Theoretical Evaluation of the Interfacial Area Between Two Fluids in Soil

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Introduction

When mass transfer occurs between immiscible fluids, it does so at an interface. It is important to understand the means by which this transfer occurs. In particular, it is important to be able to determine the interfacial area between these fluids, since it controls the rate of mass transfer. When this mass transfer occurs in a porous media, the system becomes increasingly complex because the interfacial area becomes harder to determine. Since this is the method by which non-aqueous phase liquids (NAPLs) contaminate groundwater, understanding this system could lead to better knowledge of contamination risks and cleanup strategies, since some remediation techniques also involve interphase mass transfer.

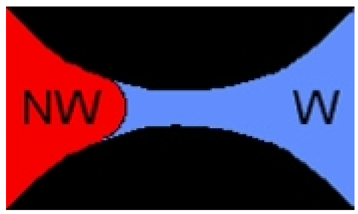

Figure 1. The Interface between a Wetting and a Non-Wetting Fluid [1].

My research involves developing quantitative models that will predict the surface area of the interface between immiscible liquids in porous media. The first step in this process involves solving the Young-Laplace equation for capillary pressure:

$$P_c = \gamma C$$

where Pc is the capillary pressure, γ is the interfacial tension between the fluids, and C is the mean curvature of the interface [1]. This solution is very simple for simple geometries; however, for a highly irregular porous medium, it can be very complex.

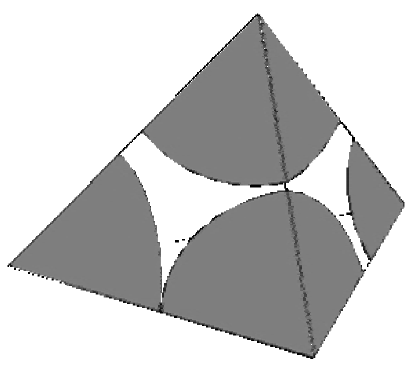

Figure 2. Irregular pore geometry [1].

In order to simplify this solution, the current model for determining the interfacial area between the fluids uses the Haines Insphere approximation. This approximation assumes that, as the interface passes through the pore throat, it is spherical. Therefore, the critical curvature is $C = 2/r_i$, where r_i is the radius of the largest circle that can be inscribed in the pore throat.

This method has merit. It is by far the simplest to use, and it *does* yield reasonable estimates of curvature; however, as Figure (3) indicates, it is not the most accurate measure of critical curvature. The meniscus that it predicts is smaller than the actual interface; therefore, the Haines Approximation provides a conservative estimate of the interfacial area and critical curvature at the interface.

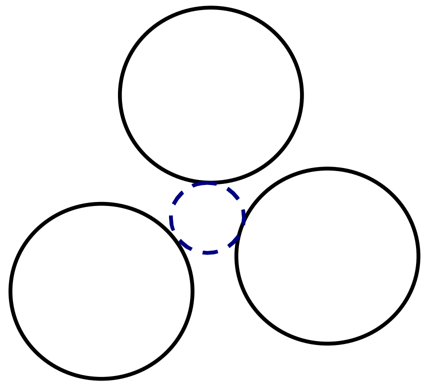

Figure 3. The Haines Insphere Approximation for 3 Spheres.

Another alternative to the Haines Insphere Approximation is the Mayer-Stowe-Princen (MS-P) approximation. This method makes the assumption that the packing surrounding the pore space is made up of an arrangement of uniform tubes or rods, rather than spheres [3]. The MS-P approximation also takes into account the presence of wedge menisci that could decrease curvature. This approximation will yield a lower critical curvature at the interface, and a better estimate of interfacial area.

Discussion

For the purpose of our study, an arrangement of three rods was chosen to approximate the system. Initially, the meniscus curvature is calculated assuming that there are no wedge menisci present. This will give the initial curvature that will be the basis for further estimates.

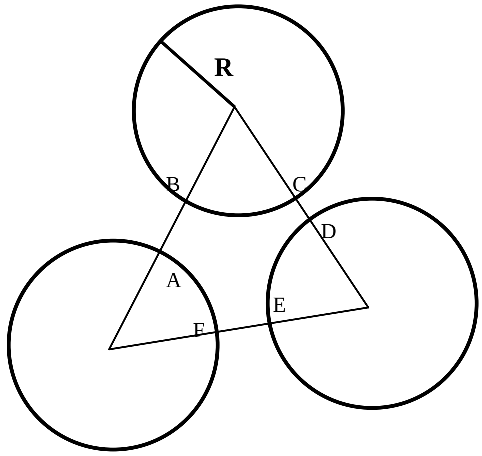

Figure 4. Rod Arrangement for Mayer-Stowe-Princen (MS-P) Approximation [2].

The meniscus curvature is found by taking the total area of the liquid supported by the solid-liquid surface tension, and dividing it by the solid perimeter where this support occurs (See Appendix A.):

$$C = 1/r_{init} \tag{1}$$

$$r = A/P \tag{2}$$

Initially, A is the area defined by ABCDEF in Figure (4), and P is the solid perimeter AF + ED + CB. Both of these values can be found using simple geometry (App. A).

The next step is to determine if wedge menisci are present, and if so, if they increase or decrease the curvature of the meniscus. Figure (5) shows a double wedge meniscus between two rods.

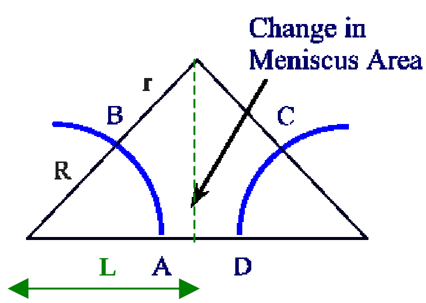

Figure 5. Double Wedge Menisci between Two Rods [2].

For this method, it is assumed that the meniscus will always adopt the lowest curvature possible; therefore if a wedge exists that *increases* curvature, it is assumed that there is no wedge at that interface. For our system, there are three separations between the rods that may contain wedge menisci. The area and perimeter of the wedge can be calculated from simple geometry:

$$\Delta A = (R+r)^2 \sin\alpha\cos\alpha - \left[R^2\alpha + r^2(90-\alpha)\right]\pi/180 \qquad (3)$$

$$\Delta P = \left[R\alpha - r(90-\alpha)\right]\pi/90 \qquad (4)$$

where r is the radius of the wedge calculated below:

$$r = (L - R\cos\alpha)/\cos\alpha \qquad (5)$$

The new area and perimeter values are then used to calculate a new meniscus radius. The new radius is only used if the result is larger than the previous calculation, indicating that the wedge results in a lower critical curvature. The normalized curvature is then calculated as the ratio of the rod radius to the new meniscus radius. Figure (6) compares the results of the MS-P method, the Haines Incircle approximation, and the Hwang approximation for a system of 4 spheres. The Hwang approximation was not discussed for this project, but it assumes that the capillary interface covers the entire cross section of a given tube, and that curvatures are inversely proportional to hydraulic radius (ratio of pore perimeter to pore area). The MS-P method clearly provides the best estimation of critical curvature, even though it assumes rod-like packing. The “point of separation” is the point where the meniscus curvature becomes higher for a pair of pores defined by three rods than that of one pore defined by four rods. If this separation cannot occur, such as when the wedge menisci are bounded, then the curve shifts to the rupture of back-to back wedges [2].

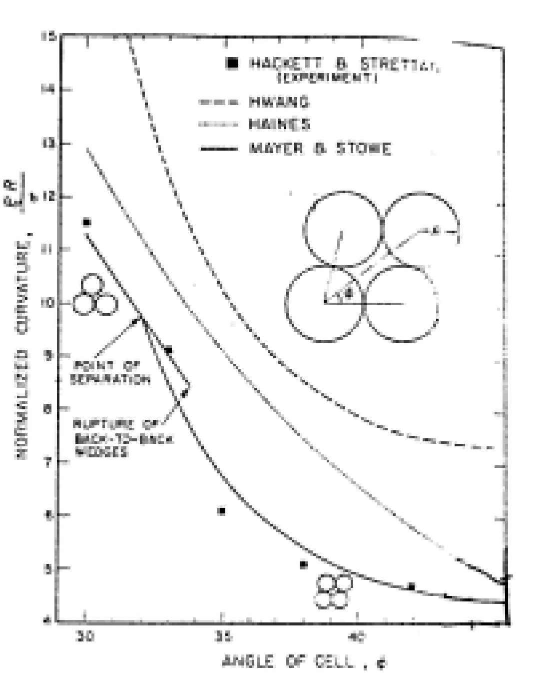

Figure 6. Comparison of Experimental Results with 3 Theoretical Approximations for 4 Rods [2].

Conclusion

The Meyer-Stowe-Princen Approximation gives a good estimate of the critical curvature of a fluid in a pore space. The pore space can be approximated by different configurations of rods, even when the packing is comprised of spheres. The Haines Insphere approximation is a simple method to use; however, it provides a high estimate of critical curvature, and a conservative estimate of interfacial area.

References

1. Bryant, S. “Theoretical Evaluation of the Interfacial Area between Two Fluids in Soil, ” AICHE Annual Meeting, Oct. 31 – Nov. 5 1999.

2. Mason, G. and N.R. Morrow, “Coexistence of Menisci and the Influence of Neighboring Pores on Capillary Displacement Curvatures in Sphere Packings,” *Journal of Colloid and Interface Science*, **100,** 519 – 535 (1984).

3. Mason, G. and N.R. Morrow, “Meniscus configurations and curvatures in non-axisymmetric pores of open and closed uniform cross section,” *Proc. Roy. Soc. London A* **414**, 111-133 (1987).