All simulations shown in this paper were performed in two-dimensions, one of the radii is effectively infinite. In 3D the Young-Laplace equation takes into account a second principal radius of curvature. Since this value does not exist in the 2D equation, an inherent discrepancy between 2D and 3D calculations in this model exists. By assuming \( r_1 = r_2 = r \), we have \( \Delta P = 2T_s/r \), which indicates that the 2D SWRC is a factor of two in magnitude less than that of the 3D SWRC. This scaling factor was used in the calculations presented here to relate the 2D Monte Carlo results to 3D systems. The experimental SWRCs for the four different saturations (Figures 3a–3d) compare favourably with those from MC simulation performed on grain positions given by the microXCT images (Figures 3e–3h). This is shown in Figure 3i with the comparison with the conventional Tempe cell method for SWRC [e.g., Lu and Likos, 2004] and the relative differences are less than 8%. These results confirm that the MC approach represents a new quantitative means for both understanding and predicting properties resulting from the intricate interfacial interactions of complex porous materials.

[8] A second important macroscopic relation is the relation between the air-liquid interfacial area and liquid saturation, often referred to as the specific surface area curve (SSAC). The SSAC characterizes, for instance, the composite tensile
strength and can be used to predict trends in the rates of biological activities [e.g., Nichols et al., 2005]. It can be readily obtained from our MC analysis by counting the number of air-water lattice contacts for clusters of water, multiplied by the length of a lattice unit and normalized by the total simulation area. Figure 3b compares results from microXCT and MC predictions. For this soil, the specific surface area peaks between 30 and 67 and 319.45,0 ppm., Intermolecular and Surface Forces, 374, 121, Mol. Phys. – specific surface area, J. Eng. Mech., Soil Sci. Soc. Am. J., unsaturated soils, 241, 44, b, J. Colloid adsorption isotherms, 20, Rev. Mod., 024708, doi:10.1063/ can now be computed without expensive and time J. Chem. Phys., 387, of the 3.521 mm × 3.521 mm cell used for Ottawa 16, J. Phys. A Math. Gen., between liquid saturation and tensile strength. interface plays a dominant role in the tensile strength of wet granular materials as a function of liquid saturation has been investigated for many years [e.g., Mason and Clark, 1965; Hornbaker et al., 1997; Pierrat and Caram, 1997]. Yet a theory that describes tensile strength for all saturations has been developed only recently [Lu et al., 2009]. The theory leads to a closed form analytical equation for tensile strength under all saturations and predicts the same non-monotonic behaviour shown in Figure 3j for sandy soils, strongly indicating that the SSAC of the liquid-air interface plays a dominant role in the tensile strength of wet granular media. The MC approach provides a direct link between liquid saturation and tensile strength.

5. Discussion

[10] Since the MC simulation is coarse-grained in lattice units, the SWRC and SSAC results can be scaled up by simply changing the lattice cell size. For example, if the dimensions of the simulation region shown in Figures 3a–3h is 1/100th of the 3.521 mm × 3.521 mm cell used for Ottawa sand, a typical scale for silty soil, and if the relative pore distribution remains the same, the corresponding capillary pressure and specific liquid-air interface area curves in Figures 3i and 3j would be simply multiplied by a factor of 100. A profound implication is that once the pore structures and pore material compositions are determined by high resolution imaging techniques such as microXCT, TEM, and SEM, the associated multi-phase and interfacial properties such as adsorption isotherms and specific surface area curves can now be computed without expensive and time-consuming macroscopic experiments.

[11] The MC methodology is thus a computationally innovative approach to quantify important structural and macroscopic constitutive relations in wet porous media. The cases above focus only on homogeneous materials, however it is straightforward to simulate regions wherein saturation varies locally (see shaded areas in the circled regions in Figures 2 and 3). The transition zones showing large variations in saturation indicate higher probabilities to shift to new interfacial configurations in response to small perturbations in capillary pressure or saturation. Quantifying such relations can provide useful information on how and where cavitation occurs, or to identify preferential flow paths in porous materials. The methodology provides a route from grain or pore scale structure to water distribution and thus macroscopic constitutive relationships that would be otherwise difficult to obtain.

References


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