



## Capillary retention of colloids in unsaturated porous media

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[1] Understanding colloid transport behavior in unsaturated porous media is important because mobile colloid-contaminant complexes and colloidal pathogens can degrade groundwater quality. Visual evidence suggests that colloids are retained at the air-water meniscus-solid ( $AW_{mS}$ ) interface in unsaturated porous media, but there is no quantitative theoretical explanation of this retention mechanism to date. A theoretical study is presented here to quantify energy potentials represented by capillary forces on colloids at the  $AW_{mS}$  interface in unsaturated porous media. Our calculations indicate that the capillary energy potentials for colloids retained in films or at the  $AW_{mS}$  interface range from  $10^7$  to  $10^8$  kt, which are several orders greater than the Derjaguin-Landau-Verwey-Overbeek energy potentials. Capillary forces for colloids at the  $AW_{mS}$  interface can be decomposed into a force that pushes the colloid back in the bulk solution and one that pins the colloid against the surface of the grain. A friction force generated between the colloid and grain can prevent the colloids from moving back into solution. When drag forces can be ignored, colloids will remain at the  $AW_{mS}$  interface as long as the static friction coefficient is greater than the tangent of the water-grain contact angle. It is independent of the surface tension.

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### 1. Introduction

[2] Recent attention given to colloid fate and transport in unsaturated porous media arises from the fact that most colloids in groundwater originate in the overlying unsaturated (vadose) zone, from which they can facilitate the transport of various contaminants (e.g., radionuclides, pesticides, trace metals, etc.), leading to deterioration of groundwater quality [Saiers and Hornberger, 1999; Williams *et al.*, 2005]. Pathogenic biocolloids (viruses, bacteria, and protozoa) are governed by similar transport mechanisms [Chu *et al.*, 2001; Han *et al.*, 2006] and their contact with drinking water aquifers similarly poses risks to public health.

[3] Progress has been made toward understanding the mechanisms governing colloid transport through unsaturated porous media [McCarthy and McKay, 2004]. In addition to the processes that dominate colloid transport in saturated porous media (e.g., surface deposition and pore straining), four additional mechanisms have been identified as essential for describing colloid transport in unsaturated porous media: air-water-solid (AWS) interface capture [Crist *et*

*al.*, 2004], water film straining [Wan and Tokunaga, 1997], storage in immobile water zones [Gao *et al.*, 2006], and air-water (AW) interface capture [Wan and Wilson, 1994b]. While AWS interfaces, water films, and immobile water zones can induce significant deposition of colloids, AW interface capture plays a lesser role in retention because these interfaces are moving with the water in the pore [Crist *et al.*, 2005; Wan and Wilson, 1994a; Zevi *et al.*, 2005]. Chen and Flury's [2005] micromodel experiments found that clay colloids did not adhere to the AW interface in moving air bubbles. Colloid retention through AW interface capture seems to occur only when air bubbles have been immobilized between larger grains in unsaturated media [Gao *et al.*, 2006; Sirivithayapakorn and Keller, 2003; Wan and Wilson, 1994b].

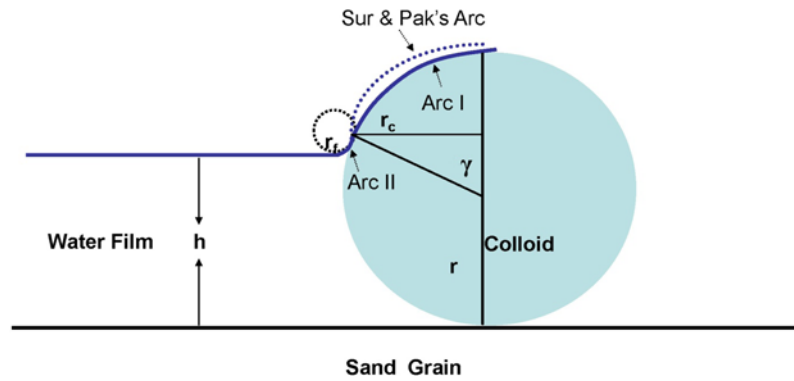
[4] Crist *et al.* [2004, 2005] visualized the transport of colloids through unsaturated silica sand flow chambers and found that hydrophilic negatively charged (anionic) colloids tended to accumulate at the air-water-solid (AWS) interface. Although the effect of evaporation on the observed rate of attachment at the AWS was debated [Steenhuis *et al.*, 2005; Wan and Tokunaga, 2005], visualization results demonstrated that colloids were retained at the AWS interface regardless of whether the chamber was covered to prevent evaporation or not [Lazouskaya *et al.*, 2006]. Further visual and experimental examinations have emphasized the importance of AWS for colloid retention in unsaturated soil [Chen and Flury, 2005; Lazouskaya *et al.*, 2006; Zevi *et al.*, 2005, 2006]. The term "air-water meniscus-solid" ( $AW_{mS}$ ) interface was proposed by Zevi *et al.* [2005] to more accurately describe the region where the water meniscus diminishes to a thin water film and where significant colloid

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**Figure 1.** Schematic of meniscus deformation with a colloid trapped in thin film.

attachment occurs. Although strong experimental evidence is available, there has not been a satisfactory mechanistic explanation of why colloids would be retained at the  $AW_mS$  interface.

[5] The coexistence of air and water within unsaturated soil pores introduces the capillary force phenomenon, which determines water configurations in soil pores and thus strongly affects water distribution, flow and transport in unsaturated porous media [Or and Tuller, 2005]. In previous studies of colloid transport in partly saturated porous media, the capillary force has been suggested to be important for colloid attachment at the AW interface [Sirivithayapakorn and Keller, 2003; Wan and Wilson, 1994b] as well as for straining in water films [Gao et al., 2006; Wan and Tokunaga, 1997]. Although studies have been conducted to investigate the capillary forces on colloidal particles bound to interfaces, liquid films and biomembranes [Kralchevsky et al., 2001; Kralchevsky et al., 2005; Kralchevsky and Nagayama, 2000; Sur and Pak, 2001], there have been only few direct investigations of how capillary forces affect colloid transport and retention in unsaturated porous media.

[6] In a review of capillary forces, Kralchevsky and Nagayama [2000] indicated a mathematical analogy between capillary and electrostatic forces, which enables one to introduce “capillary charges” on colloidal particles attached at interfaces. Under certain circumstances, the energy exerted from these charges can greatly exceed those from electrostatic forces. Notwithstanding, most theories for colloid interaction forces in unsaturated porous media are primarily formulated around electrostatic forces (e.g., Derjaguin-Landau-Verwey-Overbeek (DLVO) forces) and often exclude capillary forces [Crist et al., 2005]. Interestingly, DLVO theory cannot explain the observed deposition of colloids in a number of unsaturated flow experiments [Chen and Flury, 2005; Sirivithayapakorn and Keller, 2003]. For example, Crist et al. [2005] found that calculations based on DLVO theory could not describe why hydrophilic anionic colloids deposited at the contact line of the  $AW_mS$  interface, and concluded that the mechanisms for colloid retention at that interface thus remained unclear. In subsequent work, Zevi et al. [2005] suggested that capillary force interactions may explain the observed predominance of colloid retention at the  $AW_mS$  interface. It is clear that further examination is warranted for the role of capillary forces on colloid retention in unsaturated porous media.

[7] The objective of this paper is to show theoretically the significance of capillary forces in unsaturated porous media

on observed colloid retention at the  $AW_mS$  interface and to quantify the forces that play a role in the colloid retention at this interface.

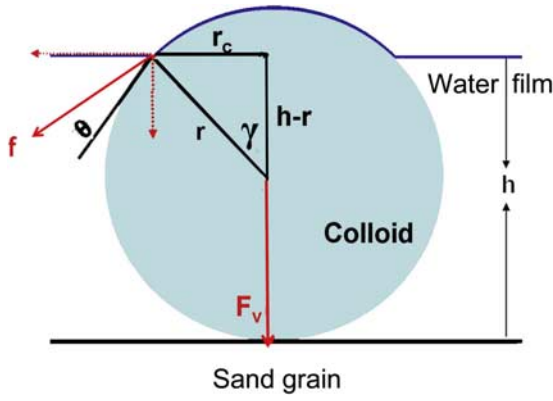
## 2. Capillary Retention

[8] Capillary retention represents the deposition of colloids in unsaturated porous media through capillary force interactions. In this section, we will demonstrate that capillary and associated friction forces are fundamental for colloid retention both within water films and at the  $AW_mS$  interface. Although these two cases are conceptually and theoretically similar, there are some significant differences and we will thus discuss the two cases separately.

### 2.1. Retention in Thin Water Films

[9] In unsaturated porous media, water may exist as pendular rings and thin water films surrounding the soil grains. According to Wan and Tokunaga [1997], anionic hydrophilic colloids may be retained on grain surfaces through film straining when the water film thickness is less than the colloid diameter. This mechanism has been confirmed by both laboratory column and pore-scale visualization experiments [Gao et al., 2006; Lenhart and Saiers, 2002; Wan and Tokunaga, 1997]. Wan and Tokunaga [1997] also suggested that the straining of colloids in the thin film was dominated by capillary forces.

[10] The presence of colloids in thin water films can result in meniscus deformation if the diameter of the colloid exceeds the film thickness [Kralchevsky, 1990; Kralchevsky and Nagayama, 2000; Sur and Pak, 2001]. Quantitative determination of the capillary force exerted on the trapped colloid within water film depends on the degree of meniscus deformation [Kralchevsky et al., 2001; Sur and Pak, 2001]. Figure 1 shows a cross section of colloid particle with radius  $r$  trapped in a thin water film with uniform thickness (depth =  $h$ ) on a mineral grain surface. For this scenario, the thickness of the water around the colloid is assumed to be negligible in comparison to the radius of the colloid. Because the colloid (diameter  $<10 \mu\text{m}$ ) is much smaller than the sand grain ( $\sim 300 \mu\text{m}$ ), the grain surface is also assumed to be flat for simplicity. According to Kralchevsky et al. [2001], the deformed meniscus can be described by two arcs as shown in Figure 1. The first arc around the colloid (referred as arc I) has the same radius as the colloid,  $r$ , and the second arc (arc II) connects the water film on grain surface (depth  $h$ ) with the water film around the colloid and



**Figure 2.** Schematic of capillary forces ( $F$ ) on colloids trapped in a thin film.

has a radius  $r_f$ . At the point of intersection of arcs I and II, the slope of arc II is equal to the contact angle of the water surface with the colloid,  $\theta$ . The contact line on the colloid with the water film forms a semicircle with radius,  $r_c$ :

$$r_c = r \sin \gamma \quad (1)$$

where  $\gamma$  is the angle associated with arc I as depicted in Figure 1.

[11] A capillary force ( $f$ ) exists at the point of contact between the water film and the colloid surface, orthogonal to the water film (Figure 2). This capillary force can be decomposed into two forces: one parallel and one perpendicular to the grain surface. The force components parallel to grain are balanced (i.e., net force equal to zero) laterally around the colloid, however, the perpendicular forces can be compiled into one force through the center of the colloid and holds the colloid against the grain surface. Given the contact angle between water and the colloid ( $\theta$ ), this capillary force ( $F$ ) for a spherical colloid with radius  $r$ ; that for a film is perpendicular to the grain surface, can be determined geometrically as

$$F = \sigma 2\pi r_c \cos\left(\theta + \frac{\pi}{2} - \gamma\right) \quad (2)$$

where  $\sigma$  is the liquid-vapor interfacial tension for water ( $0.073 \text{ N m}^{-1}$  at  $20^\circ\text{C}$ ).

[12] Equation (2) indicates that only hydrophilic colloids with a contact angle,  $\theta$ , smaller than  $\gamma$  can be trapped within the thin water film through capillary retention. Under the circumstance where  $\theta$  equals  $\gamma$ , all the capillary forces are determined to be parallel to the grain and the net capillary force will be zero. If the colloid is relatively hydrophobic and  $\theta$  is larger than  $\gamma$ , the vertical force becomes negative and the net capillary force will try to lift colloid away from the sand grain surface, an unrealistic scenario for the film straining mechanism.

[13] The determination of the location of the contact line (the exact point of intersection of arcs I and II, which in turn determines  $\gamma$  and  $r_c$ ) on the colloid is critical when calculating the magnitude of the capillary force. Obtaining this information requires knowledge of the force field within the film near the grain, which is beyond the scope of this paper.

For this reason, we will use the simplified approach for colloidal particles confined in a freely suspended liquid thin film developed by *Sur and Pak* [2001], in which it is assumed that the deformed water film can be described by a single arc (blue dashed line in Figure 1). Comparison of the authors' experimental data with their calculations indicates that this simple assumption is valid. In this paper we will use a similar approach by allowing  $r_f$  to go to 0 to calculate the capillary force. As  $r_f$  approaches zero, the capillary force generated by film deformation will reach its maximum value, where the angle  $\gamma$  and  $r_c$  can be determined geometrically as

$$\gamma = 0 \quad r_c = 0, \text{ when } h \geq 2r \quad (3a)$$

$$\gamma = \cos^{-1}\left(\frac{h-r}{r}\right) \quad r_c = \sqrt{r^2 - (h-r)^2}, \text{ when } h \leq 2r \quad (3b)$$

[14] By substituting equation (3) into equation (2), the vertical capillary force,  $F_v$ , on a colloid trapped by film straining can be written as a function of the surface tension, the colloid radius ( $r$ ), the contact angle of the water with the colloid ( $\theta$ ), and the water film height ( $h$ ) as follows:

$$F_v = \sigma 2\pi \sqrt{r^2 - (h-r)^2} \cos\left[\theta + \frac{\pi}{2} - \cos^{-1}\left(\frac{h-r}{r}\right)\right], \quad (4)$$

when  $h \leq 2r$

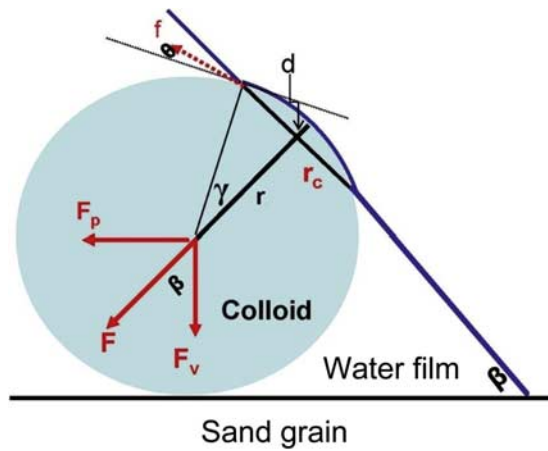
[15] Because there are no net lateral capillary forces in our system, colloids trapped in the water film will be immobile as long as the meniscus is not moving. In addition, the capillary force applies a vertical force on the grain that in turn induces a friction force (discussed in detail later) which can prevent the colloid from moving even if film flow exerts a drag force on the colloids.

## 2.2. Retention at $AW_mS$ Interfaces

[16] In unsaturated soil pores, air typically occupies the center of the pores, while water is found in thin films on grains and in pendular rings between grains. Colloidal particles flowing into this peripheral water may be retained through capillarity at the contact points, i.e., the  $AW_mS$  interfaces. *Zevi et al.* [2005] observed that in general, retention was greater for hydrophilic colloids (as compared to relatively hydrophobic colloids) and suggested that this greater retention could be explained by the additional force represented by the capillary energy potentials exerted on the hydrophilic colloids at the  $AW_mS$  interface.

[17] Figure 3 is a conceptual schematic of a spherical hydrophilic colloidal particle trapped at the  $AW_mS$  interface. Similar to Figures 1 and 2, the grain surface is assumed to be flat, and the  $AW_mS$  interface simplified as a wedge at an angle ( $\beta$ ) equal to the water-grain contact angle. The difference between Figures 2 and 3 is that the deformed water film and the colloid are rotated by an angle  $\beta$  while the grain surface remains horizontal. The net capillary force  $F$  (at an angle  $\beta$  with the grain surface) is therefore similar to equation (2).

[18] In this case, the radius  $r_c$  and the angle  $\gamma$  of the contact line of the colloid with the water "wedge" is



**Figure 3.** Schematic of capillary forces ( $F$ ) on colloid trapped at an  $AW_mS$  interface.

independent of the film thickness and can be written as a function of the distance,  $d$ , of the deformed water film from the colloid at the midpoint. From Figure 3 it is obvious that

$$\gamma = \cos^{-1} \left( \frac{r-d}{r} \right) \quad r_c = \sqrt{r^2 - (r-d)^2} \quad \text{for } d > 0 \quad (5)$$

[19] Through substitution of equation (5) into equation (2) the capillary force can be written as

$$F = \sigma 2\pi \sqrt{r^2 - (r-d)^2} \cos \left[ \theta + \frac{\pi}{2} - \cos^{-1} \left( \frac{r-d}{r} \right) \right] \quad (6)$$

[20] The net capillary force can be decomposed into a lateral capillary force ( $F_p$ ), which tends to push the colloid toward the bulk water, and a vertical capillary force ( $F_v$ ), which pins the colloid on the grain surface, viz.

$$F_p = \sigma 2\pi \sqrt{r^2 - (r-d)^2} \cos \left[ \theta + \frac{\pi}{2} - \cos^{-1} \left( \frac{r-d}{r} \right) \right] \sin \beta \quad (7)$$

$$F_v = \sigma 2\pi \sqrt{r^2 - (r-d)^2} \cos \left[ \theta + \frac{\pi}{2} - \cos^{-1} \left( \frac{r-d}{r} \right) \right] \cos \beta \quad (8)$$

[21] As noted above, the lateral force ( $F_p$ ) tends to push the colloid away from the  $AW_mS$  interface and back into the bulk water. For the colloid to remain at the  $AW_mS$ , a force is needed to resist movement. This requirement is satisfied with a frictional force, which must be at least of the same magnitude and in the opposite direction as the lateral capillary force [Tipler, 1998]. Recent theories relate friction forces to chemical bonding and “stick and slip” processes [Wu and Tung, 2002]. Using a classical approximation, friction forces can be calculated according to the grain surface roughness properties (i.e., ultra smooth or rough). For ultrasmooth surfaces, deformation of the surfaces and molecular interactions determine the magnitude of the

friction. These molecular interactions are currently used almost solely for predicting retention of colloids in regards to van der Waals and double layer potential energies. Little is known about the deformation forces for colloid grain friction.

[22] For rough surfaces, the friction force between colloid and grain surfaces can be determined through classical approximation with the Coulomb friction equation [Tipler, 1998]:

$$F_r = \mu F_v \quad \quad \quad (9)$$

where  $\mu$  is the coefficient of static friction for surfaces initially at rest relative to each other (e.g., colloids trapped at  $AW_mS$ ), and  $F_v$  is the vertical component of the capillary force that pins the colloid to the grain surface. When the colloid initially begins to move, the friction force and the lateral force are equal in magnitude but act in opposite directions (i.e.,  $F_r = -F_p$ ). Furthermore, taking equation (9) and substituting equation (8) for  $F_v$  and equation (7) for  $F_p$  we find that for colloids to remain at the  $AW_mS$  interface the following condition is required

$$\mu \cotan \beta \geq 1 \quad \text{or} \quad \mu \geq \tan \beta \quad (10)$$

[23] Equation (10) implies that the water-grain contact angle ( $\beta$ ) and the friction coefficient ( $\mu$ ) are the only factors controlling colloid retention at the  $AW_mS$  interface if the surface is rough. This retention mechanism is also independent on how far the colloid protrudes from the meniscus. Careful interpretation of equations (9) and (10) is required since we assumed that capillary force was the only force acting on the colloid. However, other forces such as imposed by the water velocity and DVLO forces may also be present. For these forces, the exact value of the vertical component of the capillary force is required because it affects the friction force. DVLO forces are discussed below.

### 3. Results and Discussion

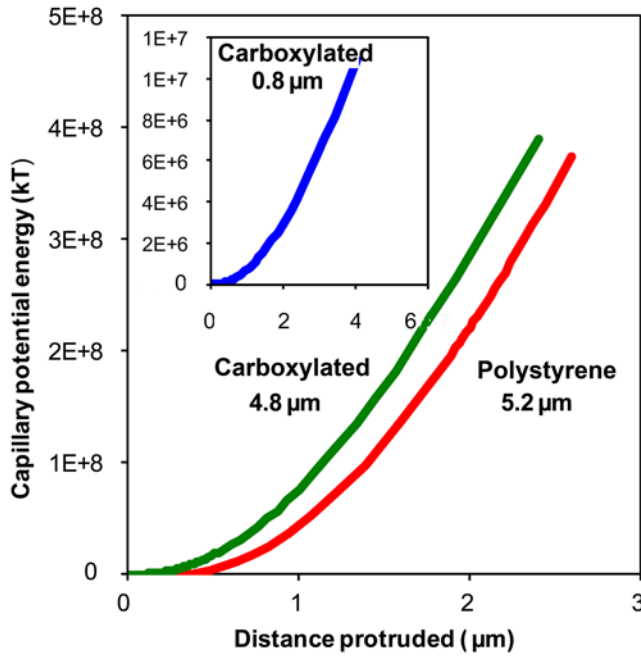
[24] To analyze the relative importance of DVLO and capillary forces for colloid retention at the  $AW_mS$  interface, we will compare the energy potentials of both carboxylated and polystyrene synthetic microspheres used in the visualization studies of Crist *et al.* [2004, 2005] and Zevi *et al.* [2005]. Table 1 lists the colloid properties.

[25] In a static system, the capillary energy potential ( $\Phi_c$ ) for a colloid that protrudes a distance  $d$  out of either a film or  $AW_mS$  can be calculated by integrating the capillary force over its path in the direction of the force through the water film. To simplify the notation we introduce a  $z$

**Table 1.** Properties of Colloids Used in Force Calculations<sup>a</sup>

Colloid Type	Diameter, $\mu\text{m}$	Zeta Potential, mV at 20°C	Contact Angle With Water, deg	Water Sand Contact Angle, deg
Carboxylated	0.8	-31.1	<10	~25
Carboxylated	4.8	-29.6	<10	~25
Polystyrene	5.2	-44.7	20-25	~25

<sup>a</sup>Crist *et al.* [2005], Zevi *et al.* [2005], and Y. Zevi (personal communication, 2007).



**Figure 4.** Capillary energy potential of colloids retained within thin water films and at the AW<sub>m</sub>S interfaces for 0.8 and 4.8  $\mu\text{m}$  carboxylated and 5.2  $\mu\text{m}$  polystyrene microspheres.

coordinate through the center of the colloid and orthogonal to original meniscus with  $z = 0$  at the surface of the colloid:

$$\Phi = \int_{z=r(1-\cos\theta)}^{z=d} Fdz \quad (11)$$

where  $F$  is the capillary force on the trapped colloids orthogonal to the original meniscus. The lower limit of the integral is where  $\gamma = \theta$  at which the net force on the colloid is zero. The capillary force,  $F$ , as a function of  $z$  for the film can be obtained from equation (4) by substituting  $z$  for  $2r - h$  and equation (6) for the AW<sub>m</sub>S interface by substituting  $z$  for  $d$ . Note that the equation is the same for the film as for the AW<sub>m</sub>S interface. Note also that in equation (11) that  $d$  is distance that the colloid protrudes out the film (as indicated in Figure 3). The capillary energy potentials calculated with equation (11) for the 0.8 and 4.8  $\mu\text{m}$  carboxylated colloids and the 5.2  $\mu\text{m}$  polystyrene colloids with contact angles,  $\theta$ , of 0 and 22.5 respectively are shown in Figure 4 for different distances that the colloids protrude from the meniscus. When the colloid diameter is less than the film thickness ( $2r < h$ ), the film is not distorted. According to equation (3a), when  $h > r(1 + \cos\theta)$  the direction of the capillary force is away from the surface and the capillary potential is negative. Thus, as discussed above,  $\Phi_c = 0$  for the carboxylated colloids (with  $\theta = 0$ ) when  $h = 2r$ . For the polystyrene colloids (with  $\theta = 22.5$ ) equation (3a) finds that  $\Phi_c = 0$  when  $h = 1.92r$  (Figure 4). When  $h \rightarrow 0$  (or  $d \rightarrow 2r$ ) the capillary energy potential increases to values ranging from  $10^7$  to  $10^8$  kJ for the colloids considered here. The capillary potential is lower for hydrophobic colloids than for hydrophilic colloids when they both protrude through the film by the same distance.

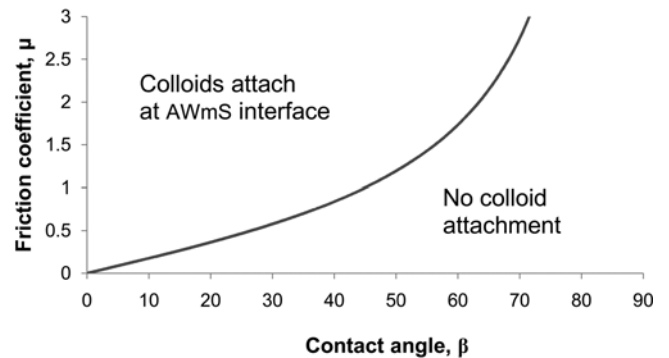
[26] The interfacial energy potential associated with DVLO forces is a function of the distance of the colloid to the grain surface. *Crist et al.* [2004] calculated for the carboxylated and the polystyrene colloids that at a distance greater than 1nm these colloids were repelled by the grain. The maximum interfacial energy potential was established at separation distances of 1 nm, and ranged from  $10^3$  to  $10^4$  kJ for the colloids studied here. At distances less than 1 nm, the particles become attractive because of the van der Waals forces. Thus, the capillary energy potential is several orders of magnitude greater than the DLVO energy potential.

[27] Equation (10) suggests that the value of the friction coefficient required keeping a colloid at the AW<sub>m</sub>S interface decreases with contact angle. Since the friction coefficients vary with surface conditions, which are not well established for colloids and grains, we have plotted in Figure 5 the relationship of grain contact angle and the friction coefficient required to retain the colloid just at the AW<sub>m</sub>S interface. According to equation (10), the line delineating the exact position can be expressed as

$$\mu = \tan\beta \quad (12)$$

Colloids at the AW<sub>m</sub>S interface where the friction coefficient,  $\mu$ , is greater than the tangent of the contact angle,  $\beta$ , (i.e., a point above the line in Figure 5) will be retained, while those that fall below the line will be pushed into the bulk solution by the capillary force.

[28] Next, we will compare if our results in Figure 5 are in accordance with the colloid retention literature available. According to Figure 5 (and equation (11)) for a zero contact angles colloid retention is independent of the sand roughness. Because this situation is represented in the earlier discussed film, we can conclude that our calculation is consistent with the theory because lateral capillary forces are absent. For contact angles of greater than or equal to 90 degrees, the friction coefficient needs to be infinite to firmly secure colloids at the interface. This is in accordance with the findings of *Crist et al.* [2004] that showed that for hydrophilic grains colloids retention occurred at the AW<sub>m</sub>S interface, but for intermixed hydrophobic grains, colloid retention at the AW<sub>m</sub>S interface was less. Finally, we consider the colloid results for the *Zevi et al.* [2005] and the *Lazouskaya et al.* [2006] experiments. Zevi measured the grain contact to be 25 degrees with a standard deviation



**Figure 5.** Relationship between grain contact angle,  $\beta$ , and friction coefficient,  $\mu$ , for colloid retention at the AW<sub>m</sub>S interface.

of 7 degrees (Y. Zevi et al., personal communication, 2007). From Figure 5, the minimum friction coefficient was calculated at 0.46 (from 0.32 to 0.62 at 1 standard deviation). This value is in the range of friction coefficients mentioned for concrete on sand [Dorf, 2004], favoring colloid retention at the  $AW_mS$  interface. Since there are very few static friction coefficients above 1, colloid retention when the contact angle is greater than 45 degrees is unlikely. The latter is in accordance with the experiments of Lazouskaya et al. [2006] in a microchannel where colloids were not retained at the  $AW_mS$  interface when the meniscus was flat (likely with a contact angle above 45 degrees) and retention took place when the contact angle was concave (contact angle much less than 45 degrees).

[29] So far, we have considered the effect of the DVLO and capillary forces separately. We will now examine their combined effect. In bulk solution, the colloids are repelled by the electric double layer DVLO forces as they usually cannot approach the grain surface sufficiently to allow attractive van der Waals forces to dominate. At  $AW_mS$  interface capillary potential forces are much greater than the electric double layer repulse forces and can push the colloid close enough to the grain surface where they are attracted to the collector through the van der Waals forces. As a result, DVLO forces actually help keep the colloids at the  $AW_mS$  interface even when the meniscus is not steady because of a small perturbation in the flow.

#### 4. Implications

[30] On the basis of the above analysis, the effect of capillary forces on colloids at the  $AW_mS$  interfaces can be expressed for both colloid retention and release.

##### 4.1. Retention

[31] A colloid particle approaching the meniscus near the solid phase can deform the meniscus if the water film is thinner than the colloid diameter. This colloid will be abruptly stopped at the  $AW_mS$  interface (as observed by Zevi et al. [2005]). On the basis of the theory proposed in section 2.1, the forward movement of the colloid is halted because of the lateral capillary force ( $F_p$ ) that acts to push the colloid back into the bulk solution (as observed by Sur and Pak [2001]). Simultaneously, a vertical capillary force ( $F_v$ ) perpendicular to the grain pins the colloid to the grain surface inducing a static friction force ( $F_r$ ), which may (depending on the surface roughness of the grain) be sufficient to offset the lateral force ( $F_p$ ). This combination would in theory result in retention of the colloid at the  $AW_mS$  interface for contact angles less than 45 degrees and the product of the static friction coefficient and the tangent of the contact angle less than 1.

##### 4.2. Release

[32] The magnitude of the static friction ( $F_r$ ) force depends on force perpendicular to the grain surface ( $F_v$ ) and the grain surface roughness (static friction coefficient). If the static friction force  $F_r$  cannot overcome the lateral force  $F_p$ , the colloid will be pushed back into the fluid. Thus colloids "caught" at the  $AW_mS$  interface will be released when the capillary force disappears, such as when the pore fills up because of a Haynes jump or otherwise by increasing the matric potential [Gao et al., 2004; Saiers and

Lenhart, 2003; Sirivithayapakorn and Keller, 2003]. Moreover, since the friction coefficient larger than 1 is an exception (rubbery surfaces have friction coefficients larger than 1), Figure 5 and equation (11) indicate that there will be no retention if the contact angle is larger than 45 degrees.

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