



The uniform capillary model for packed beds and particle wettability

Nate Stevens¹, John Ralston, Rossen Sedev*

Ian Wark Research Institute, University of South Australia, Mawson Lakes, SA 5095, Australia

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ABSTRACT

The distribution and movement of fluids in porous media are important in a variety of situations arising naturally and industrially (e.g., water migration in soils, oil recovery, chromatography, filtration and separation processes). Our specific interest is in deriving advancing and receding contact angles from capillary pressure measurements in packed beds of particles partially saturated with liquids. The simplest model of a porous medium treats the porous body as an equivalent uniform capillary giving rise to the same capillary pressure. Pressure measurements were performed successfully with advancing as well as receding liquids. For an advancing liquid front a measurement with a second liquid is needed to calibrate the equivalent capillary radius and obtain the advancing contact angle. For a receding liquid front – an additional determination of the amount of liquid trapped behind in smaller pores is required. The equivalent capillary radius is mainly determined by the porosity of the packed bed and is easily corrected to account for capillary retention. Only then can the receding contact angle be obtained reliably. This new methodology for contact angle measurement was validated with model systems and applied successfully to various real particulate systems.

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1. Introduction

The wettability of small particles is of paramount importance in many industrial processes, e.g., flotation, powder technology, paints, etc. Wettability is best quantified by the contact angle, θ , i.e. the angle of inclination of the liquid/vapor interface at the three-phase line. The contact angle is related to the interfacial tensions through the Young equation [1,2]:

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma} \quad (1)$$

where γ_{SV} , γ_{SL} , and γ are the interfacial tensions of the solid/gas, solid/liquid and liquid/gas interface, respectively. The contact angle reflects the balance between adhesive and cohesive forces in the three-phase system. According to Eq. (1) the equilibrium value of θ is entirely determined by the intermolecular interactions (accounted for by the three interfacial tensions).

It is highly desirable to be able to measure the contact angle in any three-phase system of interest. However, most of the well-established measurement techniques are suitable only for flat surfaces with relatively large areas [3,4]. The popular sessile drop technique requires a flat reflective surface of at least a few square millimeters. The standard Wilhelmy technique is applicable to plates or fibers with a fixed cross-sectional shape and length of

* Corresponding author. Fax: +61 8 8302 3683.

E-mail address: rossen.sedev@unisa.edu.au (R. Sedev).

¹ Present address: Particle Engineering Research Centre, University of Florida, Gainesville, FL 32611, USA.

about 10 mm or more. The measurement of contact angles on particles is complicated by their small size and significant curvature. Two techniques have been adapted successfully to measure the contact angle on single particles: sphere tensiometry [5–8] and colloid probe microscopy [9]. However in both cases delicate instruments and significant expertise are required; even more restrictive is the fundamental requirement for particle sphericity.

A more practical approach is to pack a large number of similar particles into a porous plug and perform a measurement related to the wettability of the solid surface. Because of the small cavities and void space between the assembled particles the packed bed possesses, as a whole, intrinsic capillary properties. According to the Laplace equation, the capillary pressure across the liquid/gas interface, ΔP , is directly proportional to the surface tension of the liquid and the mean curvature, $\frac{1}{2}(R_1^{-1} + R_2^{-1})$ (R_1 and R_2 are the principal radii of curvature), of the interface [1,2]. In a small capillary the liquid interface is approximately spherical and the capillary pressure is

$$\Delta P = \frac{2\gamma}{R} = \frac{2\gamma}{r} \cos \theta \quad (2)$$

where R is the radius of interfacial curvature and r is the radius of the capillary. Because the contact angle acts as a boundary condition for Eq. (2) it has a strong influence on the shape of the liquid surface and hence on the capillary pressure. Thus, a measurement of capillary pressure coupled with a tractable model of the porous medium can be used to estimate the contact angle.

In the simplest possible approximation, the porous medium is modeled as a single uniform capillary – Fig. 1.

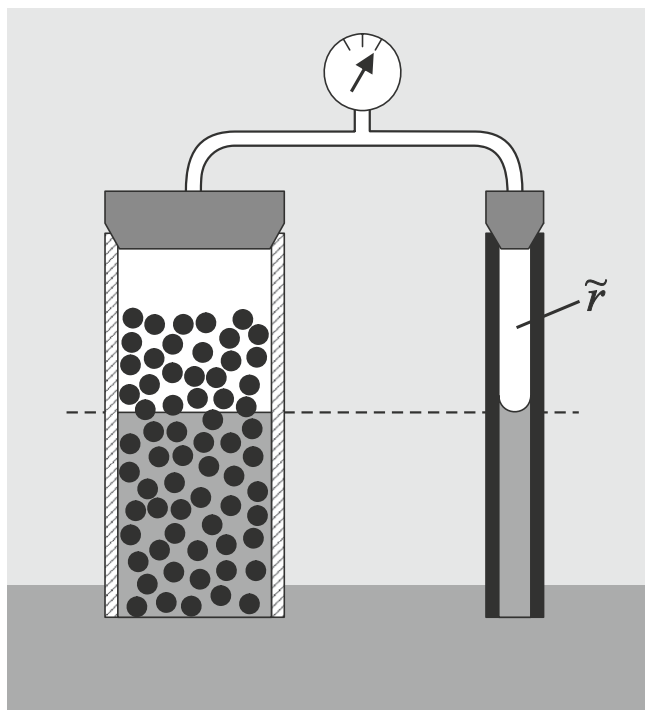


Fig. 1. Uniform equivalent capillary model of a porous body. The capillary pressure is the same in both capillary systems due to the choice of an effective capillary radius, \tilde{r} .

The radius of the equivalent capillary (effective capillary radius, \tilde{r}) is chosen so that the capillary pressure, ΔP , in the particle bed is given by the uniform capillary formula (2). The static capillary pressure technique (SCPT) for contact angle measurement consists in measuring the static capillary pressure, estimating the effective capillary radius, and calculating the contact angle with Eq. (2) (γ is known or measured independently). The SCPT was originally proposed by Bartell and co-workers [10,11]. Diggins et al. [12,13] have re-assessed the technique and also developed a compact and robust instrument which has been employed in a number of applied studies [14–17].

The most convenient determination of \tilde{r} is performed with a second liquid which is known to fully wet the powder (contact angle $\theta_2 = 0$) and the working expression for the contact angle of interest, θ_1 , is

$$\cos \theta_1 = \frac{\gamma_2 \Delta P_1}{\gamma_1 \Delta P_2} \quad (3)$$

Alternatively, the equivalent capillary radius can be obtained from the porosity of the packed bed. If the pore volume, V_V , is entirely accessible to the fluid and the pore shape is approximated by a cylinder (i.e. $V_V/A_S = r/2$, where A_S is the area of the solid surface), then

$$\tilde{r} = \frac{2V_V}{A_S} = \frac{2(1 - \phi_S)}{\rho_S \phi_S \bar{A}} \quad (4)$$

where ρ_S is the density and ϕ_S the volume fraction of the solid, and \bar{A} is the specific surface area. This effective capillary radius is essentially identical (within a 1/2 factor) to the mean hydraulic radius [18,19]. Eq. (4) can be obtained within a simple thermodynamic framework [20] in which the liquid has penetrated quasi-statically a microscopically uniform porous body [21]. Diggins et al. [12,13] have provided a detailed experimental validation of Eq. (4).

The above considerations are equilibrium ones, but in practice when the liquid has penetrated a dry bed, before stopping due to increased gas pressure, the contact angle obtained is an advancing

one, θ_A . However, in some instances the receding contact angle, θ_R , is of far greater importance. For example, in flotation the success and selectivity of the process depend on the particle–bubble contact established after the liquid film ruptures, i.e. the receding contact angle is the pertinent parameter [22]. Furthermore, when measurements are carried out with the particles that have been dried, some alteration of their surfaces and wettability may have occurred. In real systems, the contact angle hysteresis (i.e. $\theta_A - \theta_R$) can be very large and thus using the value of θ_A , even as a guide, can be misleading. It is therefore highly desirable to investigate the possibility of measuring receding contact angles together with advancing contact angles.

In this paper, we present an adaptation of the SCPT for the measurement of the receding contact angle. The major difference between a liquid penetrating into a dry porous bed and the same liquid being expelled from a bed, after liquid saturation, is that pockets of liquid are left behind the receding front – Fig. 2a.

This translates into an effective reduction in porosity and hence a smaller effective capillary radius. This radius decrease turns out to be different for different liquids (i.e. $\tilde{r}_1 \neq \tilde{r}_2$) and therefore Eq. (3) must be rewritten as

$$\cos \theta_1 = \frac{\gamma_2 \Delta P_1 \tilde{r}_1}{\gamma_1 \Delta P_2 \tilde{r}_2} \quad (5)$$

In other words, the use of a second liquid is not enough to account for the effective capillary radius. If the volume fraction of the retained liquid is ϕ_L , then the effective porosity is $1 - \phi_S - \phi_L$ (rather than $1 - \phi_S$ as for a dry particle assemblage) and the working expression for the contact angle becomes

$$\cos \theta_1 = \frac{\gamma_2 \Delta P_1 (1 - \phi_S - \phi_{L1})}{\gamma_1 \Delta P_2 (1 - \phi_S - \phi_{L2})} \quad (6)$$

Furthermore, because the liquid has receded during the measurement the contact angle in this case is a receding one.

We describe in this paper the determination of the parameters required in Eq. (6), namely $\Delta P_{1,2}$, ϕ_S and $\phi_{L1,2}$ (where $\gamma_{1,2}$ are considered known). Measurements were performed on three size fractions of clean (hydrophilic) and methylated (hydrophobic) glass spheres. Preliminary results for irregularly shaped quartz particles are also included. Reasonable values for both advancing and receding contact angles are obtained with this capillary pressure technique.

2. Materials and methods

2.1. Particles

Spherical glass beads were obtained from Potters Industries in sieved fractions. Angular quartz particles were obtained by crushing quartz rocks using a pan mill (Rock Labs CH-1). The particles were then dry sieved using woven wire sieves (Endecotts) into the same fractions as the spheres above. Particle sizing was carried out with a laser diffraction-based instrument (Mastersizer X, Malvern Instruments) and the results are listed in Table 1.

All quartz particles were repeatedly cleaned in a HNO_3 :HCl mixture (2:1) for 2 h at 80 °C until the acid showed no further coloration during the procedure. Particles were then rinsed five to six times with pure water (resistivity $\geq 18 \text{ M}\Omega \text{ cm}$; UHQPS, Elgastat) and dried at 125 °C in a clean furnace (Vulcan 3-400HTA, NeyTech). The dry particles were stored in clean Schott bottles.

Prior to their use the particles were further cleaned with hot KOH (30%) for 1 min, rinsed five to six times with pure water and dried at 125 °C. Finally the particles were plasma cleaned (Plasma cleaner PDC-002, Harrick) immediately before use.

A SEM image of the glass spheres is shown in Fig. 3a. Most of the particles are spherical and rather uniform in size. Only a small percentage of the particles are ellipsoidal. Physical defects such as

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