

PORE SCALE MODELLING OF CO₂ SEQUESTRATION

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Abstract

Geological sequestration of CO₂ in porous sedimentary medium filled with saline water requires a clear view of the gas behavior as a function of topology of the hosting pores, linked to capillary phenomena. The sedimentary medium is modeled as a random packing of equal spheres giving rise to 3D network of pore bodies and throats. The injected CO₂ pushes the water from pores of the reservoir. The scenario is simulated by the increase of the curvature of the liquid/CO₂ interface. Eventually a critical state is reached where the liquid is drained from pores. When the liquid counteracts this first drainage step (imbibition), there is a progressive decrease of the interfaces curvature until they merge together, eliminating the CO₂ from pores. This pore-scale investigation of the mechanisms possibly occurring after a gas injection is studied.

Keywords: Drainage, imbibition, surface evolver, capillary pressure, porous media

Introduction

In recent decades, the CO₂ concentration in the atmosphere has rapidly increased¹ with a wondering correlation with global climate changes². As a consequence, increasing efforts have been directed towards finding solutions to mitigate the CO₂ concentration in the atmosphere. One of the most serious solutions is offered by the CO₂ injection directly inside deep geological formations. The formations are potentially capable to store many thousands of gigatonnes of gas, possibly over several thousand years. Meanwhile, large sedimentary basins with easy access (depth around 800 m) are widely distributed worldwide, having tremendous pore volume, capped by impermeable rocks, and containing saline water of no use³. The injected CO₂ invades the porous space leading to non-saturated state and the system converges towards a quasi-equilibrium state, wherein major portion of initial CO₂ is

persisting as disseminated air pockets, part is dissolved inside the contacting solution, and part is mineralized by turning into carbonates.

The CO₂ sequestration in geological formation is the outcome of two key processes: drainage and imbibition. Drainage process occurs during the period of CO₂ injection, the CO₂ bubble disperses inside the pore spaces because the gas-liquid interface advances against the liquid (drainage). Depending on the topology of the pores network, the initially continuous bubble can penetrate the whole network (splitting of bubble sticky CO₂ plume), turning into a series of smaller bubbles, or just slides inside the media depending on the minimization of the interface mean energy (slippery CO₂ plume⁴). In the post injection period, imbibition process initiates. The gas-liquid interfaces recede inside the pore spaces due to the increasing liquid pressure related to the drainage event (imbibition). In the drainage process, different pathways are possible depending on the pore's topology inside the sedimentary reservoir. As a consequence, the drainage and imbibition processes are governed by the capillary pressure at the two fluids which determines the partitioning between liquid and CO₂ saturation in the reservoir, under the final conditions.

We are using below the basic laws of capillarity to understand which processes at the pore scale determine the gas trapping or the out gassing. The interface (meniscus) between the non wetting and wetting phases is curved expressing the capillary pressure between the two contacting phases (Young Laplace equation). The associated surface area and volume of the liquid and gas which share the pore space provide a quantitative estimate of the gas/liquid trapping state of the pores network. These calculations as well as the building of the model pores network is performed through the Surface Evolver software.

Surface Evolver Software

The Surface Evolver software was developed by Brakke⁵ to study the soap film surface shape and minimize its energy according to different constraints, like surface tension, geometry, gravity effects, all parameters related to the stability of one interface under a certain degree of curvature (capillary interface). These characteristics make it a suitable tool to study the effect of these parameters in the CO₂ sequestration strategies, when the injected gas (CO₂) meets the resident aqueous solution (in general, a long-time resident brine). The software requires as inputs the initial surface location, different characteristics of the surface, and the surface dependent energy function. Actually, it operates on surfaces which consist of geometric elements plus auxiliary data such as constraints, boundaries and forces. The basic elements used to represent a surface are vertices (points in Euclidean 3D-space), edges, facets

and bodies. The coordinates of the vertices are the parameters that determine the location of the surface, and are changed according to the minimization procedure. The surface is implemented as union of flat triangles, so that the smoothness of a sphere depends on the number of triangles (Fig. 1). The total surface energy quantity results from the surface tension and other terms like gravitational energy. Then, the software makes the surface to change under these given constraints to obtain the equilibrium configuration (minimum energy). Finally, the shape of interface under equilibrium conditions is displayed and corresponding surface area and volume can be obtained. One of the interesting feature of this software is that the minimization is done without directly applying Young Laplace equation, though it is inherently satisfied. Thus, it can be applied to complex geometries which are difficult to model through a direct use of the Young Laplace relation.

Pore-scale Model of Sedimentary Media

To model the physical processes occurring during the CO₂ sequestration such as drainage/imbibition, an adequate knowledge of the pore space geometry is essential. Natural media have complicated pore space geometries, which are also heterogeneous from place to place. Many models, even sophisticated, are unable to satisfactorily describe the behavior of two immiscible fluids in three-dimensional pore space⁶⁻⁸. To concentrate ourselves on the physical laws without geometrical complexities, we used a model of random packing of equal spheres^{9,10}. The random packing of equal spheres gives rise to a network of pore bodies, the largest pore spaces, connected by throats, the thinnest pore spaces, which coexist permanently and host a continuous liquid or a liquid-gas biphasic mixture (Fig. 1). The pores could be described in terms of tetrahedral sub units, centers of four spheres lying on the vertices of a tetrahedron. The void space inside the tetrahedron corresponds to a pore body while the cross section of each face corresponds to a pore throat. An interface located at the pore throat can accept capillary conditions which makes it to collapse if hosted in the pore body. It becomes obvious that the way the whole reservoir drains or imbibes, meaning that the way each pore empties or fills, will influence the stability of liquid/gas trapped in the pore bodies or pore throats. Our aim is to clearly decipher the main steps and mechanisms in these processes, and renew the basics of the real systems modeling.

This configuration where thin spaces directly coexist with larger spaces is very often called the ink-bottle arrangement by the soil scientists. It makes possible the coexistence of gas and liquid at equilibrium even under pressure, owing to the cohesion of the liquid capillary

bridges which can take place either across the thinnest (high capillary conditions) or across the largest (low capillary conditions) pore spaces. A direct first conclusion is that the throats can host more capillarized liquid than the bodies, while coexisting with gas filled pore body. In other words, we can say that once the pore bodies have been emptied, a re-emptying stage requires a significant change of the local conditions. As a consequence, during a succession of drainage-imbibition events, naturally there is a range of conditions along which a bubble can be trapped in the bodies while the contacting throats are imbibed under varying pressure.

Capillary Pressure

The capillary properties of the pores and throats determine the drainage/imbibition. According to the Young Laplace law, the capillary pressure is the pressure difference (P) across a curved interface between the wetting and the non-wetting phases. It is directly proportional to the surface tension between the two phases, and inversely proportional to the size of the bridge.

$$\Delta P = P_{NW} - P_W = \gamma_{LV} \times \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \quad (1)$$

Where P_{NW} and P_W are the pressures of, respectively, the non-wetting (CO_2) and the wetting (aqueous solution) phases. LV is the surface tension between the two phases. r_1 and r_2 are the main radii of curvature of the meniscus, and for spherical meniscus: $r_1 = r_2$. The two radii are connected to the radius of the hosting pore, through the contact angle made by the meniscus on the solid wall (noted θ), $r_{PORE} = r_{MENISCUS} / \cos(\theta)$, and it is also connected to the curvature of the interface (noted C) by: $C = 1/r_{PORE}$.

The CO_2 is injected in the sedimentary media deeper than 800m, at pressure higher than 10MPa while the temperature ranges over 35-60°C. The critical pressure of CO_2 is 7.39 MPa and the critical temperature is 31.1°C, hence, the CO_2 penetrates the reservoirs as supercritical fluid. Along these P,T conditions, the interfacial tension between CO_2 and brine remains almost constant close to 26 mN/m¹¹ and this value was used in all simulations. Moreover, the wetting phase was assumed to completely wet the solid spheres, i.e. the meniscus sticks to the solid wall with a nil contact angle. That means the solid is hydrophilic enough for the liquid to slip on it without energy cost. In physical chemistry terms, that translates in the following Young Dupré relation:

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cdot \cos\theta \quad (2)$$

where the subscript defines between which phases the surface tension is considered. When

the liquid-to-vapor surface tension (γ_{LV}) is equal to the difference between the two other surface tension (solid-to-vapor γ_{SV} , and solid-to-liquid γ_{SL}), the contact angle is zero. This is the case of the perfect wetting, characteristic of the surfaces with high γ_{SV} owing to their large cohesion energy (glasses, metals, oxides). On the contrary, the low γ_{SV} solids will have a very high contact angle (organic solids, like Teflon, for instance).

Eventually, the capillary pressure appears entirely governed by the configuration of pore or throat. The smaller the pore, the larger the capillary pressure, and therefore, the most stabilized can be the liquid by the capillary effects. With the presently used ink bottle geometry, it appears that the liquid should persist at the pore throat while the CO₂ should more easily invade the pore body. Our primary objective is to illustrate how such basic heterogeneity controls drastically the evolution and the amount of the gas trapped inside the media, all together with the local (P, T) conditions.

Building Diversely-filled Pores Network

As discussed above, the knowledge of the geometrical distribution of the two immiscible fluids within the pores is of the utmost importance to predict the capillary pressure saturation relationships of the porous media, and therefore, play the primary role in the key processes of drainage, imbibition, and dissolution. First, the exact size of the wall-to-wall distance where a liquid-gas interface takes place also controls the limiting curvature which interface might attain during the varying capillary pressure. Each time the interface curvature exceeds the limit, obeying the Young Laplace relation (equation (1)), the interface collapses and moves to another more favorable place. We assume the Young Laplace equilibrium throughout in our simulation, though it is experimentally known that it can be trespassed¹²⁻¹⁵. Second, spatial characteristic, of consequence in our reasoning, is the surface area of the interface between wetting and non-wetting phase i. e. between the brine solution and the CO₂ phase: it is termed hereafter the bridge area or interface area and is of primary importance while considering the other storage process i.e. gas dissolution in brine solution. On the practical side, the gas or liquid volume present in the pores network are expressed relative to the pore volume itself: this is termed as saturation ratio, a common way to express the liquid/gas partitioning in the usable volume. To do such calculations, and also to evaluate the corresponding capillary pressure, we need to choose a peculiar grain size. In simulation, the spherical grains are considered of diameter of 10 micron, a choice which corresponds to pore diameters around 2

μm . Also, the hydraulic connectivity is assumed to be everywhere, meaning that a change in the pressure conditions make the whole reservoir to react: hydraulic gradient is everywhere active on the transport processes and capillary pressure adjustments.

Liquid Bridge between Two Equal Spheres: Pendular Ring

Let us begin with the simplest situation where a liquid volume is held between two equal spherical grains against the gravity (suspended water) forming a capillary liquid bridge. The bridge is characterized by a constant mean curvature having pendular shape (Fig. 2).

Some part of the spherical grain comes in contact with the wetting phase of the pendular ring. However, in the remaining part of the grain, the liquid spreads over the grain surface in the form of a thin adsorption film. This thin film provides the hydraulic connectivity of the liquid phase throughout the whole packing of spheres. Negligible liquid volume is contained inside the thin film in comparison to the pendular ring. However, in addition to liquid bridge, the film realizes a liquid- CO_2 interface necessarily required for gas dissolution. Hence, the total interface area is taken as the sum of the water thin film area and the ring area, and is expressed (Fig. 3) relative to the area covered by a water monolayer over the two grains. As for the liquid bridge, the two key parameters (Fig. 3) are the curvature of the interface (depending on the capillary pressure, namely the pressure difference across the interface), and the associated volume delimited by the interface, which characterizes the liquid amount wherein any dissolved solutes (like aqueous CO_2 or any weathering products) can settle in. Investigating the pore scale from these two sides, area and volume, allows to get a simultaneous view of the surface/volume ratio, which is directly connected to the trapping/dissolution behaviors.

The amount of liquid held in pendular ring is expressed relative to the liquid volume contained between the two spheres at nil capillary pressure. With increasing capillary pressure, the curvature of the pendular ring goes on increasing, thereby decreasing the liquid amount while the total interface area increases. At this stage, do notice that we normalized the interface area to the area occupied by a monolayer of water (assumed 0.3 nm thick) covering all the solid surfaces. Otherwise, when the value of the normalized interface area comes closer to 1, the water is only present as adsorption films, while a decreasing value points to an increasing amount of water trapped as capillary bridge. The curves (Fig.3 left) can be subdivided into three parts according to the local slope of the characteristic curves. In the first region the slope is very steep indicating that liquid is loosely held and can be carried

away by compensating small capillary traction, while the removal of liquid increases the interface area (Fig.3 right).

In the second region, the local slope gradually varies with capillary pressure: the liquid is more strongly bounded by capillary force, but keeps significant volume trapped as capillary bridges. Yet, the relative total interface area gradually increases with increasing capillary pressure.

In the third region, the slope remains almost constant: the liquid volume is almost zero and the relative interface area close to one. In this domain, the contact between the two fluids is maximal, but the amount inside which one may trap dissolved gas is reduced to one monolayer of water molecules (0.3 nm).

In terms of drainage/imbibition processes, the two-spheres scheme illustrates that it is not possible to dry completely the grain packing, due to the special stability of adsorption films. On complete drainage, the system is left as network of pendular rings trapping a continuous CO₂ bubble. Thus, the liquid remaining in pendular rings contributes towards the residual liquid saturation of the sedimentary systems.

One interesting point, though it is not developed below, is that in the first and the second region, the CO₂ is interacting with water experiencing a certain capillary pressure. And the in gassing effect of the capillarized water at high suction is well-referenced¹⁶⁻²¹.

Liquid Bridge Adhering to Three Spheres: Drainage and Imbibition in Pore Throat

A situation where liquid phase adheres to three spheres allows coming closer to three dimensional pores network. Three sphere configuration corresponds to the faces of a tetrahedral subunit, at the location termed above the pore throat (Fig. 4), opposite to the pore body (center part of the tetrahedron).

The pore throat provides entrance for the liquid-gas interface inside the pore body, so the dimensions of the pore throat determine the capillary retention (imbibition) or the hydraulic movement (drainage) of the interface. Initially, liquid in the form of a continuous phase adhering to three spheres in contact with CO₂ from all sides. The increasing capillary pressure causes the interface to become more curved. On reaching the “critical curvature” the interface splits into three interfaces (Fig. 4). Simulation was carried by successively increasing the capillary pressure expressing the progressive invasion of CO₂ (Fig. 5). At critical curvature, the CO₂ is able to penetrate the central cavity of the throat, which traps therefore a gas bubble in an equilibrium state. Before reaching the corresponding capillary conditions, the liquid phase occupies most of the throat volume, filled after this threshold by

CO₂ ($V_{CO_2} = 0.49$). Do notice that the liquid phase is initially continuous, and the gas bubble is concentrated in the exterior medium, while after the CO₂ invasion, it turns into a biphasic mixture of two immiscible fluids (CO₂ brine) coexisting in the throat spaces.

In drainage, CO₂ invades from one face. At the critical curvature, CO₂ passes through triangular hole, and gets connected to the reservoir. In imbibition, on decreasing capillary pressure, pendular rings start growing and finally merge together spontaneously, eliminating CO₂ from triangular hole so that the CO₂ phase gets disconnected.

After drainage, the (small) liquid volume remains in the pendular rings even with increasing capillary pressure, meaning that the amount of trapped CO₂ negligibly changes (Fig. 6). These pendular rings contribute towards what is called the residual water saturation, namely the water amount always persisting in natural media.

The imbibition process defines the stage where after a drainage period (normally, up to the critical curvature), the capillary pressure starts decreasing, and the liquid-gas interface recedes towards the pore. In a real medium, this stage is afforded when the liquid pressure has sufficiently increased due to the drainage step, to reverse the driving force. At imbibition, the pendular rings start growing up to special capillary conditions at which the rings merge with each other forming a single liquid bridge adhering to the three spheres: the cavity is filled with liquid throwing out the CO₂ from the central portion, and the CO₂ phase now gets discontinuous (Fig. 6). On further decreasing the capillary pressure, the CO₂ amount decreases in a gradual fashion with the gradual decreasing curvature of the liquid gas interface.

The drainage and imbibition processes obviously follow different paths (Fig. 6), and the CO₂ amount trapped at a particular capillary pressure depends on the pathway. During imbibition process, and before attaining the critical curvature, there is a capillary pressure range along which the CO₂ trapped as stable bubbles is drastically larger than that present along the drainage process (Fig. 6; $V_{CO_2} \sim 0.6$).

The Four Spheres Case: Pore Body Drainage and Imbibition

A truly 3-dimensional pore network can be sketched by dealing with the liquid bridge(s) adhering to four spheres tetrahedrally arranged. In this case, each series of three grains displays a pore throat and wedge-shaped contacts (Fig. 7). The CO₂ can enter in the pore body through any the four throats.

Conclusion

In the present work we have carried out pore-scale investigation for CO₂ sequestration in deep saline aquifer media through capillary equilibria integrating the capillarity laws to understand the CO₂-brine interface behavior along the different steps of the post injection period, pressure associated to the drainage process, and its related equilibria towards the gas pressure, these mutual changes controlling the behavior of the global bubble.

The heterogeneity which is well-known to exist in real reservoirs is simply assumed through the equal-size of the constituting spheres, and varying sphere-to-sphere distance. It would be straightforward to introduce a certain degree of varying sphere size, the combination of possibilities becoming infinite of course.

In the present study, we used the “Surface Evolver” software, avoiding the direct implementation of the Young-Laplace law though it is being inherently satisfied. As a consequence, the present strategy and calculations could be extended to complex geometries, as those defined through the packing of grains having varying and complex individual shapes. Study was started with the simplest situation where a liquid volume is held between two equal spherical grains against the gravity (suspended water) forming a capillary liquid bridge of pendular shape characterized by a constant mean curvature. With increasing capillary pressure, the curvature of the pendular ring goes on increasing, thereby decreasing the liquid amount held.

The graph between liquid volume in pores versus capillary pressure can be subdivided into three parts according to slope of the curve. In the first region of very steep slope indicates that liquid is loosely held which can be removed by capillary pressure. The removal of liquid increases the interface area. In the second region is characterized by gradually varying slope indicating more strongly bounded liquid requiring more capillary force, significant volume remains trapped. The relative total interface area gradually increases with increasing capillary pressure. In the third region, the slope remains almost constant, large capillary pressure is needed to remove the liquid volume. In terms of drainage/imbibition processes, the two-sphere scheme illustrates that it is not possible to dry completely the grain packing. On complete drainage, the system is left as network of pendular rings trapping a continuous CO₂ bubble. Thus, the liquid remaining in pendular rings contributes towards the residual liquid saturation of the sedimentary systems.

The pore throat provides entrance for the liquid-gas interface inside the pore body. With the increasing capillary pressure the interface becomes more & more curved and at the “critical curvature” splits into three interfaces causing CO₂ penetration in the central cavity thereby causing CO₂ trapping. The system becomes a biphasic mixture of two immiscible fluids (CO₂-brine) coexisting in the throat spaces. During the imbibition process the capillary pressure starts decreasing, the pendular rings start growing eventually rings merge with each other forming a single liquid bridge adhering to the three spheres. The cavity gets filled with liquid throwing out the CO₂ from the central portion, and the CO₂ phase now gets discontinuous. Simulation of the situation where liquid phase adheres to three spheres. The drainage and imbibition processes follow different paths. The CO₂ amount trapped at a particular capillary pressure is pathway dependent. During imbibition process, before attaining the critical curvature, for certain capillary pressure range during which the CO₂ trapped as stable bubbles is drastically larger than that present during the drainage process.

Figures:

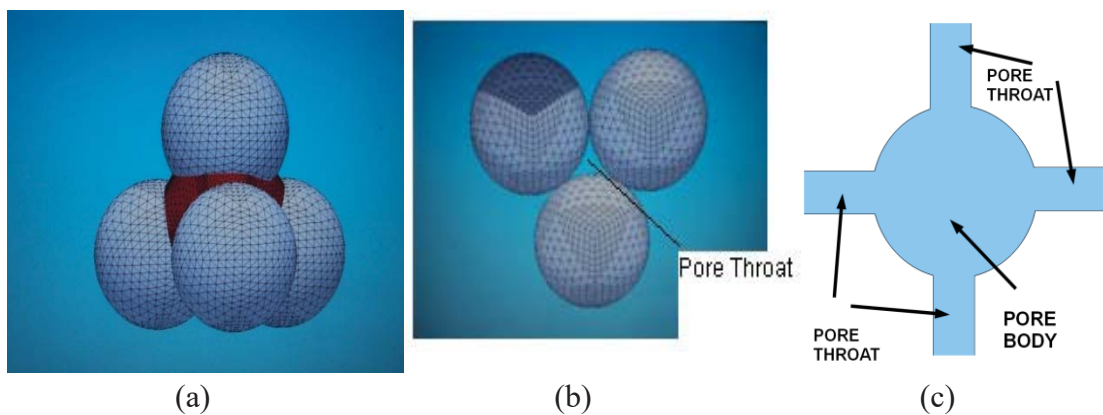


Figure 1. Left, four spheres tetrahedrally arranged, delimiting pore bodies. 'b', pore throat formed by three spheres. 'c', 2D schematic representation of pore body and pore throat.

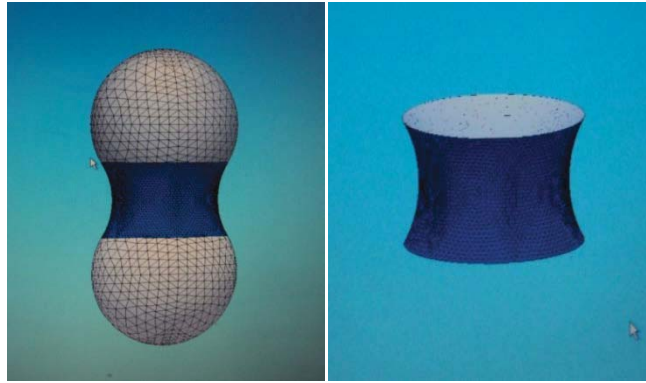


Fig 2. A simulated pendular ring between two equal spheres (left) and the sectional view (right).

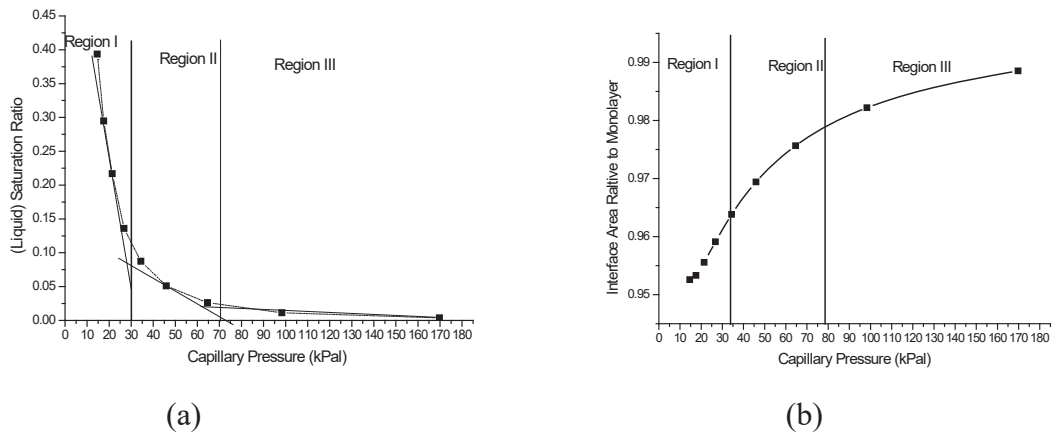


Figure 3. Pendular ring between two spheres. 'a' liquid volume in pores with capillary pressure. 'b' gas-liquid interface area relative to the monolayer area (see text) with capillary pressure.

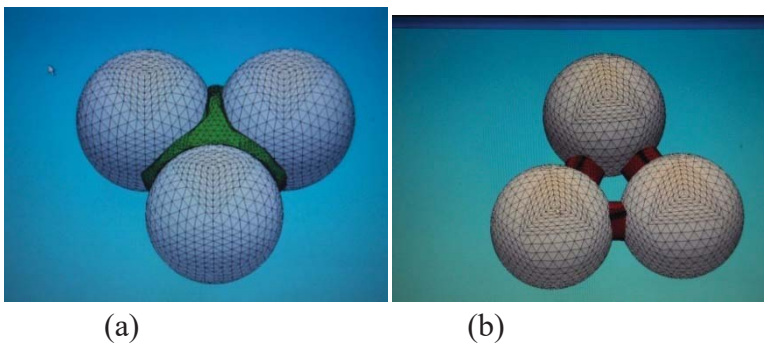


Figure 4. A typical simulated liquid bridge adhering to three equal spheres; before drainage (a) and after drainage (b).

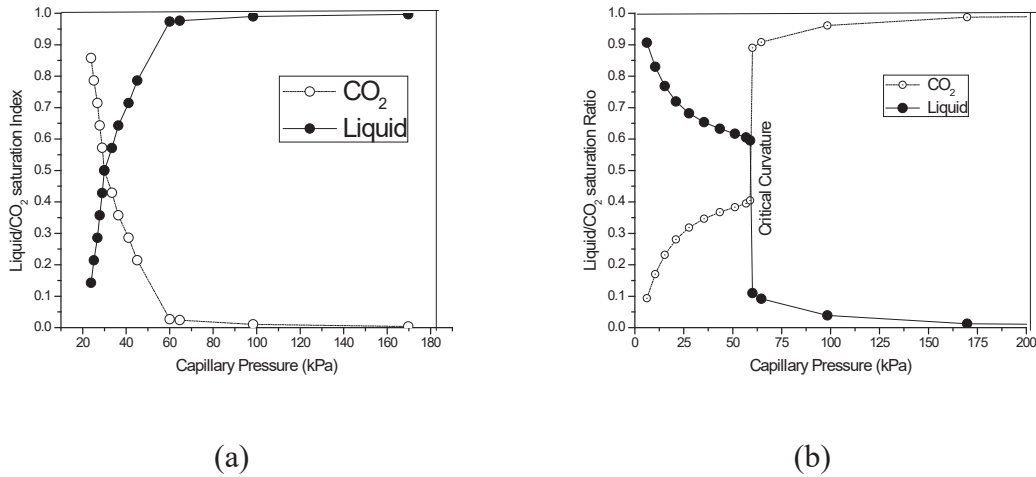


Figure 5. The key processes for pore throat formed by three grains. Drainage(a), Imbibition(b)

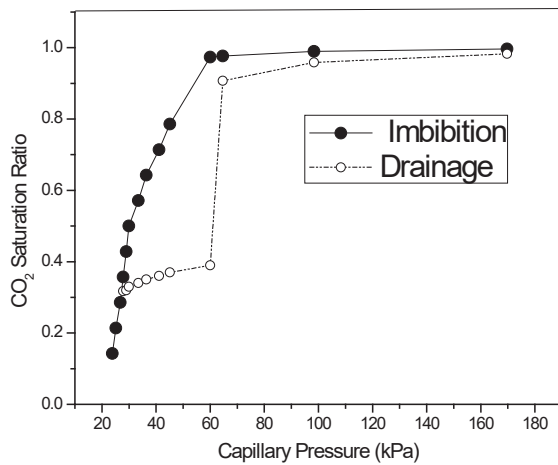


Figure 6. Comparison of volume of CO₂ trapped during drainage and imbibition processes in the pore throat formed by three equal spheres.

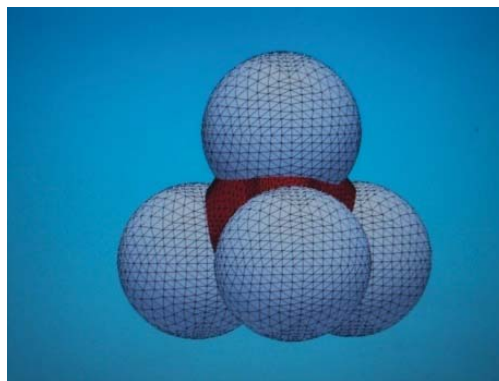


Figure 7. Liquid bridge adhering to four spheres arranged in a tetrahedral configuration.

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