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Citation for published version:

Beckett, CTS & Augarde, CE 2013, 'Prediction of soil water retention properties using pore-size distribution and porosity', *Canadian geotechnical journal*, vol. 50, no. 4, pp. 435-450. <https://doi.org/10.1139/cgj-2012-0320>

Digital Object Identifier (DOI):

[10.1139/cgj-2012-0320](https://doi.org/10.1139/cgj-2012-0320)

Link:

[Link to publication record in Edinburgh Research Explorer](#)

Document Version:

Peer reviewed version

Published In:

Canadian geotechnical journal

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Journal:	<i>Canadian Geotechnical Journal</i>
Manuscript ID:	cgj-2012-0320 .R1
Manuscript Type:	Article
Date Submitted by the Author:	09-Nov-2012
Complete List of Authors:	Beckett, Christopher; University of Western Australia, School of Civil and Resource Engineering Augarde, Charles; Durham University, School of Engineering and Computing Science
Keyword:	Pore size distribution, Suction, Cavitation



Prediction of soil water retention properties using pore size distribution and porosity

Christopher T. S. Beckett and Charles E. Augarde

Abstract:

Several models have been suggested to link a soil's pore size distribution to its retention properties. This paper presents a method which builds on previous techniques by incorporating porosity and particles of different sizes, shapes and separation distances to predict soil water retention properties. Mechanisms are suggested for the determination of both the main drying and wetting paths which incorporate an adsorbed water phase and retention hysteresis. Predicted results are then compared to measured retention data in order to validate the model and to provide a foundation for discussing the validity and limitations of using pore size distributions to predict retention properties.

Key words: Pore size distribution; suction; cavitation.

1. Introduction

The soil water retention curve is the relationship between suction and the water content (or degree of saturation) of an unsaturated soil and is a key factor in determining its behaviour (Nuth and Laloui, 2008; Tarantino, 2010; Gens, 2010). Suction arises due to the formation of curved water menisci at the air-water interfaces within soil pores. The simplest example of this effect is the phenomenon of

Received April 10, 2012. Revision received . Accepted . Revision accepted .

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capillary rise, where water in a free reservoir will spontaneously rise to a height in a thin tube of radius r_{tube} . The corresponding suction, ψ , for a given height rise h is calculated using

$$\psi = u_a - u_w = -h\rho g = -\frac{2\gamma}{\kappa} = -\frac{2\gamma \cos(\theta_{slv})}{r_{tube}} \quad (1)$$

13 where u_a and u_w are the air and water pressures respectively, γ is the air-water surface tension, θ_{slv} is
14 the solid-liquid contact angle in the presence of a vapour (in this case air) and κ is the meniscus radius
15 of curvature. It is commonly assumed that $\theta_{slv} = 0$, so that the meniscus curvature equals the tube
16 radius, and that $u_a = 0$. This phenomenon, although simplistic, nonetheless demonstrates the direct
17 link between suction and the size of the body (i.e. the pore) in which the water is held.

18 As the direct determination of a soil's retention properties can be time consuming or difficult, sev-
19 eral models have been suggested to relate a soil's pore size distribution (PSD) to its retention properties
20 (Ghanbarian-Alavijeh and Liaghat, 2009). The simplest of these is the Bundle of Cylindrical Capillar-
21 ies (BCC) model, where each pore size is considered to be a capillary tube of a certain diameter, with
22 suction calculated according to Eqn 1 (Millington and Quirk, 1961; Mualem, 1976). The disadvantage
23 of the basic BCC model, however, is that pores are required to be either completely filled or com-
24 pletely empty, so that the unsaturated soil effectively becomes a combination of a completely dry and a
25 completely saturated material (Tuller and Or, 2004; Baker and Frydman, 2009). Observations of water
26 regimes in unsaturated soils made by Lourenço et al. (2012) using environmental scanning electron
27 microscopy (ESEM) show that water and air exist simultaneously in a pore of a given size, with water
28 occupying both a bulk and an adsorbed phase. Adsorption is the mechanism whereby water molecules
29 readily adhere to the surfaces of soil particles due to short-range solid-water interaction mechanisms
30 (including van der Waals attractions, exchangeable cation hydration and electrical field polarisation)
31 (Philip, 1977; Derjaguin et al., 1987; Lu and Likos, 2004). The presence of adsorbed films in cylindri-
32 cal pores was considered by Shull (1948) for correcting obtained PSD data from nitrogen adsorption
33 techniques (for example the BET method) and by Collet et al. (2008) for predicting PSDs of hemp-
34 based materials from retention properties determined using vapour-equilibrium, however these works
35 did not then go on to use measured PSDs to predict retention properties.

36 A more advanced model for predicting retention properties which incorporates both bulk and ad-
37 sorbed water regimes was suggested by Tuller et al. (1999), wherein pore spaces were assumed to be

38 angular voids joined by narrow slits, as shown in Figure 1. The bulk and adsorbed phases were sepa-
39 rated for ease of calculation into menisci present in the pore corners and adsorbed films in the narrow
40 slits. The disadvantage of this model, however, is that calculations are dependent on the “angularity
41 factor” of the pores, which is information not usually available (Baker and Frydman, 2009).

An improvement to the model suggested by Tuller et al. (1999) is to consider the geometry and arrangement of soil particles surrounding the pore space as well as the water regime. An example of a water meniscus suspended between two granular soil particles is shown in Figure 2, along with adsorbed films of exaggerated thickness. A meniscus suspended between two particles has both concave and convex curvatures in the meridional and azimuthal directions respectively, properties which are not possible in the model of Tuller et al. (1999) due to the columnar pore assumption (Butt, 2008). Although the shapes of granular particles are complicated, simplifying them allows suctions generated in the suspended menisci to be calculated. Lu and Likos (2004), Mayer and Stowe (2006), Grof et al. (2008) and Likos (2009) suggested models wherein granular particles are assumed to be spherical and in contact, with toroidal menisci suspended between particles of equal size. These assumptions allow suction to be calculated via

$$\psi = \gamma \left(\frac{1}{\kappa} - \frac{1}{l} \right) \quad (2)$$

42 where κ and l are the meridional and azimuthal radii respectively and are each functions of particle size
43 (these functions will be discussed in a later section) and pore size is assumed to be the diameter of the
44 interstitial sphere, as shown in Figure 3. Water is assumed to exist either in bulk or as menisci suspended
45 between particles and, in the case of Likos (2009), in the form of thin films adsorbed onto the particle
46 surfaces. This paper aims to improve on these models by assuming a more realistic arrangement of
47 soil particles which accounts for material porosity, whilst retaining the effect of adsorbed water on the
48 SWRC introduced in Tuller et al. (1999) and Likos (2009). Predictions made using the model are then
49 compared to measured data in order to investigate the limitations present when predicting retention
50 properties using PSD data.

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51 2. Soil skeleton approximations

52 2.1. Particle shape

As suction is determined by the shapes of menisci suspended between soil particles, it is important to consider particle shapes which can reproduce the retention properties of pores of varying sizes. A method to determine the suitability of an approximation to a particle shape is to consider the assumed particle's specific surface area (SSA). Figure 4 shows calculated SSA values for different particle sizes as compared to measured data, where the SSA of a spherical particle is calculated via

$$SSA_{sphere} = \frac{4\pi R^2}{\frac{4}{3}\pi R^3 \rho} = \frac{3}{\rho R} \quad (3)$$

where ρ is the particle density, assumed to be 2650 kg/m³, and the range of values of R used is as given in Table 1. Although the spherical particle assumption closely matches those SSA values measured for larger particles (\geq silts), Figure 4 shows that it fails to capture the higher SSA values of clay particles, so that suctions predicted for pores surrounded by these particles will suggestably not be representative of the real material (Iwamatsu and Horii, 1996). Instead, images of clay particles, for example as shown in Figure 5, suggest that these particles might be more appropriately modelled as being cuboidal in shape. The SSA of such a cuboidal particle can be calculated using

$$SSA_{cuboid} = \frac{L^2(2 + 4\alpha)}{L^3\alpha\rho} = \frac{2(1 + 2\alpha)}{L\alpha\rho} \quad (4)$$

53 where L and α (the particle side length and height-to-length ratio respectively) are as given in Table 1
 54 and are dependent on clay mineralogy. Note that these are the SSA values for individual particles
 55 only, i.e. no particle-particle contact area is considered. Figure 4 shows, by assuming that particles
 56 smaller than silts are cuboidal in shape, that a much closer approximation to measured SSA values is
 57 achieved for little increase in geometrical complexity. Note that, here, one value of α is used to describe
 58 clay particles of a given mineralogy. As clay particle arrangements are known to change with water
 59 content, however, it might be that a more appropriate representation of the clay particle structure can
 60 be achieved by having the value of α change with water content. However, as this would also result in a
 61 change in the pore size between the particles, a single value of α is considered here to enable measured
 62 PSDs to be used to directly determine retention properties for small pores. A variable value of α could,

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63 however, be a topic for further study. Therefore, the assumption is made here that larger particles (silts
 64 and above) can successfully be modelled as spheres, as assumed by previous authors, and clay particles
 65 as cuboids. For convenience, pores surrounded by particles modelled as spheres are said to belong to
 66 the *macro region*, whilst those surrounded by cuboids belong to the *micro region*.

67 2.2. Particle arrangement

68 2.2.1. Macro region

As the volume of voids present within a soil determines the amount of water present at saturation, it is essential that soil particle geometry is modelled so that material porosity is maintained. This is not possible if it is assumed that all particles are in contact as the porosity is then set by the efficiency of the chosen packing regime. If, however, a separation distance D is specified between particle surfaces, as shown in Figure 6, then a range of material porosities n can be incorporated, as calculated via

$$n = 1 - \frac{4\sqrt{2}\pi R^3}{3(2R + D)^3} \quad (5)$$

69 where R is the particle radius. Note that a tetrahedral packing regime is used here, as opposed to
 70 the cubic regime used by previous authors, as the improved packing efficiency allows for a greater
 71 range of porosities to be modelled (cubic packing has a minimum porosity, i.e. where $D = 0$, of
 72 0.476, whereas that of tetrahedral packing is 0.260). Another advantage of this approach is that, by
 73 setting $D > 0$, the effects of particle surface asperities, which would impede contact during packing,
 74 can also be incorporated, so that results for smooth-surfaced particles can be related to those for real,
 75 rough-surfaced materials (Molenkamp and Nazemi, 2003; Butt, 2008). As for previous models, it is
 76 assumed that menisci all reside between particles of equal size for a given pore size in order to maintain
 77 the simple packing geometries shown in Figure 6. Although a simplification, as menisci in real soils
 78 are likely to reside between dissimilarly-sized particles, an effective particle radius ($R^* = \frac{R_1 R_2}{R_1 + R_2}$
 79 where R_1 and R_2 are the radii of the two subtending particles) must then be used to determine that
 80 meniscus' retention properties, so that, in effect, the calculation still considers menisci between equal-
 81 sized particles. Therefore, the assumption that menisci reside between equal-sized particles only is
 82 suggestably justified.

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83 Given the required porosity, interstitial pore size r can be found using

$$r = R \left(\frac{\sqrt{6}}{2} - 1 \right) + \frac{\sqrt{6}}{4} D. \quad (6)$$

84 so that R and D can be solved for using Eqns 5 and 6, for a given value of r from the PSD. As a result
85 of this approach, particle grading and porosity are linked via

$$V_s(R) = V_v(r) \left(\frac{1}{n} - 1 \right) \quad (7)$$

86 where $V_s(R)$ is the volume of solids of particle size R and $V_v(r)$ is the volume of voids of radius r , so
87 that the PSD and modelled particle grading are simple transformations of each other. It should be noted,
88 however, that it is not the function of this model to accurately predict the material particle grading but
89 rather to model an arrangement of particles surrounding the pores which give rise to similar retention
90 properties as seen in real materials.

91 Pore interconnectivity is discussed in Haines (1929), who suggested that porous media contain two
92 pore types, namely cavities and throats, with large cavities being separated and connected by the much
93 narrower throats. This structure results in hysteresis between wetting and drying water contents on a
94 change in suction, as drying is controlled by the emptying of the narrow throats (i.e. at high suctions),
95 whereas wetting is controlled by the filling of the larger cavities (i.e. at lower suctions) (Everett, 1967;
96 Rojas et al., 2010). However, by considering pores to be in isolation, hysteresis of the wetting and
97 drying retention properties can no longer be considered in this manner. This is a necessary simplifi-
98 cation, however, as the modelling of a connected pore network would be computationally unfeasible.
99 Instead, hysteresis is introduced by considering different wetting and drying mechanisms, based solely
100 on the modelled geometry of the individual pore; these mechanisms will be discussed in the following
101 sections.

102 2.2.2. *Micro region*

103 Cuboid particles are assumed to be stacked one on top of the other, with pore spaces in between, so
104 that the unit cell comprises a single pore flanked by two particles of half width (i.e. $\frac{\alpha L}{2}$) as shown in
105 Figure 7. Therefore, the porosity of the micro region is controlled by mineralogy only. Although this
106 might be considered a shortfall of the model, porosity is a global value and is not representative of the

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107 void ratio at different scales (i.e. local fluctuations are not considered). The lack of a consideration of
 108 porosity in the micro region is therefore arguably justifiable when considering overall material retention
 109 properties

110 3. Main drying path calculations

111 3.1. Cavitation

Water under an applied suction is in a metastable state, in that it remains in liquid form despite pressures being lower than its vapour pressure (Or and Tuller, 2002). Cavitation is the process of the formation and subsequent expansion of vapour bubbles within a liquid on a change in liquid pressure (Young, 1989). Homogeneous cavitation (also called homogeneous nucleation) is the formation of cavities (bubbles) of pure liquid vapour in the surrounding liquid. If it is assumed that random thermal motion of the water molecules leads to the formation of a spherical cavity between them of a diameter equal to the minimum distance between water molecules in liquid water (0.35 nm), then the subsequent liquid pressure required for equilibrium can be found using Eqn 1:

$$u_w = u_a - \frac{2\gamma}{\kappa} = 2.3 \text{ kPa} - \frac{0.1454}{0.175 \times 10^{-6}} = -830.6 \text{ MPa} \quad (8)$$

where γ has been calculated using $\gamma = 0.1171 - 0.0001516T$, where T is the absolute temperature, set to 293 K, and $u_a = 2.3 \text{ kPa}$ is the vapour pressure of water at 293 K (Edlefsen and Anderson, 1943; Marinho et al., 2008). This suction value, however, is rarely achieved in experiments due to heterogeneous cavitation, namely the formation of bubbles of dissolved gas which vaporises at significantly lower suctions. Cavitation of liquids containing dissolved gases was discussed in Or and Tuller (2002), who suggested that the energy required (ΔE) to form a bubble of radius r in a liquid can be calculated from the sum of the interfacial energy of the bubble surface and the opposing work done by the fluid on the volume of the resulting bubble according to

$$\Delta E = 4\pi r^2 \gamma - \frac{4\pi}{3} r^3 \psi, \quad (9)$$

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which has a minimum at

$$\frac{\partial \Delta E}{\partial r} = r^* = \frac{2\gamma}{\psi}, \quad (10)$$

so that r^* is the minimum bubble radius required in order for the creation of a bubble to be energetically favourable and ψ is the corresponding cavitation suction. The pressure equilibrium between the gas in the bubble and the surrounding fluid can then be determined via the Kelvin equation

$$\psi = \frac{R_u T}{v_m} \log \left(\frac{p}{p^*} \right) \quad (11)$$

112 where R_u is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), v_m is the specific molar volume of the
 113 fluid ($\text{m}^3 \text{ kg}^{-1} \text{ mol}^{-1}$) and p and p^* are the vapour pressure and saturated vapour pressure (i.e. that
 114 under free conditions) of the fluid in the gas respectively. It follows from Eqn 10 that pores smaller
 115 than $r^*(\psi)$ must remain filled for that value of ψ , as bubbles of sufficient size for the mechanism to
 116 be energetically favourable cannot form. An example of this is shown in Figure 8 for a range of pore
 117 sizes, where suction increases from Figure 8(a) to Figure 8(c). An advantage of the use of a cavitation
 118 mechanism is that it does not require a continuous water phase in order to be valid, as it arises due to
 119 an air-water interface only (i.e. suction is continuous and uniform in a discontinuous (but static) water
 120 phase) (Or and Tuller, 2002). Therefore, it is compatible with the modelling of pores in isolation, as
 121 discussed in the previous section.

Attraction between water molecules and particles results in a film of adsorbed water being developed on particle surfaces, as previously discussed. The thickness of an adsorbed film, t , on a single, isolated surface is given by

$$t = \sqrt[3]{\frac{A_{svl}}{6\pi(\rho_l - \rho_v)\Delta\mu}} \quad (12)$$

where $A_{svl} = -6 \times 10^{-20} \text{ J}$ is the Hamaker constant for solid-vapour interactions through an intervening liquid, ρ_l and ρ_v are the liquid and vapour densities respectively and $\Delta\mu$ is the change in chemical potential (μ) associated with a change in vapour pressure, which can be calculated via

$$\Delta\mu = kT \log \left(\frac{p}{p^*} \right) \quad (13)$$

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where k is Boltzman's constant (Iwamatsu and Horii, 1996). The value of $A_{svl} = -6 \times 10^{-20}$ J has been selected following the work of Or and Tuller (1999), who suggested that such a value is suitable for adsorption in soils containing mixed clays, although it should be noted that this value generally varies between -10^{-19} and -10^{-20} depending on soil mineralogy (Frydman and Baker, 2009). Given that k is related to R_u via

$$k = \frac{R_u}{N_A} \quad (14)$$

where N_A is the Avogadro constant and that $\Delta\mu$ is related to ψ via

$$\Delta\mu = \frac{\psi}{\rho}, \quad (15)$$

Eqns 14 and 15 can be substituted into Eqn 13 to give

$$\psi = \frac{R_u T}{v_m} \log\left(\frac{p}{p^*}\right) \quad (16)$$

i.e. Eqn 11 as before (Tuller et al., 1999). Therefore, given that $\rho_l \gg \rho_v$, adsorbed film thickness can be related to the suction present in the fluid via

$$t(\psi) \approx \sqrt[3]{\frac{-A_{svl}}{6\pi\psi}}. \quad (17)$$

Eqn 17 can be used to determine the thickness of an adsorbed film on the surface of a spherical particle provided $t \ll R$ (Tuller et al., 1999; Likos, 2009). Given the presence of this film, the minimum cavitation radius r^* in a pore of radius r must therefore be modified as shown in Figure 9 to incorporate that water surrounding the pore space which cannot cavitate (as it is bound to the particle surface), according to

$$r^* = r - t(\psi) \quad (18)$$

122 so that the cavitation suction ψ for that pore size r can then be found using Eqn 10 (Shull, 1948; Collet
123 et al., 2008).

124 Although it is assumed above that adsorbed water is in the form of thin films covering particle
 125 surfaces, it was shown in Lourenço et al. (2012) that water instead exists on the surface of rough
 126 granular particles in the form of droplets. Results presented in Lourenço et al. (2012) also suggest,
 127 however, that successive wetting and drying cycles result in a coalescence of these surface droplets, so
 128 that they progressively become more film-like. As it is assumed here that materials are first dried from
 129 a saturated state, it is therefore likely that water will remain in continuous films on particle surfaces
 130 rather than as discontinuous bodies, so that the use of films to represent adsorbed water is suggestibly
 131 justified. However, the effect of surface droplets on the retention properties of granular particles and
 132 methods to predict their shapes is an interesting topic of ongoing research.

133 3.2. Cavitation and adsorption in slit-shaped pores

A water meniscus trapped between two cuboidal particles is shown in Figure 7 and in more detail
 in Figure 11. The thickness of adsorbed water films in a slit-shaped pore, t_{ss} , at a given suction ψ is
 given by

$$\psi = -\frac{A_{svl}}{6\pi(2r - t_{ss}(\psi))^3} + \frac{A_{llv}}{48\pi(r - t_{ss}(\psi))^3} - \frac{A_{svl}}{6\pi t_{ss}(\psi)^3} \quad (19)$$

where r is the pore radius (given by the PSD) and $A_{llv} = 3.7 \times 10^{-20}$ J is the Hamaker constant for
 liquid-liquid interactions through an intervening vapour (Iwamatsu and Horii, 1996). Note that Eqn 19
 has been converted from the original expression given in Iwamatsu and Horii (1996) to be in terms of
 ψ , as discussed in the previous section. The suction required to cavitate the pore is given by Eqns 10
 and 18 as

$$\psi = \frac{2\gamma}{r^*} = \frac{2\gamma}{(r - t_{ss}(\psi))} \quad (20)$$

134 so that Eqns 19 and 20 can be solved to find $t_{ss}(\psi)$ and so ψ . Films of thickness $t_{ss}(\psi)$ remain adsorbed
 135 to the surfaces of the slit-shaped pore after the pore has cavitated (Shull, 1948).

136 4. Main wetting path calculations

137 4.1. Liquid bridges

138 Cavitation of the water contained within a pore results in the formation of menisci, often referred to
 139 as *liquid bridges* due to their shape, suspended between the surrounding soil particles. On re-wetting,
 140 those liquid bridges expand up to the point that their boundaries touch, whereupon the pore fills with
 141 water (Likos, 2009). Suction in the liquid bridges is given by Eqn 2, where κ and l are the meridional
 142 and azimuthal radii given by

$$\kappa = \frac{2R_{mod}(1 - \cos(\beta)) + D_{mod}}{2 \cos(\theta_{slv} + \beta)} \quad (21)$$

$$l = R_{mod} \sin(\beta) - \kappa(1 - \sin(\theta_{slv} + \beta)) \quad (22)$$

143 where $R_{mod} = R + t(\psi_w)$, $D_{mod} = D - 2t(\psi_w)$ ($t(\psi_w)$ is found using Eqn 17) and β is the filling
 144 angle, as shown in Figure 12. Suction in the liquid bridge given by Eqn 2 is now termed ψ_w as it is
 145 to be used to determine wetting suctions. At the moment of cavitation, suction in the liquid bridge
 146 is equal to the cavitation suction ψ as calculated using Eqn 10, so that it can readily be shown from
 147 Eqns 17, 18, 10 and 2 that $\kappa < r^*$, as shown in Figure 13(a) for cubically-packed spheres (for ease
 148 of demonstration). A reduction in suction immediately following cavitation therefore does not result
 149 in the immediate filling of the pore space, as individual liquid bridges are not in contact, but instead a
 150 gradual growth in liquid bridge volume with reducing suction until the point at which they coalesce.
 151 Liquid bridge coalescence occurs at $\beta = 30^\circ$ for tetrahedrally-packed spheres, assuming that $\theta_{slv} = 0$,
 152 so that the suction at coalescence can be found for a given value of r , R and D using Eqn 2 (Likos,
 153 2009). It should be noted that $\theta_{slv} = 0$ for wetting and drying due to the presence of adsorbed films on
 154 the smooth particle surfaces, which are therefore perfectly wetting (Lourenço et al., 2012). Hysteresis
 155 between wetting and drying suctions is often attributed to different wetting and drying θ_{slv} values,
 156 due to assumed “advancing” and “retreating” conditions respectively (Haines, 1929, 1930; Lourenço
 157 et al., 2012); however, by incorporating different mechanisms for wetting and drying (i.e. meniscus
 158 coalescence and cavitation respectively), this model is therefore also able to include suction hysteresis
 159 despite the $\theta_{slv} = 0$ restriction.

160 If $D > 0$, it is possible that $\kappa \geq l$ for some values of β , as shown in Figure 14. This condition
 161 is undefined, as the geometry shown in Figure 12 cannot be maintained. It is therefore assumed that

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162 if the condition $\kappa \geq l$ is met for a given pore size, the liquid bridges surrounding that pore rupture,
 163 so that only adsorbed water remains. $\kappa \geq l$ is also possible if too high a value of n is selected, as
 164 this results in high values of D and so a ‘stretching’ of the liquid bridge geometry. The maximum
 165 porosity that can be supported by the assumed tetrahedral geometry can be determined by setting $\kappa = l$
 166 and solving between Eqns 21, 22 and 5, resulting in $n_{max} = 0.519$, so that materials of porosities
 167 $0.276 \leq n \leq 0.519$ can be modelled using tetrahedral packing.

168 4.2. Filling of slit-shaped pores

The suction below which a slit-shaped pore will fill is given by

$$\psi_w = -\frac{1}{2(r - t(\psi_w))} \left(\frac{A_{svl}}{6\pi t(\psi_w)^2} + \frac{A_{llv}}{48\pi (r - t(\psi_w))^2} - \frac{A_{svl}}{6\pi (2r - t(\psi_w))^2} - 2\gamma \right) \quad (23)$$

169 where $t(\psi_w)$ is found using Eqn 17 (as bulk and adsorbed water phases are not interacting, so that
 170 Eqn 19 is not required). Again, Eqn 23 has been converted from the original Iwamatsu and Horii
 171 (1996) expression to be in terms of ψ_w .

172 5. Water content calculations

173 5.1. Drying of macro-region pores

174 Pores between spherical particles are either filled or occupied by adsorbed films and liquid bridges
 175 (unless they have ruptured), depending on the applied suction and pore size. The volume of water in
 176 filled pores of size r can be found directly from the soil PSD, given by the cumulative volume of pores
 177 of that size. The volume of water contained in a liquid bridge immediately following cavitation, V_{LB} ,
 178 is given by

$$V_{LB} = \pi R_{mod}^* (4\kappa^2 c^2 - (D_{mod} - 2t(\psi(r)))^2) \quad (24)$$

$$c = \frac{\cos(\theta + \beta) + \cos\theta}{2} \quad (25)$$

where $R_{mod}^* = \frac{R_{mod}}{2}$ and $t(\psi(r))$ is as found using Eqn 17. β , κ and l are found using Eqns 2,
 21 and 22 for a given value of $\psi(r)$. Note that although Eqns 24 and 25 refer to liquid bridges, the
 cavitation suction ψ and not the coalescence suction ψ_w is used for volume determination in this case
 as conditions are for drying. Cavitation leads to the formation of $(6 \times \frac{1}{2}) + (6 \times \frac{1}{4}) + 9 = 27$ liquid

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bridges in the enlarged tetrahedral cell (Figure 6), so that the volume of water contained within the liquid bridges, expressed as the ratio of water volume in the liquid bridges, $V_{LB_{cell}}$, to volume of voids in the cell, $V_{v_{cell}}$, is given by

$$\frac{V_{LB_{cell}}}{V_{v_{cell} \text{ tet}}} = \frac{27V_{LB}}{(3\sqrt{2}(2R + D)^3 - 8\pi R^3)}. \quad (26)$$

Note that R_{mod} and D_{mod} are not required in Eqn 26 due to the use of the volume of voids for the total unit cell. The corresponding water content for liquid bridges surrounding all pores of size r is therefore given by

$$V_{LB_r} = v_p(r) \left(\frac{V_{LB_{cell}}}{V_{v_{cell}}} \right) \quad (27)$$

179 where $v_p(r)$ is the volume of pores of size r , found from the soil PSD.

180 As liquid bridges can be present above the cavitation suction, the total volume of water contained
181 within all liquid bridges, $V_{T_{LB}}$, is found by summing V_{LB_r} over all pore sizes $\geq r$, all determined
182 at suction $\psi(r)$ (i.e. the currently-considered cavitation suction), noting that V_{LB_r} can equal 0 if the
183 applied suction is too high for that pore geometry (i.e. the liquid bridges have ruptured).

The volume of water contained in an adsorbed film surrounding a particle of radius R is given by

$$V_{film} = 4\pi R^2 t(\psi(r)). \quad (28)$$

The total surface area for adsorption is $(12 \times \frac{1}{6}) + (2 \times \frac{1}{2}) + 3 = 6$ spheres in the expanded tetrahedral unit cell, so that the total volume of adsorbed water in the unit cell expressed as the ratio of water volume in the adsorbed films $V_{film_{cell}}$ to volume of voids is given by

$$\frac{V_{film_{cell}}}{V_{v_{cell} \text{ tet}}} = \frac{6V_{film}}{(3\sqrt{2}(2R + D)^3 - 8\pi R^3)} \quad (29)$$

so that

$$V_{film_r} = v_p(r) \left(\frac{V_{film_{cell}}}{V_{v_{cell}}} \right) \quad (30)$$

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gives the adsorbed water content for all pores of that pore radius. Again, the total volume of water contained within adsorbed films, $V_{T_{film}}$, is given by the sum of $V_{film,r}$ over pore sizes $\geq r$. The total volume of water present in the soil at a given drying suction ψ is therefore given by

$$V_T = \sum_{<r} v_p(r) + V_{T_{LB}} + V_{T_{film}} \quad (31)$$

184 5.2. Drying of micro-region pores

It is assumed that slit-shaped pores of size r remain filled at suctions below $\psi(r)$, so that the water content of filled pores is again given by $v_p(r)$. The total volume of water remaining in a slit-shaped pore of size r after cavitation is given by

$$V_{ssr} = v_p(r) \frac{t_{ss}(\psi)}{r} \quad (32)$$

where t_{ss} is found using Eqn 19 for that suction ψ . Note that the particle length L and height αL do not feature in Eqn 32, as the assumption that pores are rectangular in cross section results in pore water content being determined by the ratio of film thickness to pore radius only. The total volume of water contained within adsorbed films between slit-shaped pores, $V_{T_{ss}}$, is given by the sum of V_{ssr} over all pores $\geq r$. The total volume of water at a given suction ψ , considering cavitation of the slit-shaped pores, is therefore given by

$$V_T = \sum_{<r} v_p(r) + V_{T_{LB}} + V_{T_{film}} + V_{T_{ss}} \quad (33)$$

185 5.3. Wetting calculations

The total volume of water present in the macro region during wetting is calculated using Eqns 24 to 27 at $\psi_w(r)$, determined using to Eqn 2. The total water content is then given by

$$V_T = \sum_{\leq r} v_p(r) + V_{T_{LB}} + V_{T_{film}} \quad (34)$$

186 i.e. as for Eqn 31, however now pores are considered to be filled at ψ_w . As $\psi_w(r) < \psi(r)$, the volume
 187 of water on wetting is lower than that during drying, as pores can maintain liquid bridges to lower
 188 suctions, so that hysteresis is expected between the filling and emptying.

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Similarly, the total volume of water present in the micro region is calculated using Eqns 25 to 27 and Eqn 32 at $\psi_w(r)$ for slit-shaped pores. Total water content during wetting is then given by

$$V_T = \sum_{\leq r} v_p(r) + V_{TLB} + V_{Tfilm} + V_{Tss}. \quad (35)$$

189 Again, this results in a lower volume of water due to lower wetting than drying suctions for slit-shaped
190 pores. A summary of all of the model calculations is given in Figure 15.

191 6. Model performance and discussion

192 6.1. SWRC prediction

193 SWRCs for five colluvial soils formed from a naturally decomposed granitic soil were presented
194 in Zhang and Li (2010), as well as corresponding PSDs for those soils under zero applied suction
195 as shown in Figure 16. Mercury Intrusion Porosimetry (MIP) was used to determine soil PSDs using
196 freeze-dried samples (Penumadu and Dean, 2000). Material was as used for SWRC analysis, but was
197 sieved to pass 10 mm due to the size limit on MIP samples (15 cm³ for the device used). Modified and
198 original particle grading curves for each soil are shown in Figure 17, indicating that whilst the grading
199 of soil CL was unchanged by this process, the grading of the remaining soils changed considerably
200 due to particle removal. Compacted densities were modified to account for the removed material, so
201 that the final densities of the MIP and SWRC test samples, and so their resulting pore structures,
202 were comparable. A disadvantage of the use of MIP to determine PSDs is that the range of pore sizes
203 accessible is dependent on the pressure range of the apparatus. PSDs found by Zhang and Li (2010)
204 for compacted and saturated samples (selected as this is the starting condition for experimental SWRC
205 analysis) identified pore diameters between 6 nm and 146 μm and results suggest that no pores smaller
206 than 6 nm were present in any of the samples, which is consistent with the larger pores expected in
207 kaolinitic clays (Diamond, 1970). Only soil GW-GM showed a significant volume of pores larger than
208 146 μm .

209 SWRCs predicted from those PSDs shown in Figure 16 are shown in Figures 18 to 22. A summary
210 of the model input and output data (for the main drying curves only) is given in Table 2. Approxima-
211 tions to the SWRC made using Eqn 1 (which are identical to those predicted in Zhang and Li (2010))
212 are also shown in Figures 18 to 22, showing that, whilst similar, the model developed here predicts

213 higher suctions for a given water content; this is due to the effective reduction in pore size due to the
214 presence of adsorbed films, as shown by Eqn 18. Note that although it is usual to show SWRCs in terms
215 of degree of saturation, it is not possible in this case due to the use of different sample sizes between
216 SWRC and PSD testing; the use of gravimetric water content removes this restriction. Figures 18 to
217 22 also show predicted main wetting curves and adsorbed water contents for each PSD shown in Fig-
218 ure 16. Unfortunately, PSDs were not determined in Zhang and Li (2010) for wetting conditions, so
219 that those main wetting curves shown in Figures 18 to 22, calculated using drying PSDs, are illustrative
220 of the model's ability to predict hysteresis between drying and wetting only. Similarly, adsorbed water
221 contents were not measured in Zhang and Li (2010), so that those adsorbed water contents shown are
222 also only indicative of how adsorbed water content might change with overall water content and suc-
223 tion. Confirmation of predicted wetting retention properties and adsorbed water contents is a topic of
224 ongoing study.

225 Figures 18 to 22 indicate that the best match to measured data was achieved for soil CL; this is
226 suggestibly due to the use of identical material during SWRC and PSD testing, as shown in Figure 17,
227 unlike those used for the other soil types. However, they also show that predicted values all show a
228 characteristic overshoot in the low suction range, where significantly higher suctions are predicted for
229 given water contents than were found experimentally. The exception to this is soil GW-GM (Figure 19),
230 which shows a good match between predicted and measured data in the low suction range but a poorer
231 match at higher suctions; this is likely due to the significant volume of pores larger than $146 \mu\text{m}$ which
232 could not be measured using the selected MIP device (Zhang and Li, 2010).

233 A potential source of the apparent overshoot is "pore trapping", which occurs when pores of differ-
234 ent radii lie on the mercury intrusion path and which has also been suggested as a contributing factor
235 towards hysteresis observed between drying and wetting retention properties (Cuisinier and Laloui,
236 2004; Rojas and Rojas, 2005). An example columnar pore is shown in Figure 23. If mercury intrudes
237 the from the left, the larger pore region (radius r_1) will fill at some suction $\psi(r_1)$ and the smaller re-
238 gion (radius $r_2 < r_1$) at a higher suction $\psi(r_2)$, with the change in the intruded volume of mercury
239 being attributed to pores of sizes r_1 and r_2 respectively. However, if mercury intrudes from the right
240 the larger region cannot be filled due to the higher intrusion pressure of the smaller region. Instead,
241 both regions are intruded at $\psi(r_2)$, with the change in the intruded volume for both regions being at-
242 tributed to pores of size r_2 only (Simms and Yanful, 2001). The effect of trapped pores on MIP results

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243 is therefore an underestimation of the volume fraction of larger pores and a subsequent overestimation
244 of that of smaller pores, resulting in higher and lower water contents for a predicted drying suction
245 respectively, as is seen in Figures 18 to 22 (Meyer and Klobes, 1999). Pore trapping could therefore
246 be responsible for the characteristic overshoot seen in Figures 18 to 22 and so demonstrates the need
247 to use multiple methods to determine soil PSDs, in order to minimise the impact of one single test on
248 measured results (Hajnos et al., 2006).

249 **6.2. Soil fabric evolution and SWRC prediction limitations**

250 The effect of changing suction on the fabric of double-structure soils has been investigated by
251 several authors. Simms and Yanful (2001) used MIP to measure the PSDs of freeze-dried samples of a
252 clayey glacial till (compacted wet of optimum) after the application of a suction and found that, with
253 increasing suction, void ratio decreased and the modal large pore size and volume reduced, whilst the
254 small pore mode remained at a constant size but grew in volume. The change in PSD with suction was
255 attributed to the constriction of larger soil pores and so a reduction in pore accessibility with increasing
256 suction.

257 Cuisinier and Laloui (2004) used a pressure plate to subject samples of a morainic sandy-loam
258 soil (compacted on the dry side of optimum) to successively increasing suction levels to determine the
259 effect of suction on soil fabric. Material was removed from the samples on reaching suction equilibrium
260 and freeze-dried so that PSDs could be determined using MIP as shown in Figure 24. As was found by
261 Simms and Yanful (2001), increasing suction resulted in a reduction in the volume of large pores, with
262 the large pore modal size decreasing slightly with increasing suction, and an increase in the volume
263 of smaller pores, again with no significant change in the small pore modal size. Soil void ratio again
264 reduced with increasing suction although changes in soil PSD occurred at near-constant void ratios
265 at higher suctions. Cuisinier and Laloui (2004), and later Tarantino (2010), suggested that observed
266 results were due to the application of suctions only high enough to drain the larger pores, so that only
267 larger pores were subjected to changes in water content and subsequently constricted, whilst smaller
268 pores remained filled at all suction levels tested.

269 Results found by these authors therefore show that the fabric of a soil changes whilst undergoing
270 SWRC testing, so that retention properties predicted from one PSD alone, as was done in the previous
271 section, cannot capture the material behaviour at different suction levels. Instead, a single PSD can

272 only reliably predict material retention properties at the suction value at which it was found, so that
273 numerous PSDs are required to determine a more complete SWRC (Nuth and Laloui, 2008). This
274 can be investigated by comparing measured SWRC values to predictions made using a succession of
275 PSDs, determined over a range of suction values, as shown in Figure 25 for PSDs given in Figure 24.
276 Although the model considers particles to be rigidly arranged for purposes of the analysis, the use of
277 a different PSD per suction level prediction accounts for a changing (i.e. non-rigid) particle structure.
278 Figure 25 shows that although predictions made using a single PSD do not capture the measured
279 retention properties, a good match to predicted data can be achieved by combining predictions for
280 each PSD for that PSD's suction level. The large difference between measured and predicted water
281 contents shown in Figure 25 is due to the significant difference between the saturated water content
282 found for SWRC testing (370 mL/g) and the maximum intruded volume of mercury found at zero
283 suction (305 mL/g), suggestibly due to a large volume of pores not being intruded during MIP testing,
284 either due to the limit on intrusion pressures inherent in the device or pores not being accessible to
285 mercury during testing (Cuisinier and Laloui, 2004; Koliji et al., 2006). Also given in Figure 25 are
286 results found using Eqn 1, again showing how Eqn 1 significantly underpredicts suction values for a
287 given water content. Results given in Figure 25 therefore show that a good approximation to measured
288 SWRC data can be achieved by this model through the use of multiple PSDs, determined over a range of
289 applied suctions. This result unfortunately diminishes the power of the use of soil PSDs for predicting
290 retention properties, however, as a large number of PSDs is therefore required in order to get a good
291 match to experimental data. The use of PSDs to predict retention properties nonetheless remains a
292 powerful tool, but predictions must be limited to those suction values investigated.

293 7. Conclusions

294 This paper has presented a new method for determining a material's retention properties from its
295 PSD and has discussed the limitations on the use of PSDs to predict retention properties.

296 The model presented here offers several advantages over those techniques used by previous authors:

- 297 • Particles are modelled either as spheres or cuboids in order to more accurately model retention
298 properties at different pore scales;
- 299 • Material porosity, determined from the material PSD, is included as a model variable, incorpo-

- 300 rated by assuming a finite separation distance between modelled particles;
- 301 • The effects of adsorbed water on both wetting and drying suctions are included by assuming that
302 particles are covered by thin adsorbed films, with a subsequent improvement to the accuracy of
303 predicted retention properties;
 - 304 • Cavitation and liquid coalescence are used as mechanisms to explain pore drainage and filling
305 respectively, which allows the model to predict hysteresis between drying and wetting conditions
306 in the presence of adsorbed films without the need to consider the effects of pore interconnectiv-
307 ity.

308 The effect of changing suction on soil fabric was discussed and it was shown that the match to
309 experimental data is significantly improved if predictions are made using PSDs determined over a
310 range of suction values. This result unfortunately diminishes the power of the ability to predict retention
311 properties using PSD data, as multiple PSDs, determined for the entirety of the suction range of interest,
312 are required. Although currently a time-consuming process, developments in non-destructive testing
313 equipment, for example X-Ray Computed Tomography, might improve the speed of PSD determination
314 to the point that retention property prediction from PSD data becomes viable. Regardless, the use of
315 PSDs to predict retention properties has been shown to be a useful and accurate alternative to direct
316 SWRC measurement provided suitable PSDs are available.

317 **8. Acknowledgements**

318 The first author was supported by a studentship awarded by the School of Engineering and Com-
319 puting Sciences, Durham University, during this research. The first author would like to thank Profs.
320 Alessandro Tarantino and David Toll for their comments on this work.

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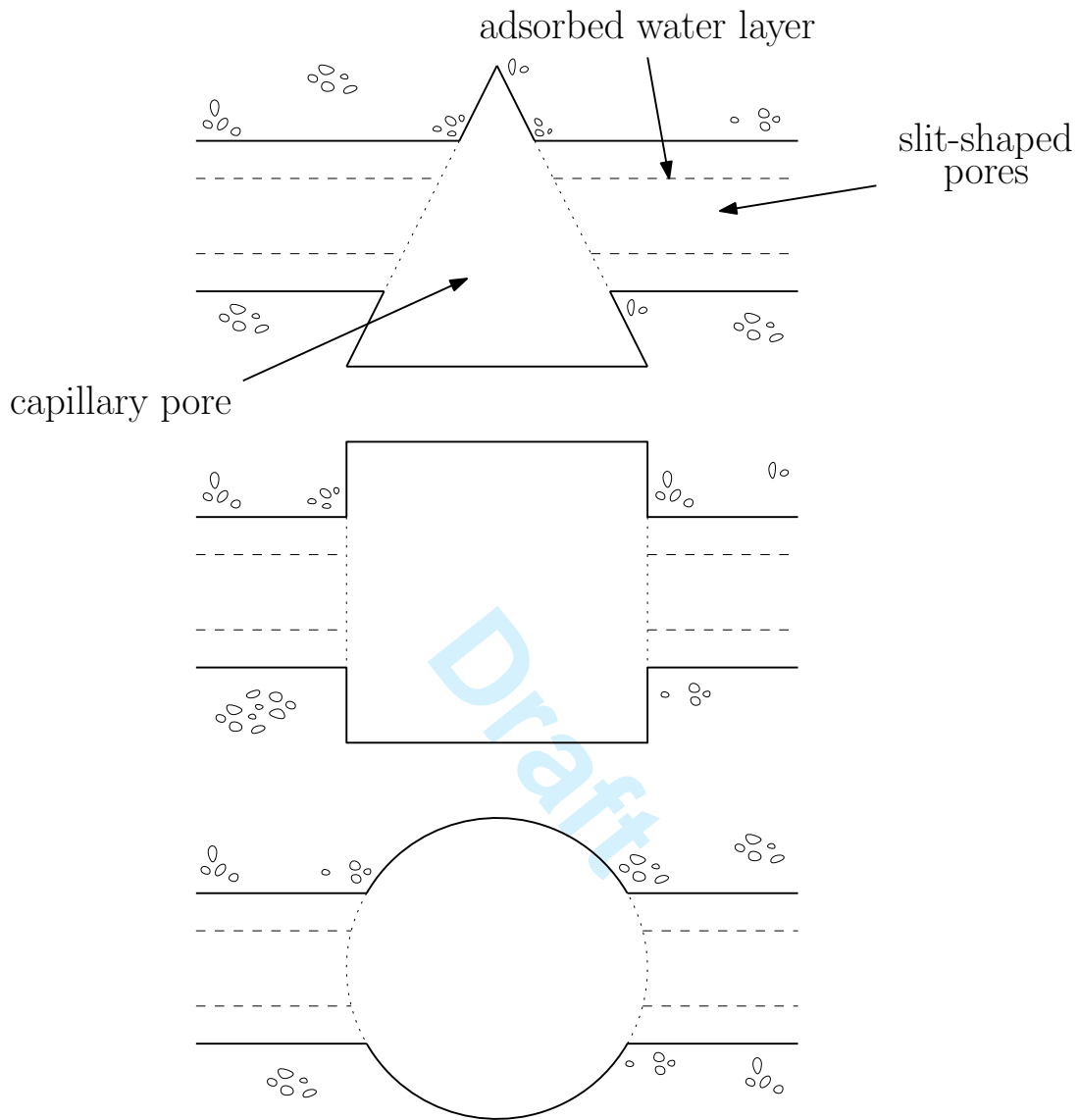


Fig. 1. Examples of pore shapes considered in Tuller et al. (1999), showing decreasing angularity

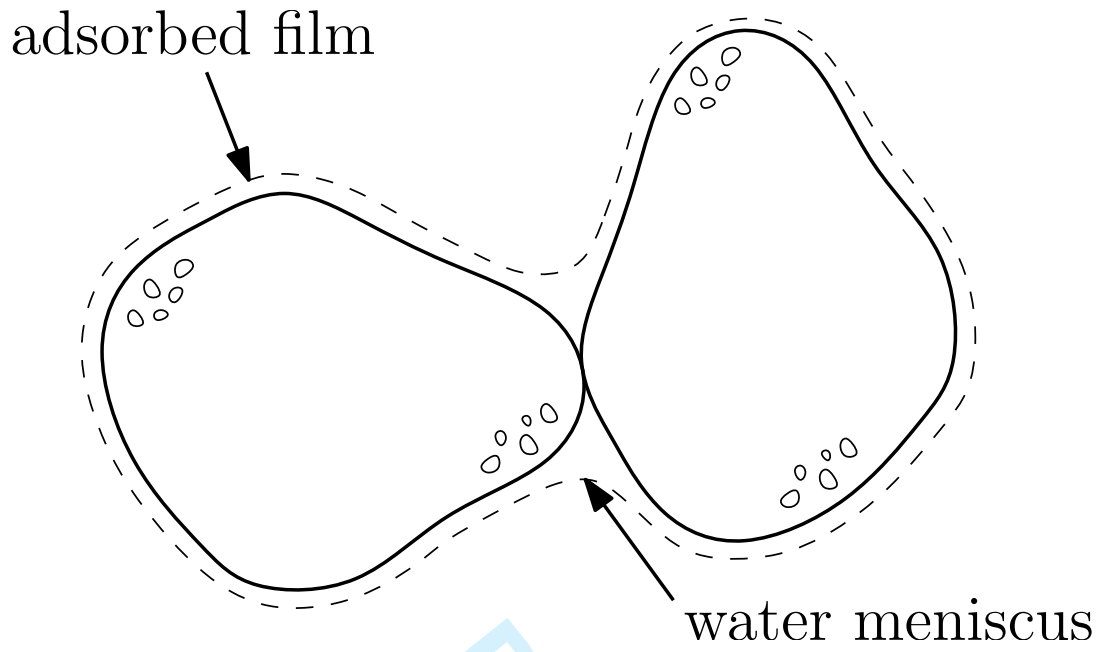
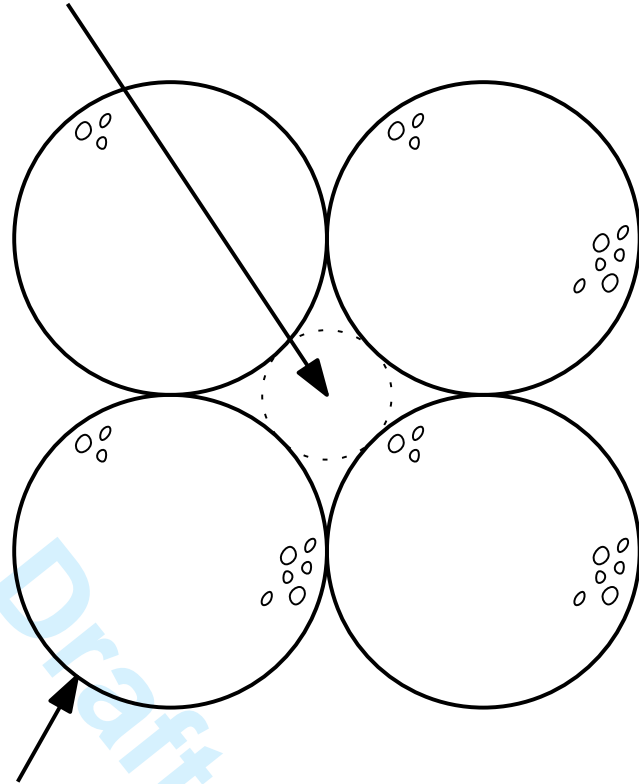


Fig. 2. Water meniscus and adsorbed films between two example granular particles

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2-D interstitial site



spherical particle

Fig. 3. Interstitial pore space between cubically-packed spherical particles

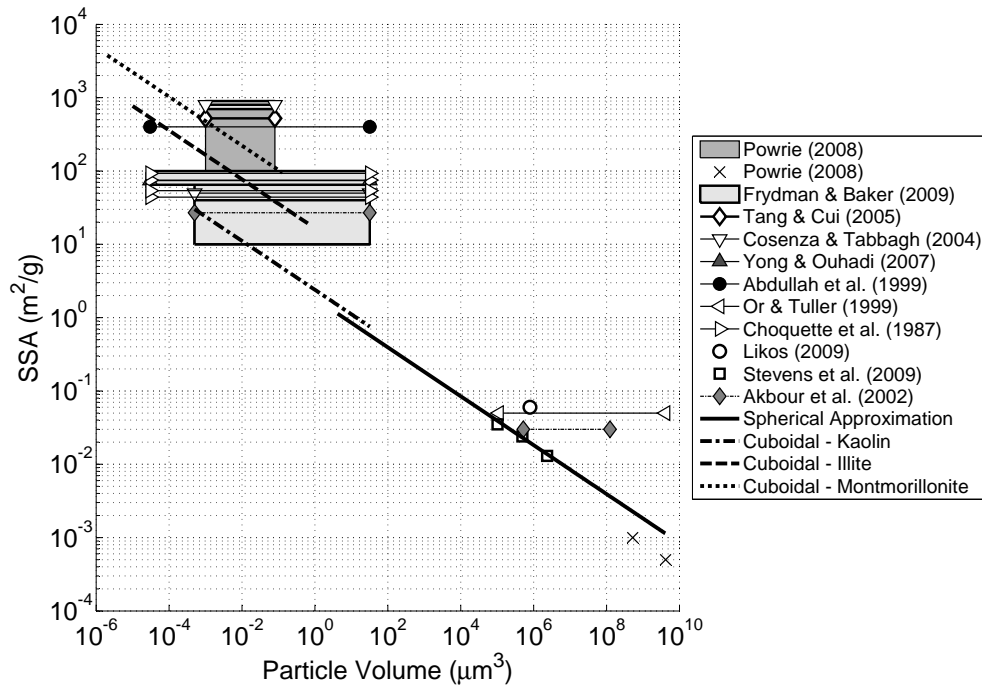
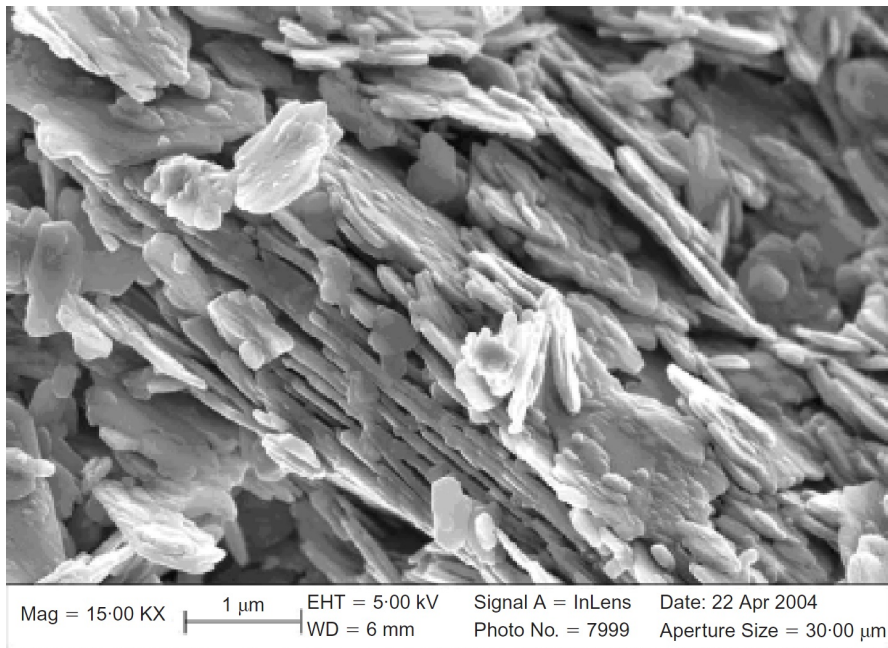


Fig. 4. Specific surface area data (sources given in the figure) compared to spherical and cuboid particle shape approximations



approximated

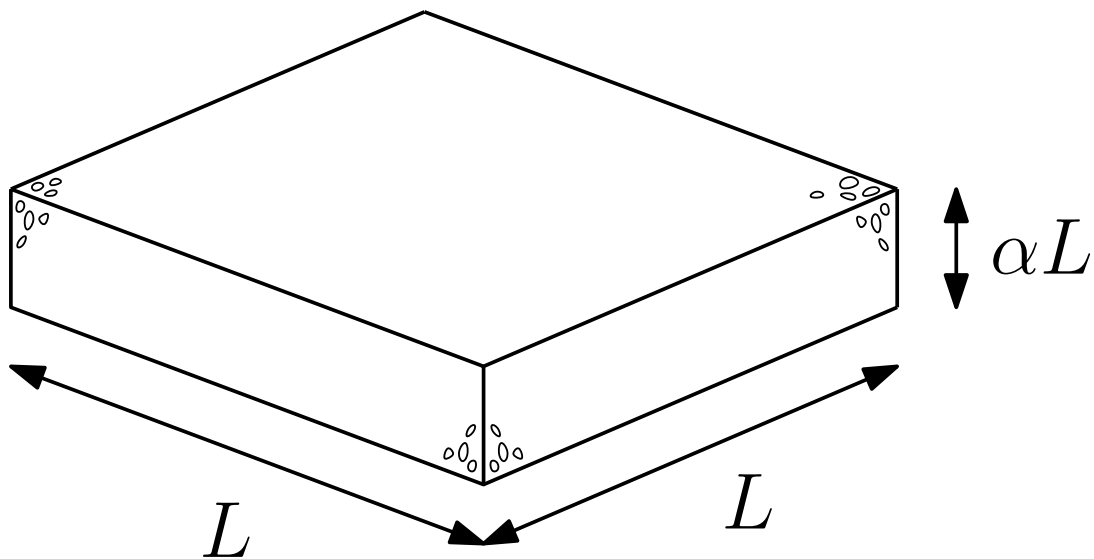


Fig. 5. Cuboidal shape assumption for plate-like particles

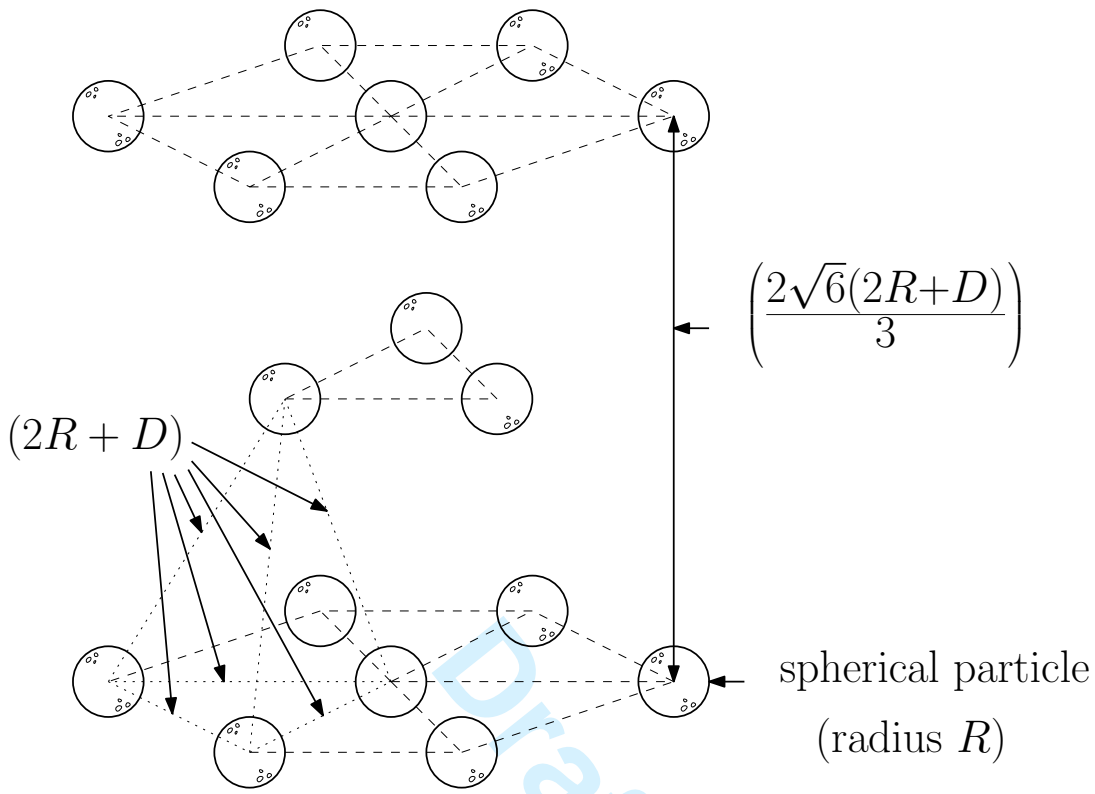


Fig. 6. Enlarged unit cell for tetrahedral sphere packing. Dotted lines show the shape of a single tetrahedral unit cell.

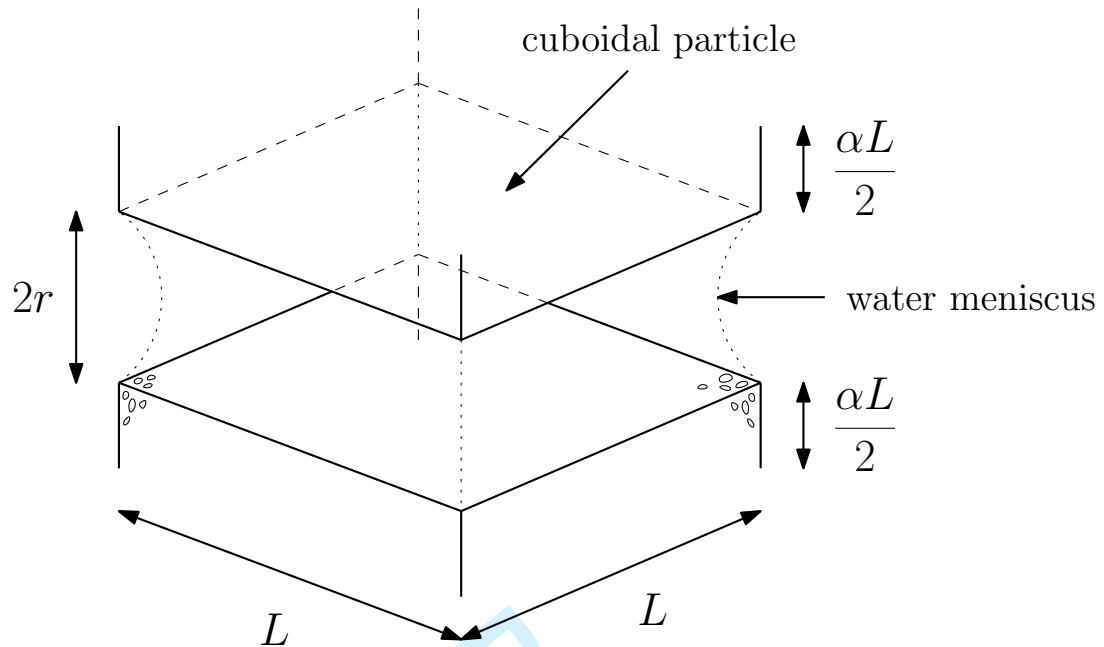


Fig. 7. Cuboidal particle unit cell (assumed example water menisci profiles also shown)

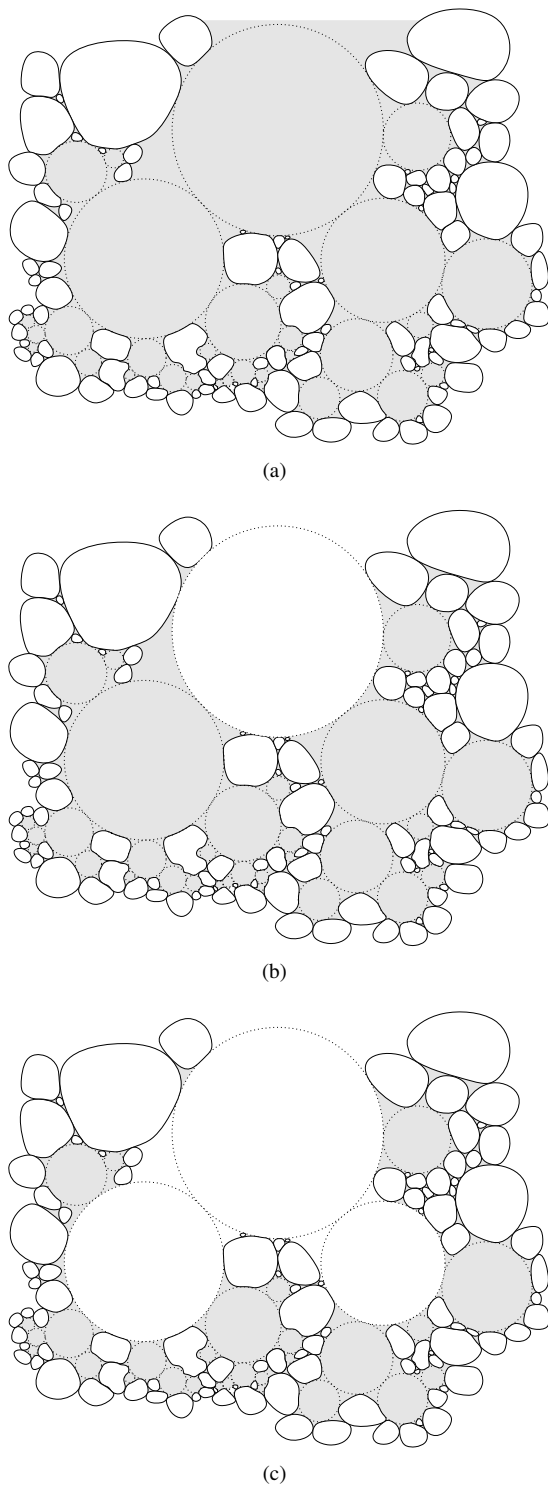


Fig. 8. Desaturation of an example granular soil comprising rounded particles through cavitation of spherical interstitial pores: a) saturated; b) initial desaturation; c) progressive cavitation at higher suctions

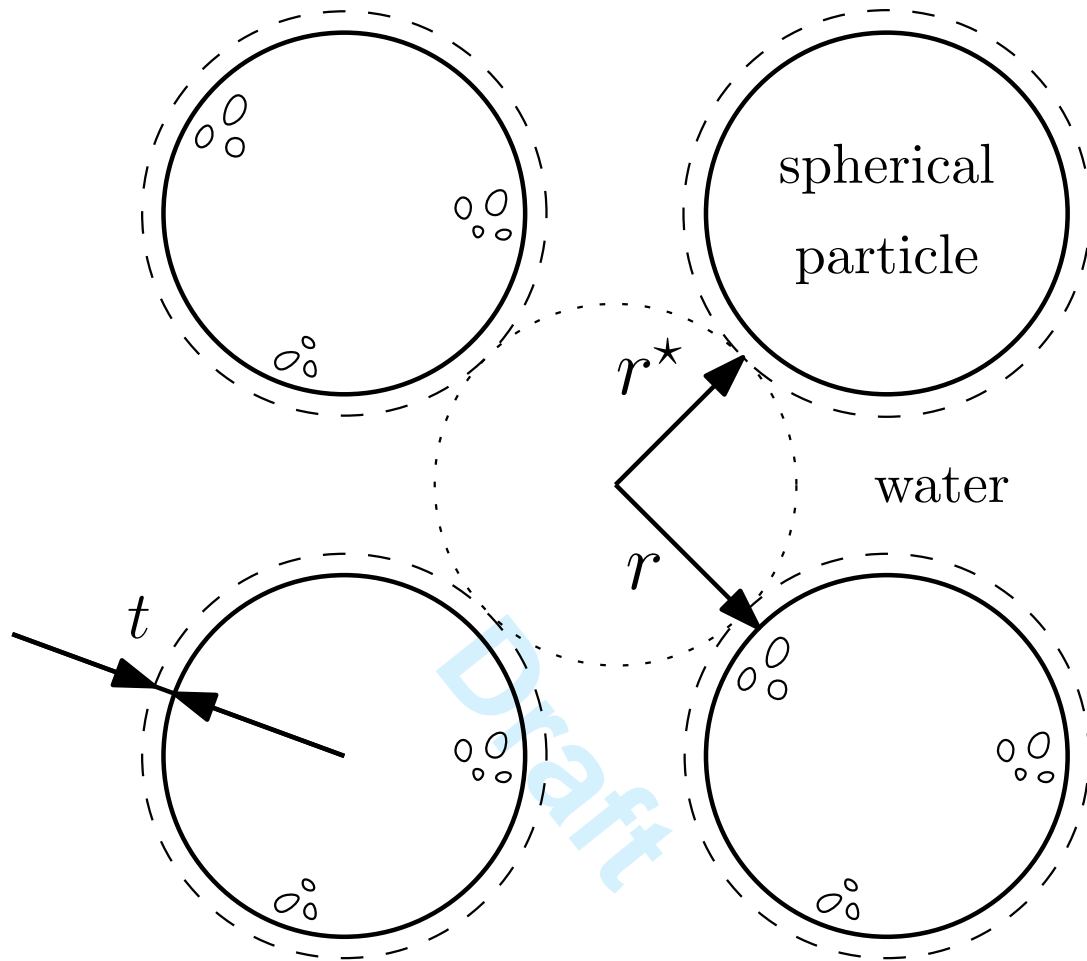


Fig. 9. Reduced cavitation radius due to adsorbed films

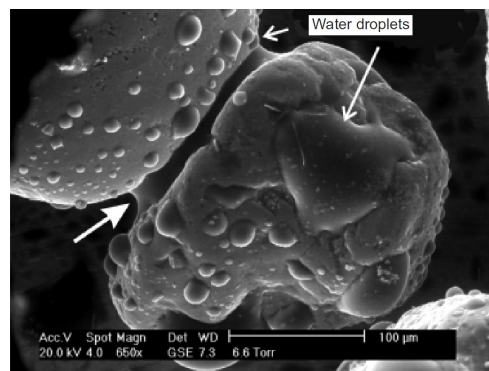


Fig. 10. ESEM micrograph of granular particles undergoing wetting (Lourenço et al., 2012)

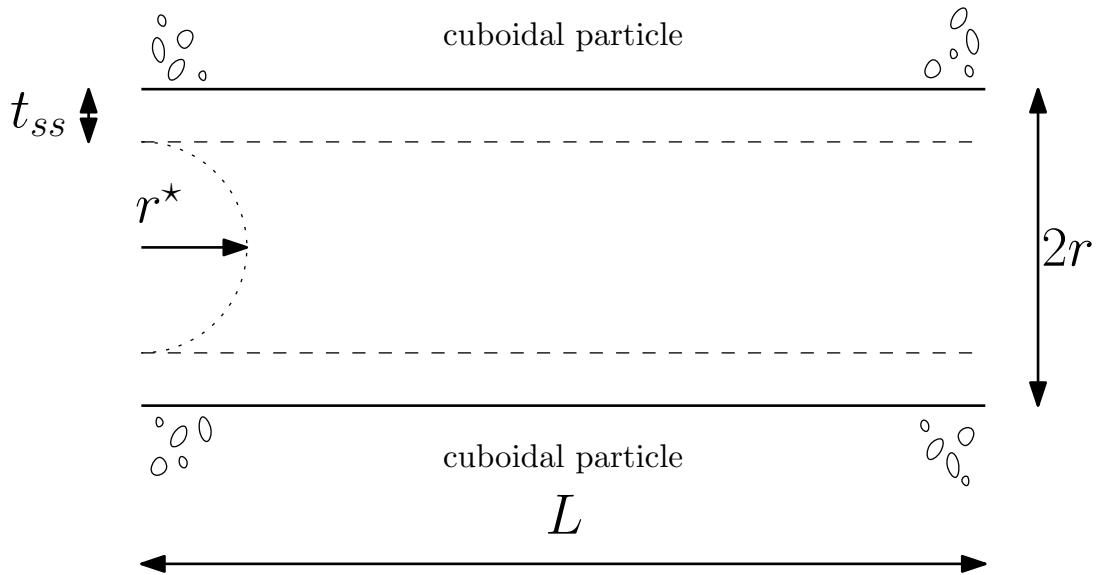


Fig. 11. Cavitation in a slit-shaped pore containing two adsorbed films

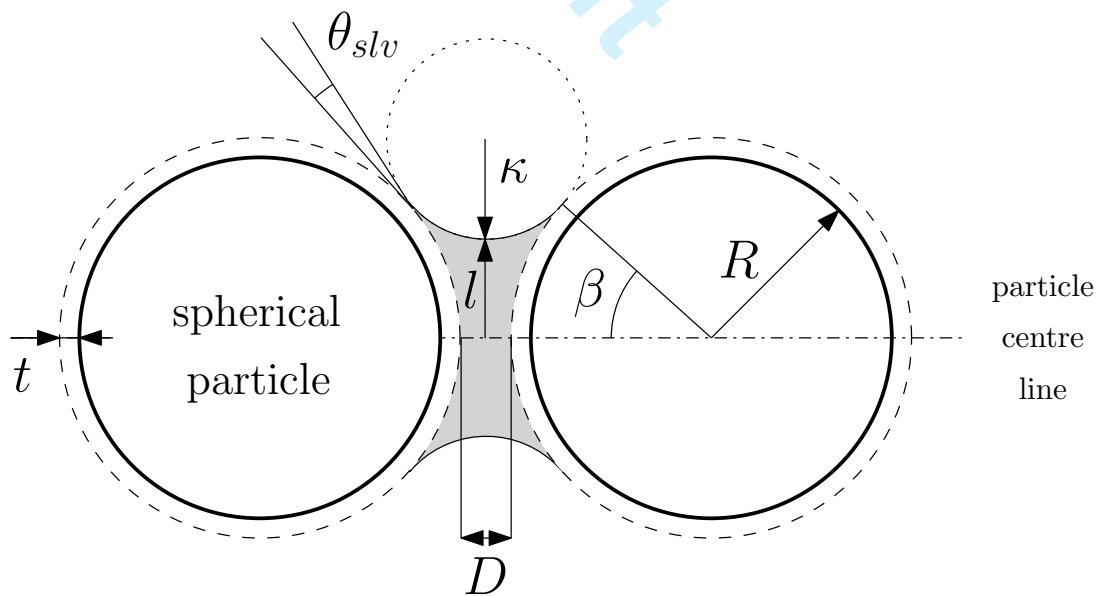


Fig. 12. Liquid bridge parameters

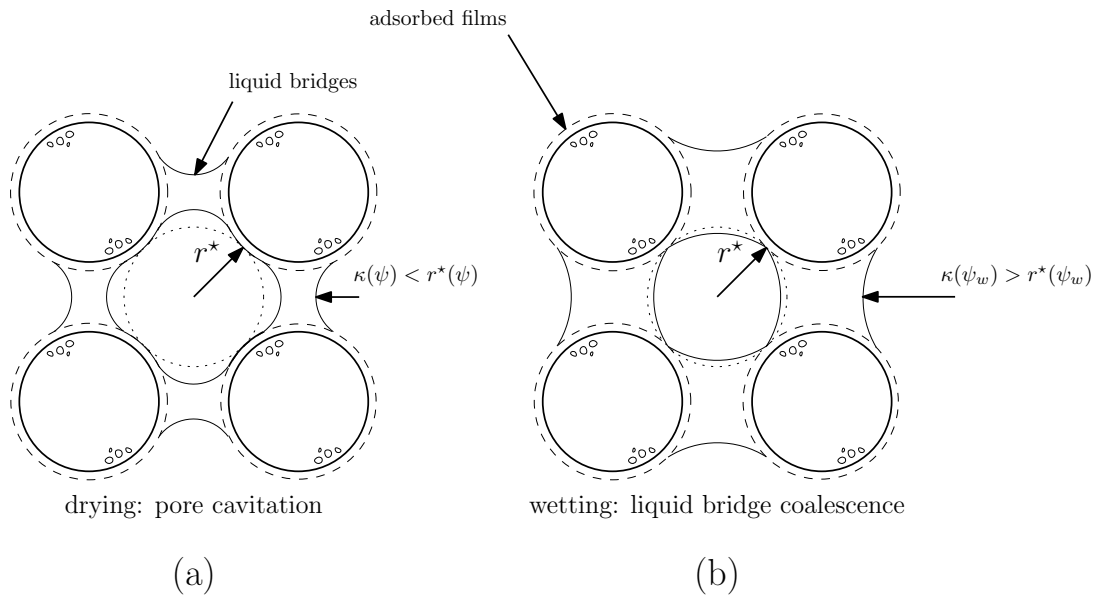


Fig. 13. Drying and wetting liquid bridge configurations

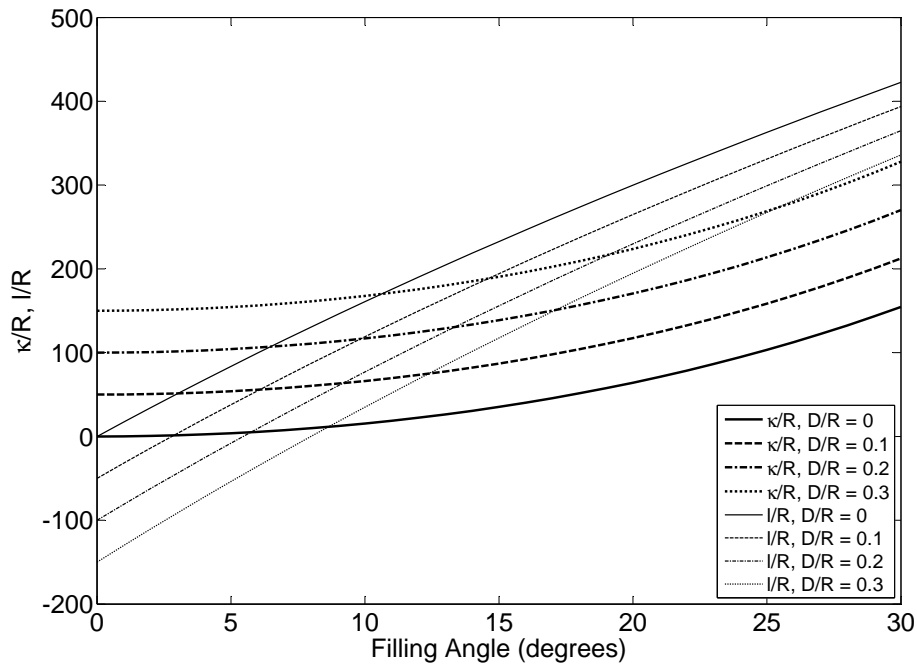


Fig. 14. Effect of separation distance on κ and l , normalised against particle radius R .

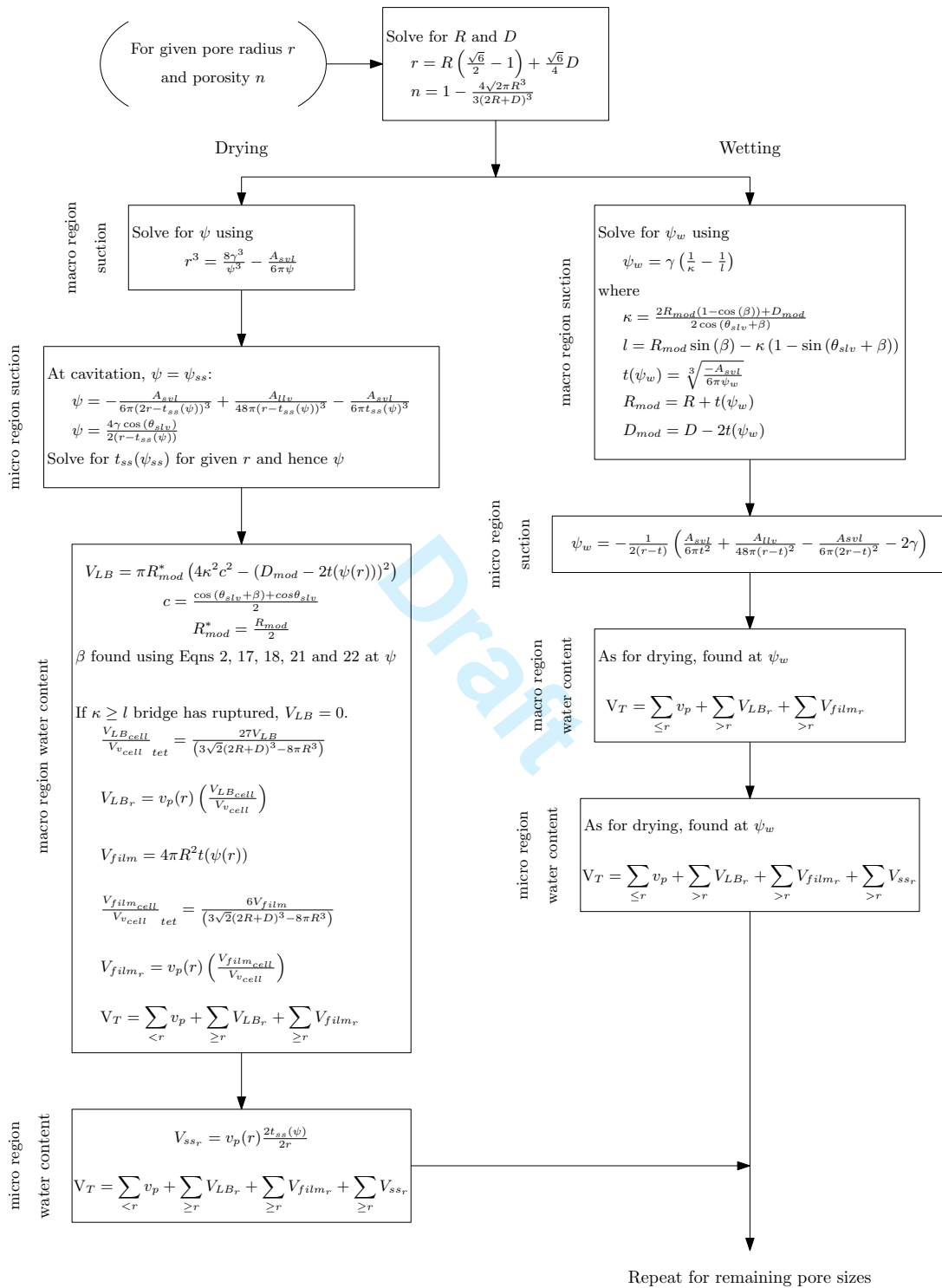


Fig. 15. Summary of equations used to determine the SWRC for a given pore size r and porosity n

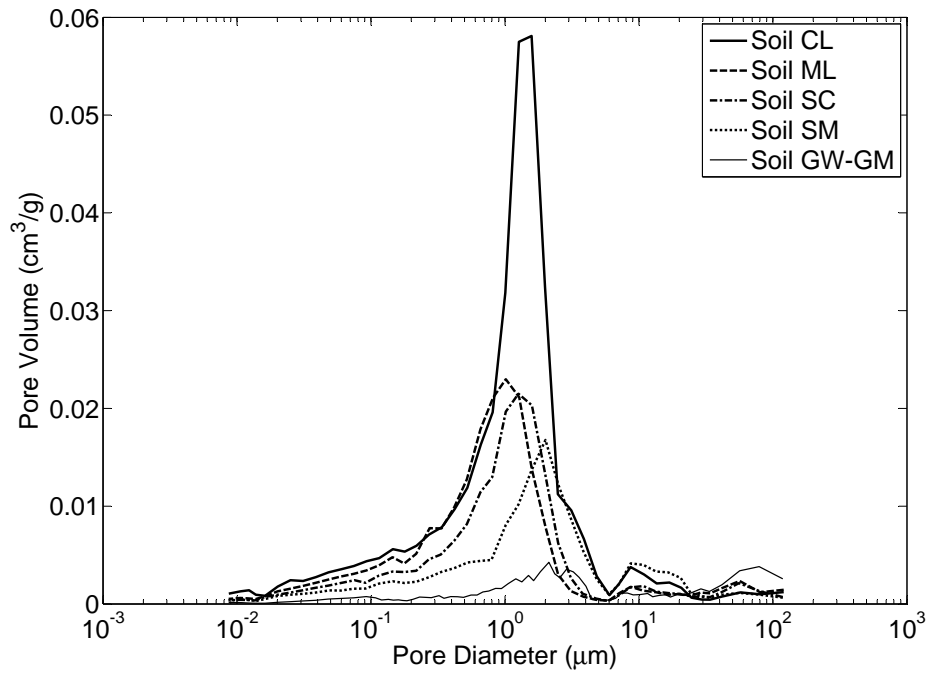


Fig. 16. Pore size distributions for five colluvial soil types post compaction and saturation Zhang and Li (2010)

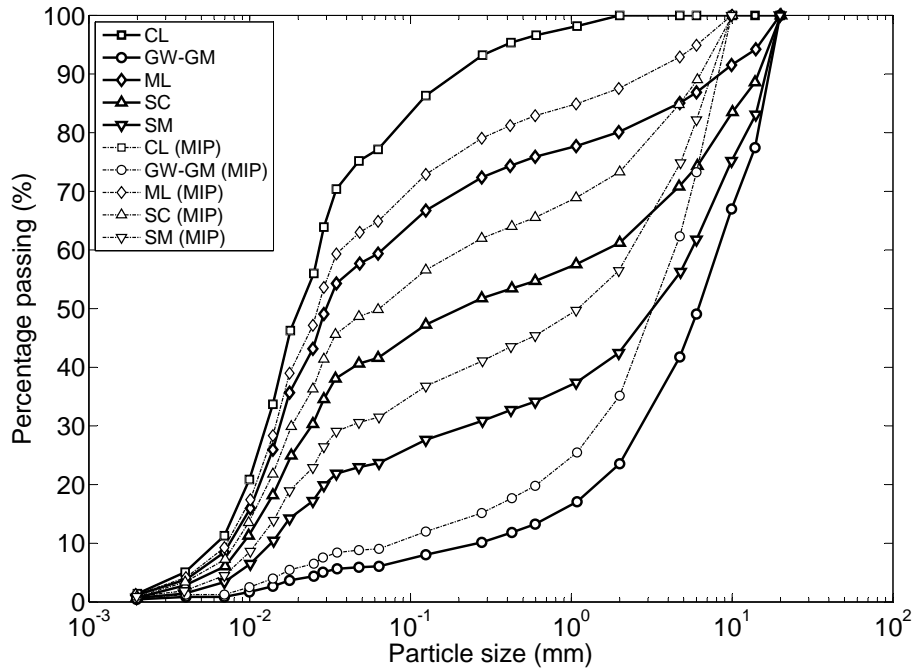


Fig. 17. Particle grading curves for soils tested in Zhang and Li (2010)

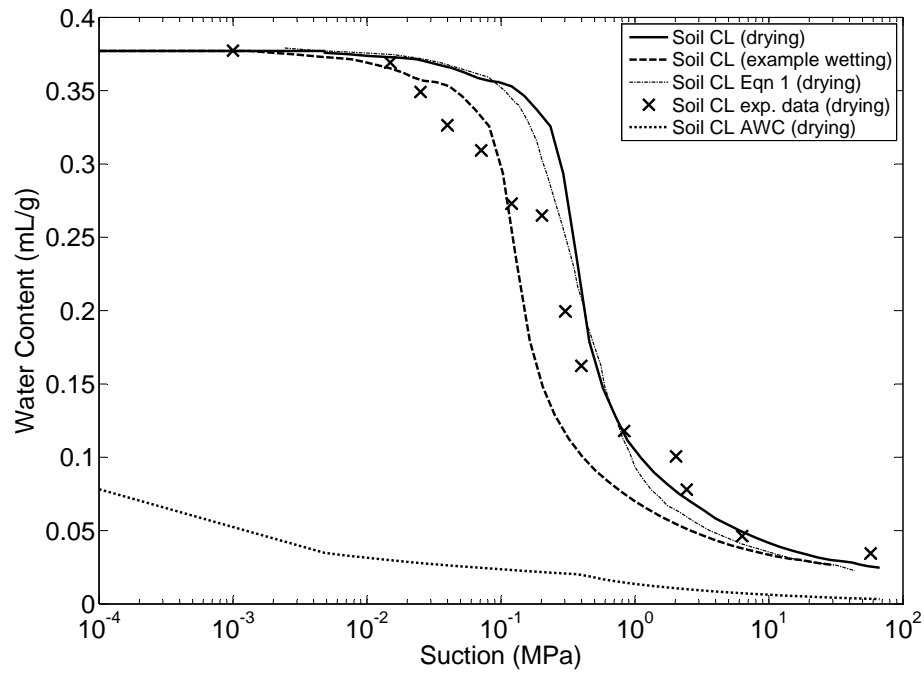


Fig. 18. Predicted SWRCs for soil CL

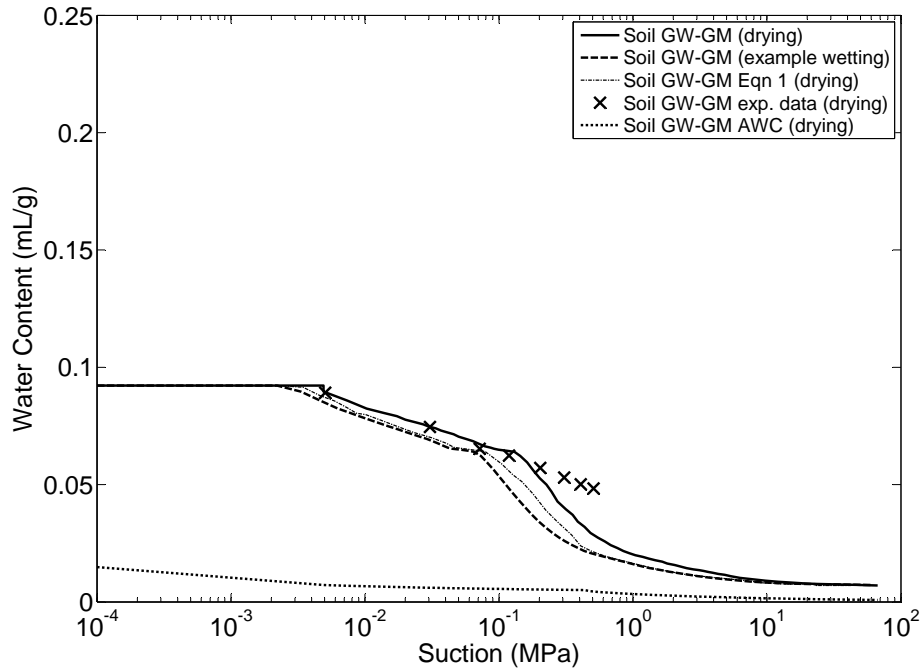


Fig. 19. Predicted SWRCs for soil GWGM

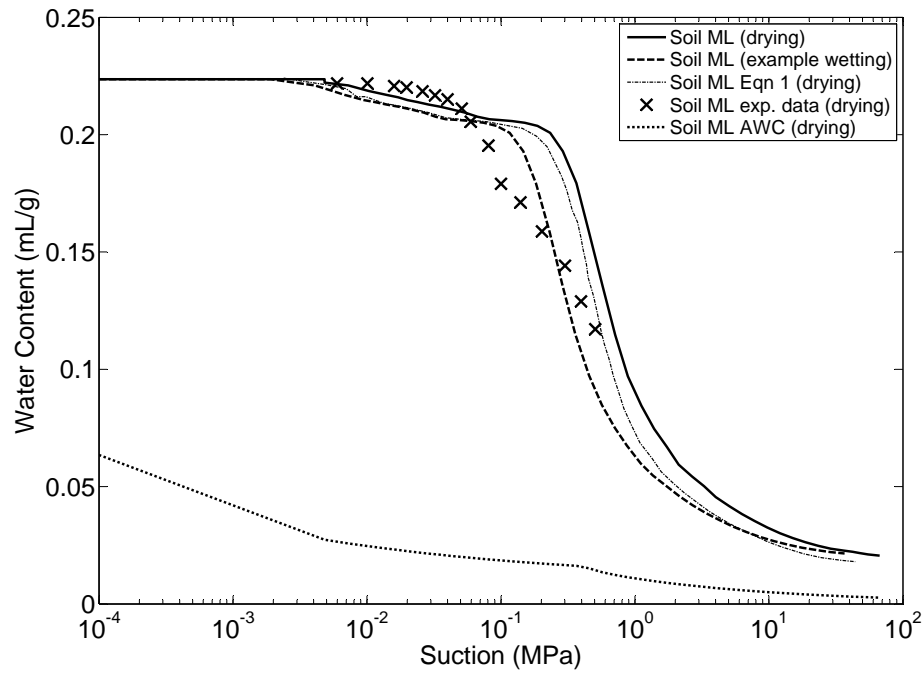


Fig. 20. Predicted SWRCs for soil ML

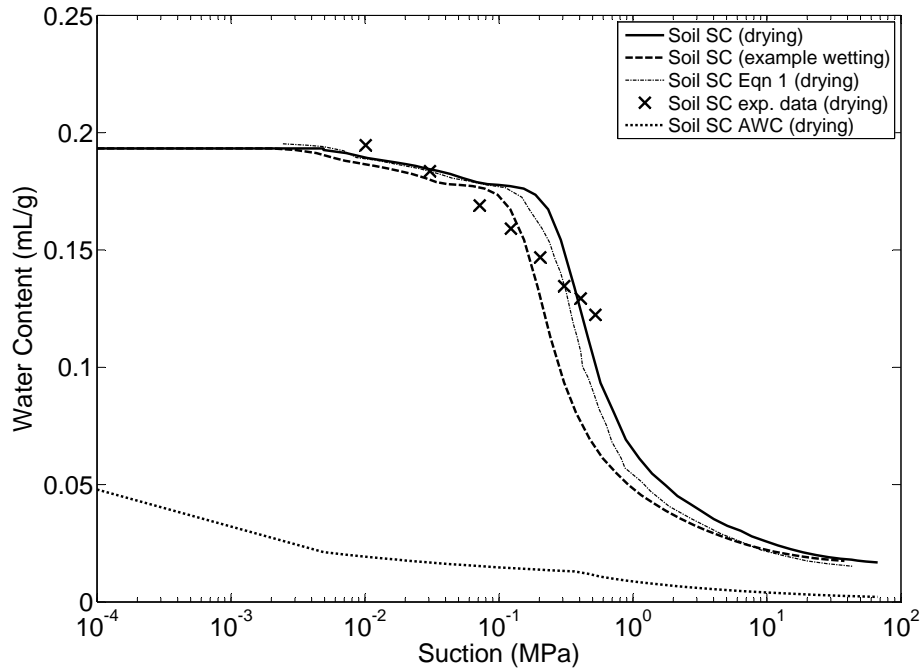


Fig. 21. Predicted SWRCs for soil SC

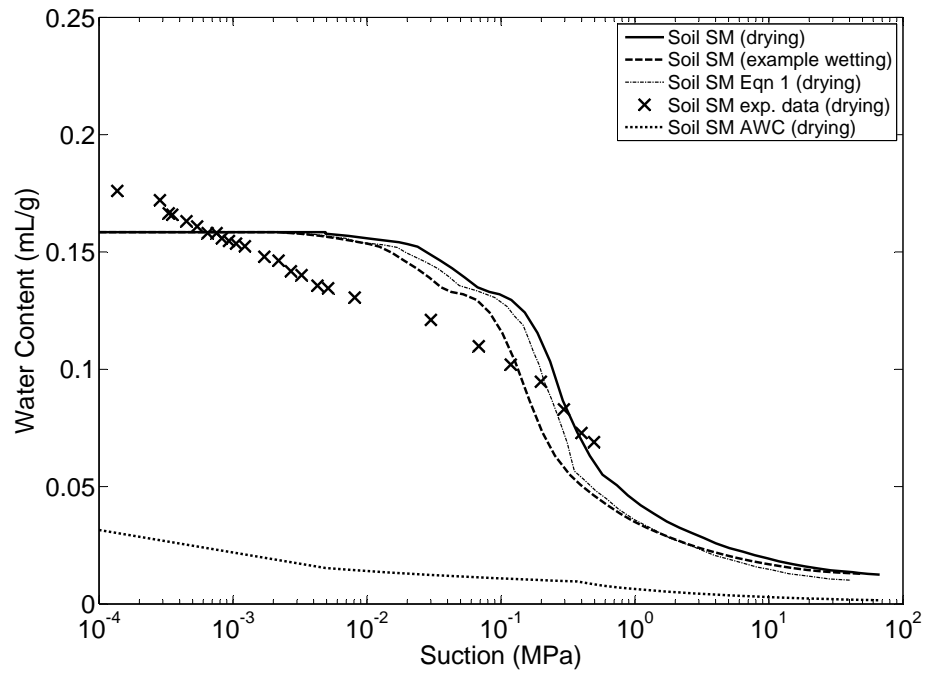


Fig. 22. Predicted SWRCs for soil SM

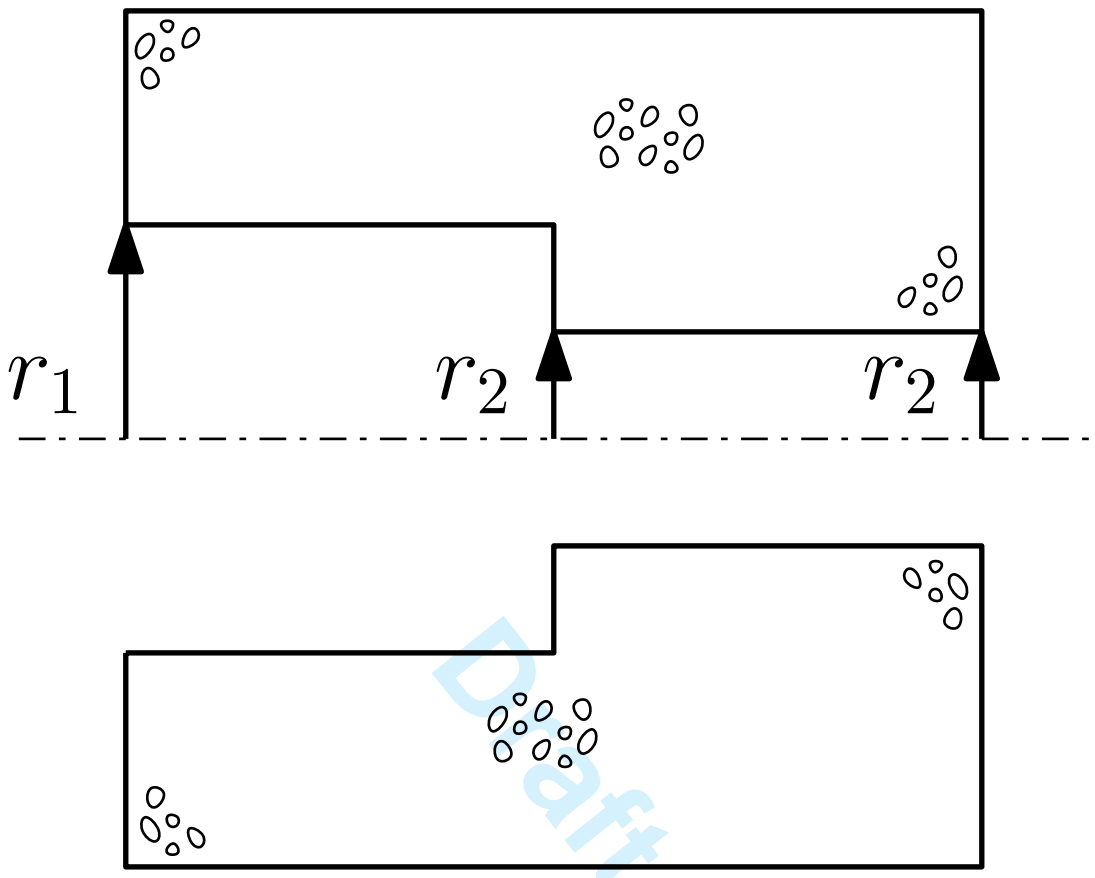


Fig. 23. Changing pore radii in a columnar pore

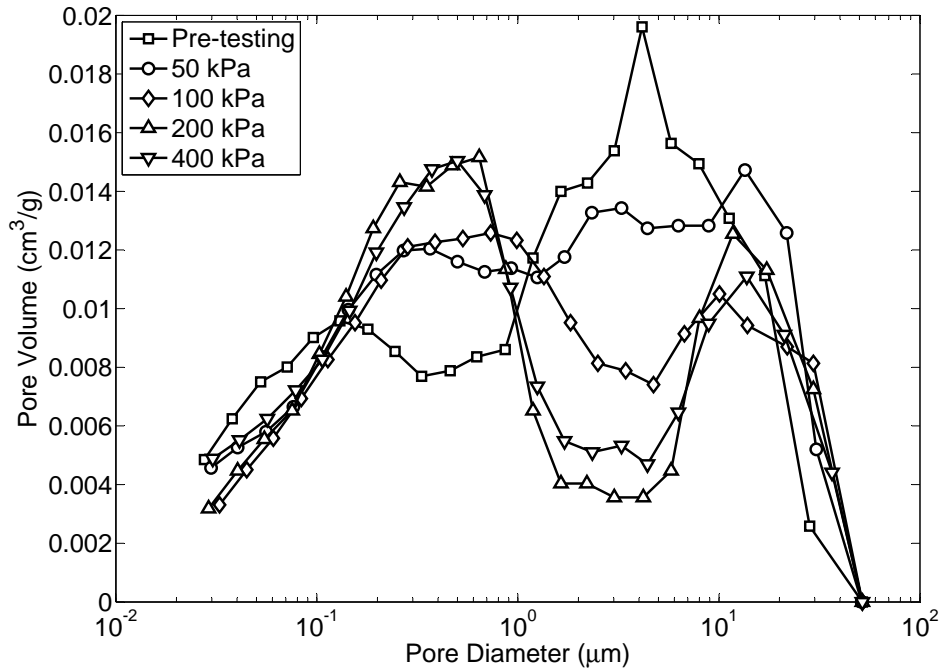


Fig. 24. PSDs for morainic sandy-loam soil after the application of suctions of 0, 50, 100, 200 and 400 kPa (Koliji et al. (2006) after Cuisinier and Laloui (2004))

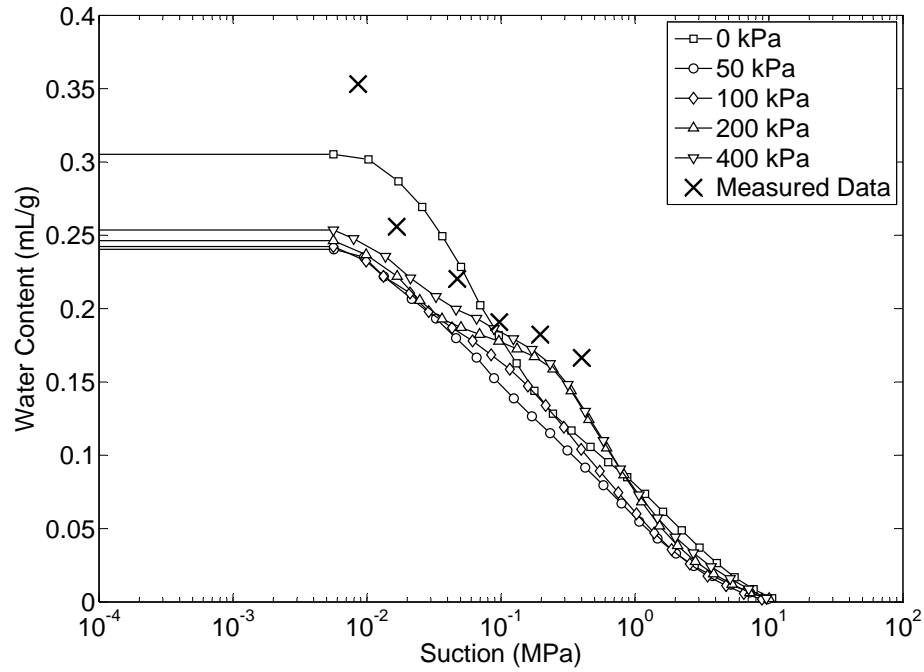


Fig. 25. Predicted SWRCs as compared to measured values (Cuisinier and Laloui, 2004)

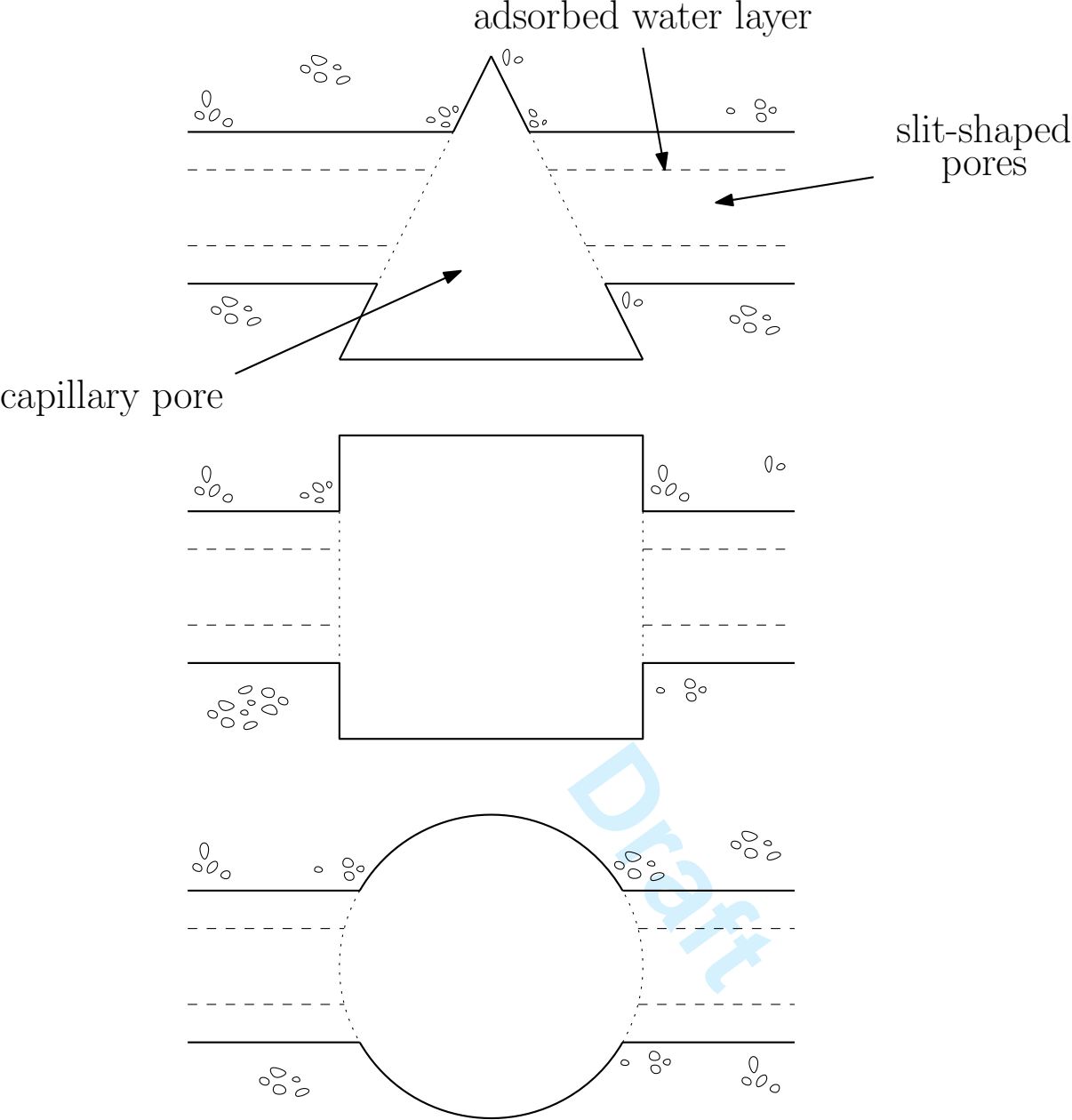
Table 1. Particle size values (Powrie, 2008)

Mineral Group	Particle Length (μm)	Particle Thickness (μm)	R (μm)	L (μm)	α
Silt and sand	2 to 2000	2 to 2000	1 to 1000	N/A	N/A
Kaolinite	0.1 to 4	0.05 to 2	N/A	0.1 to 4	0.5
Illite	0.1 to 4	≥ 0.003	N/A	0.1 to 4	0.01
Montmorillonite	1 to 2	0.001 to 0.02	N/A	0.1 to 4	0.002

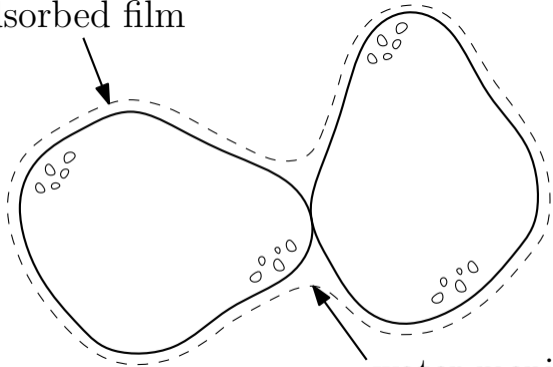
Draft

Table 2. Model input (n and θ_{slv}) and output values ($\frac{r}{R}$, $\frac{r}{D}$, r_{lim} and WC_{lim}) for predicted drying curves

Soil	n	θ_{slv}	$\frac{r}{R}$	$\frac{r}{D}$	r_{lim} (μm)	WC_{lim} (mL/g)	ψ_{lim} (MPa)
CL	0.50	0	0.40	1.42	0.40	0.0822	1.72
GW-GM	0.30	0	0.25	6.55	0.25	0.0150	2.28
ML	0.37	0	0.29	2.62	0.29	0.0594	2.12
SC	0.35	0	0.28	3.27	0.28	0.0452	2.15
SM	0.32	0	0.26	4.51	0.26	0.0325	2.15

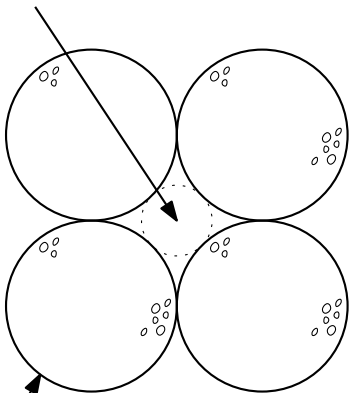


adsorbed film

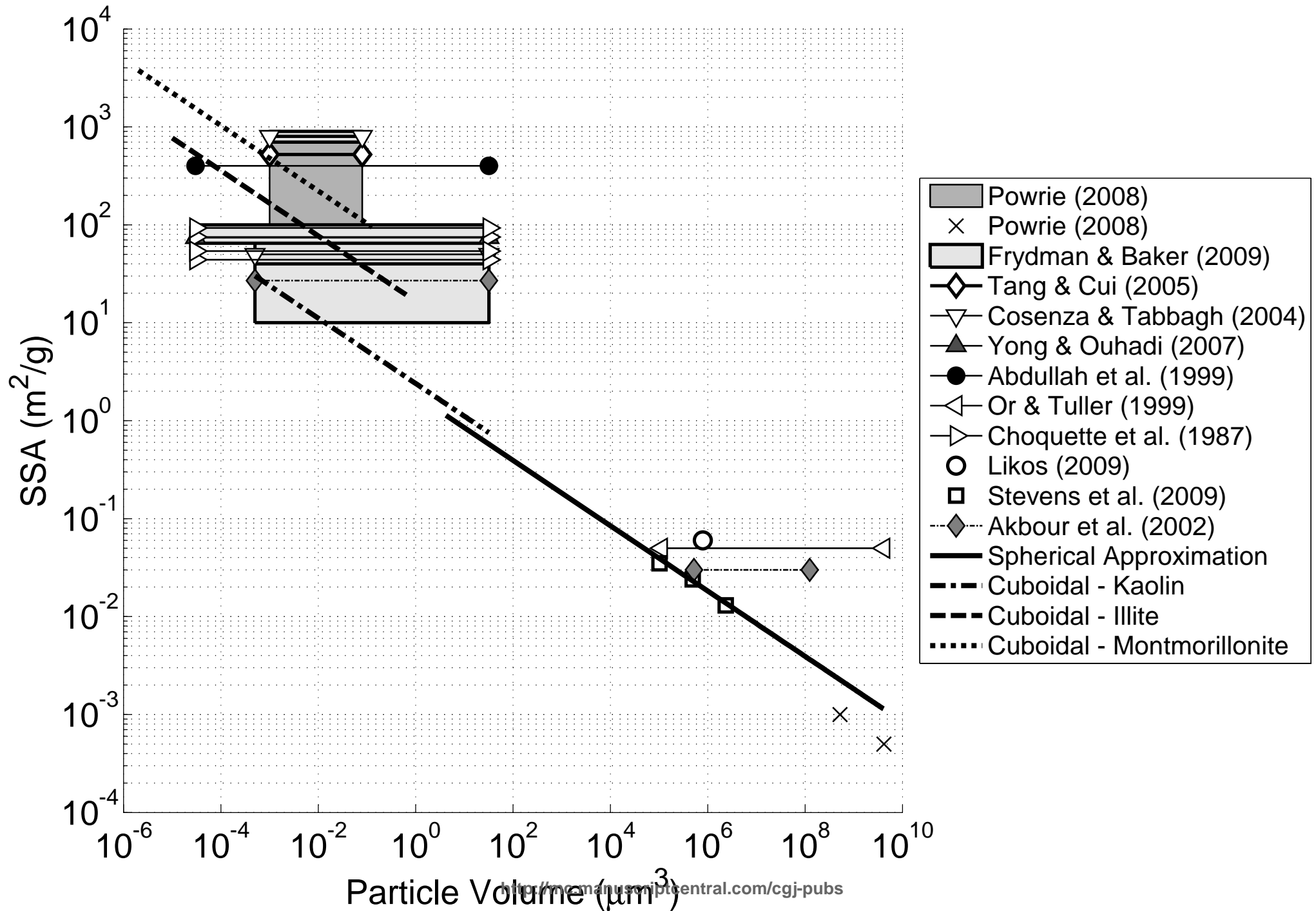


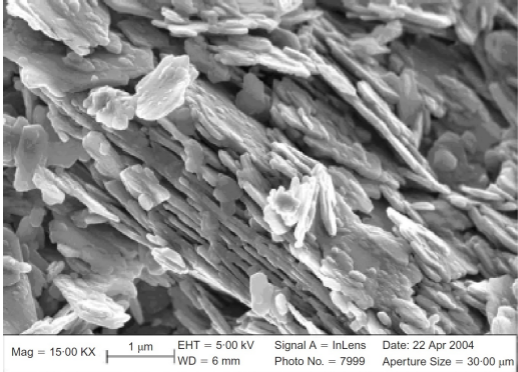
water meniscus

2-D interstitial site

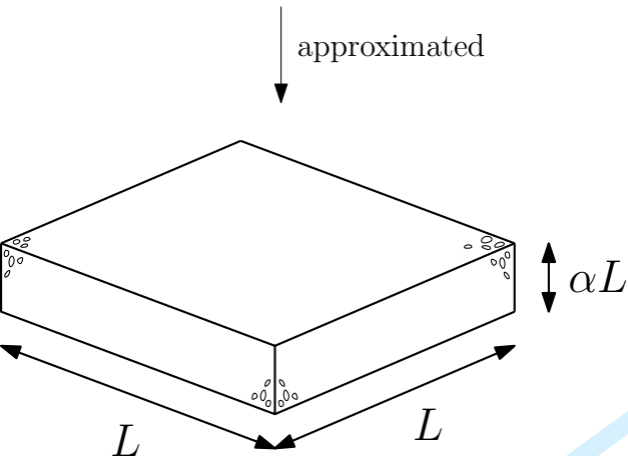


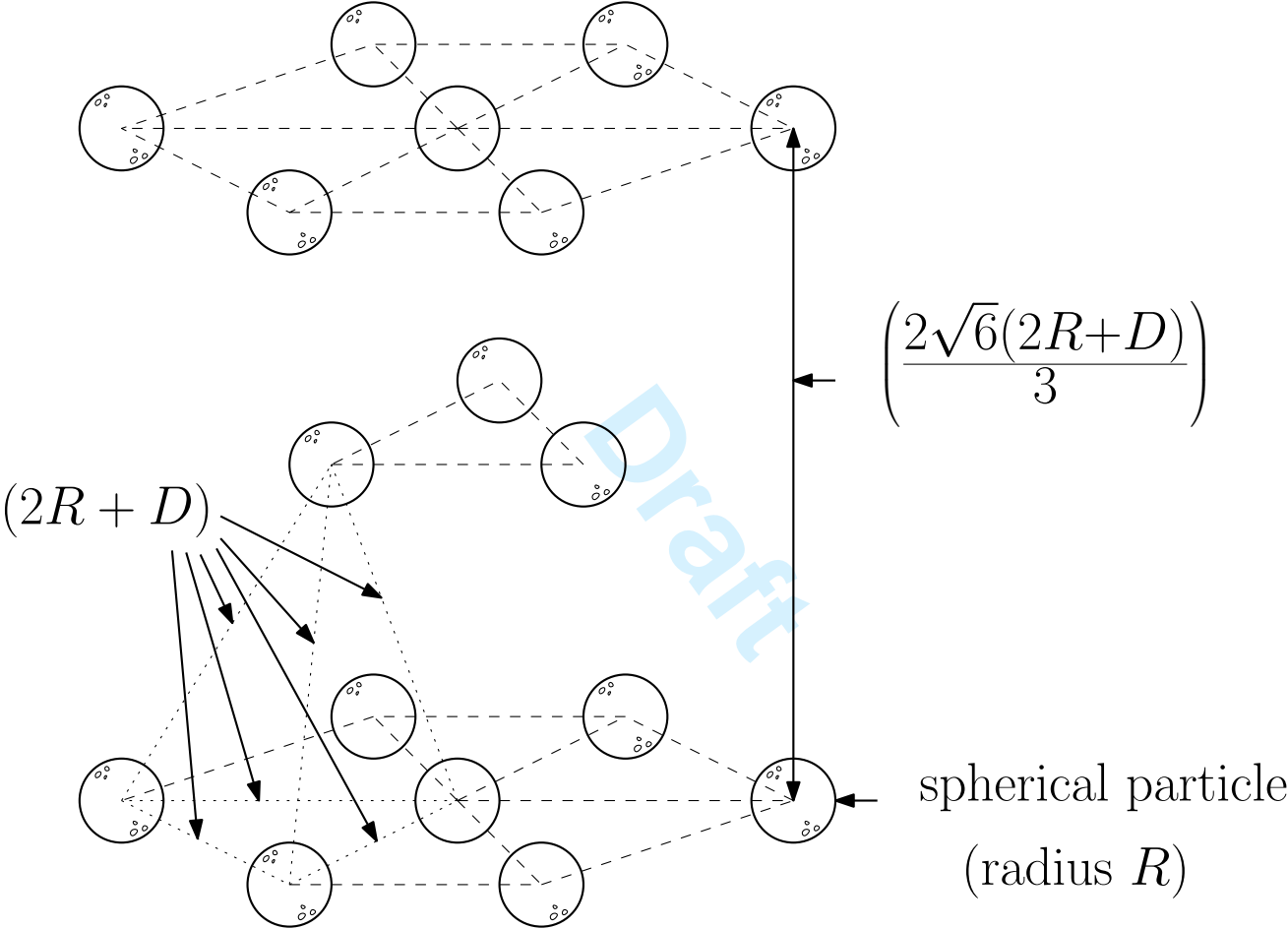
spherical particle

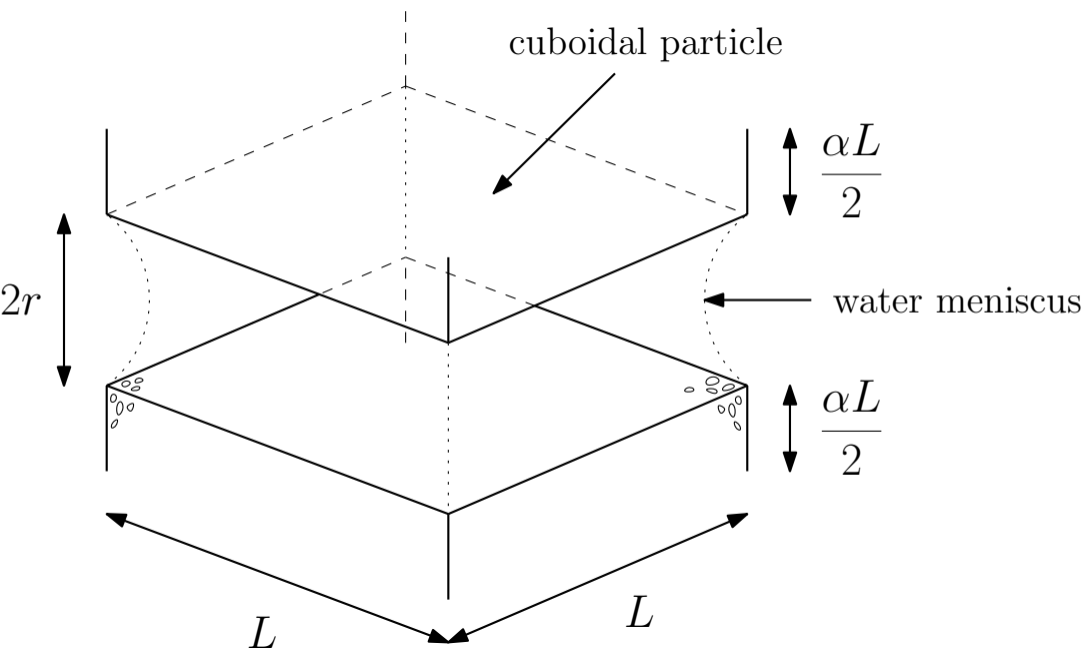


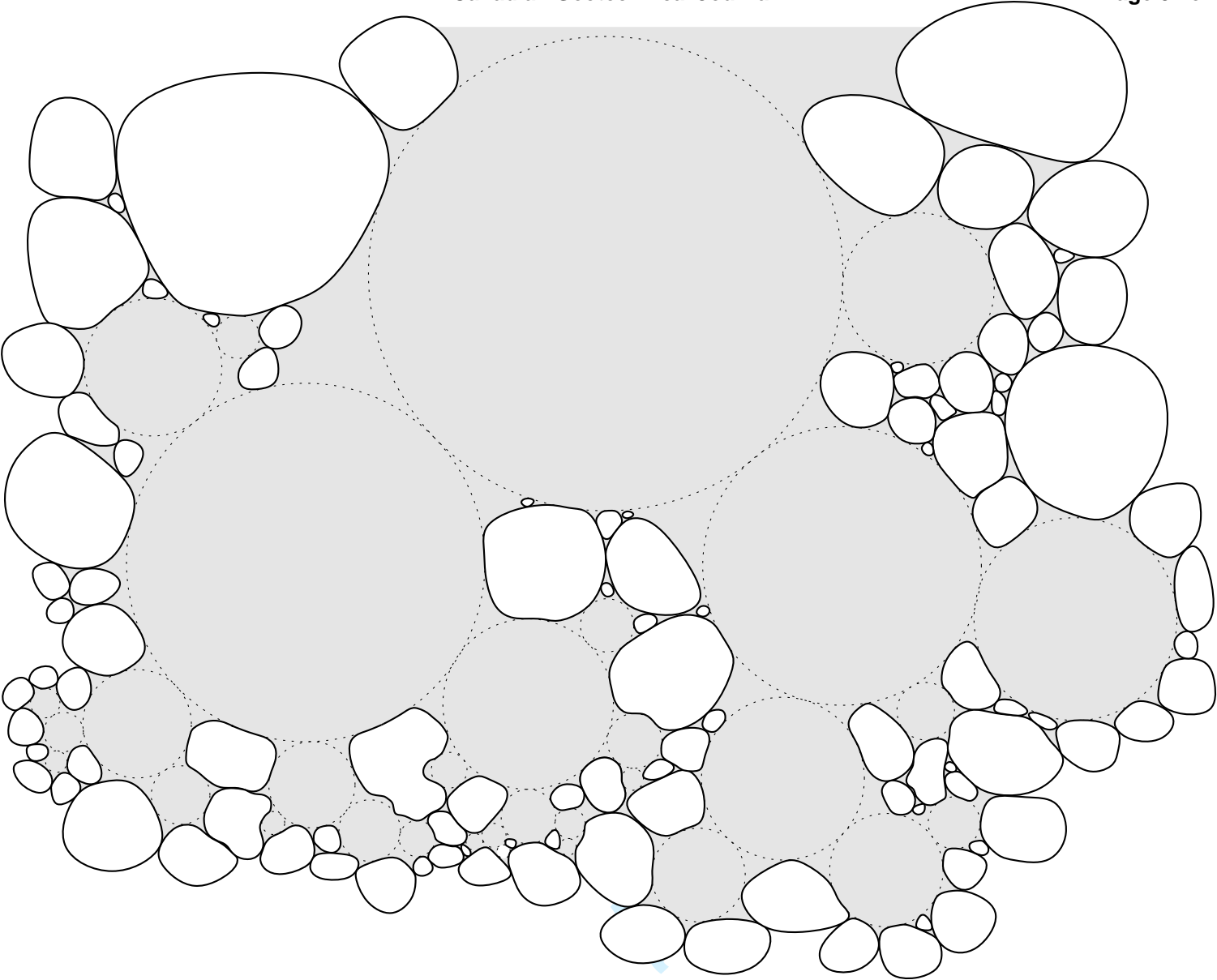


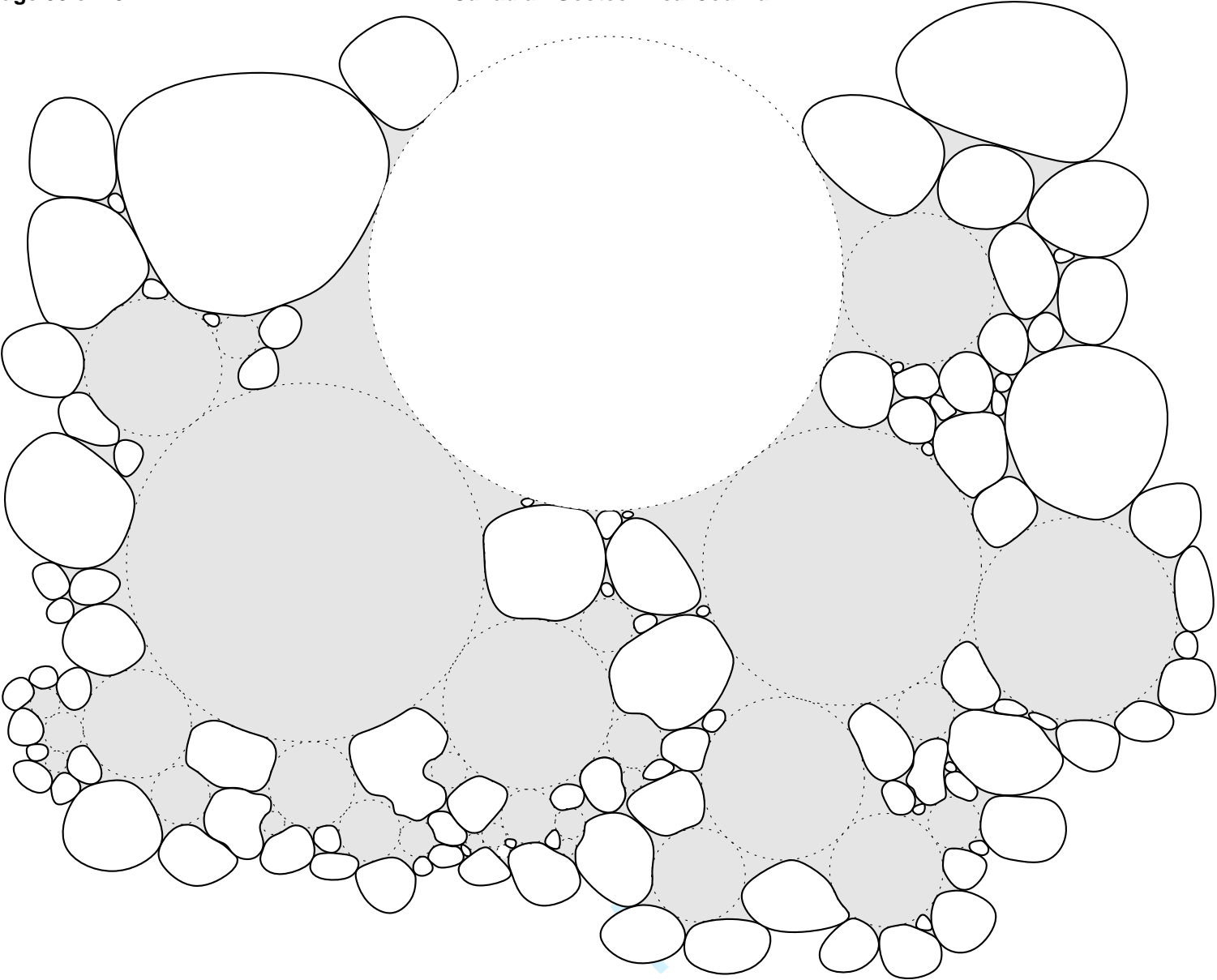
approximated

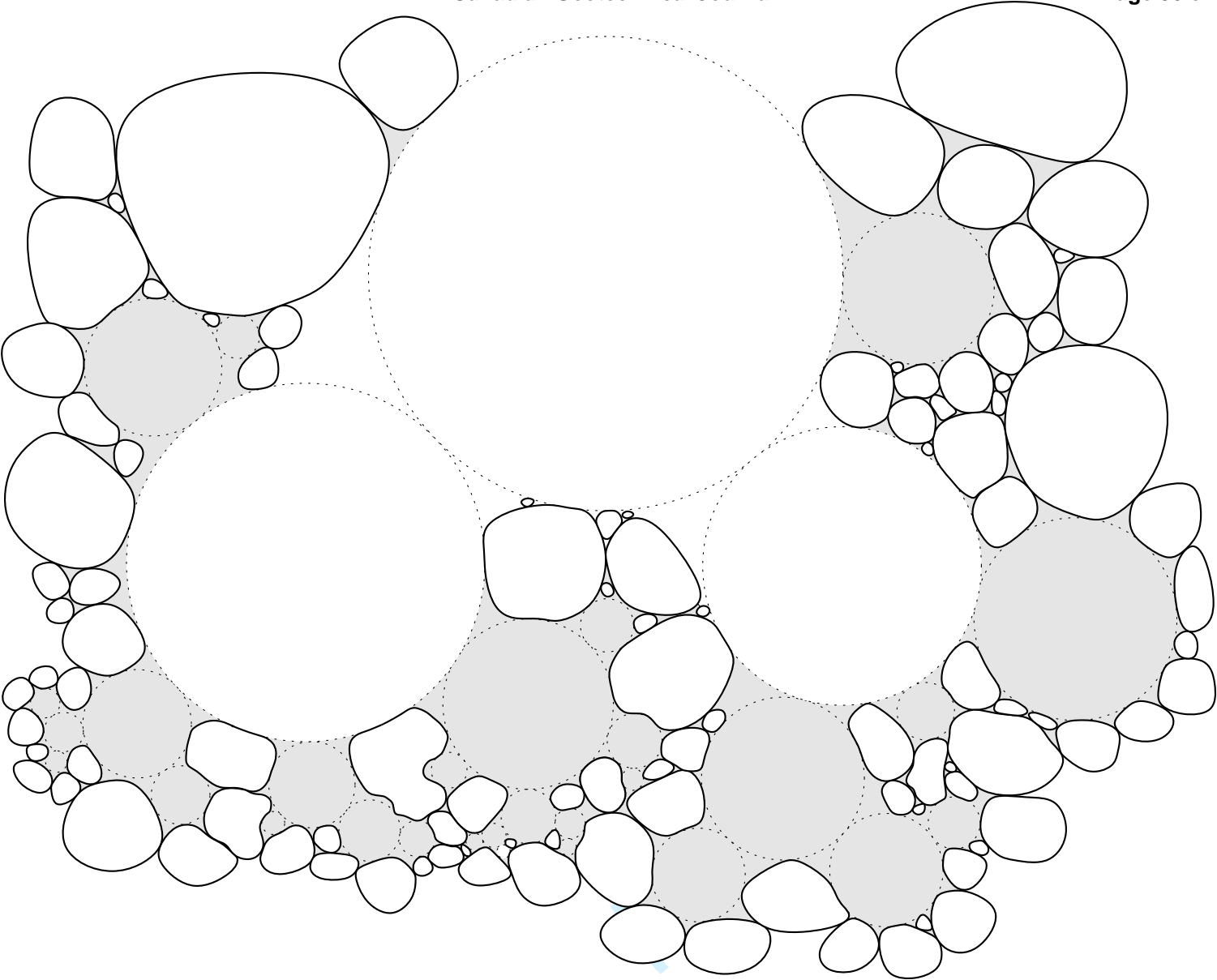


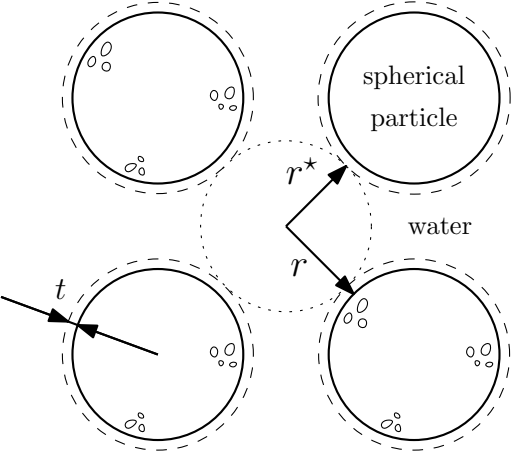


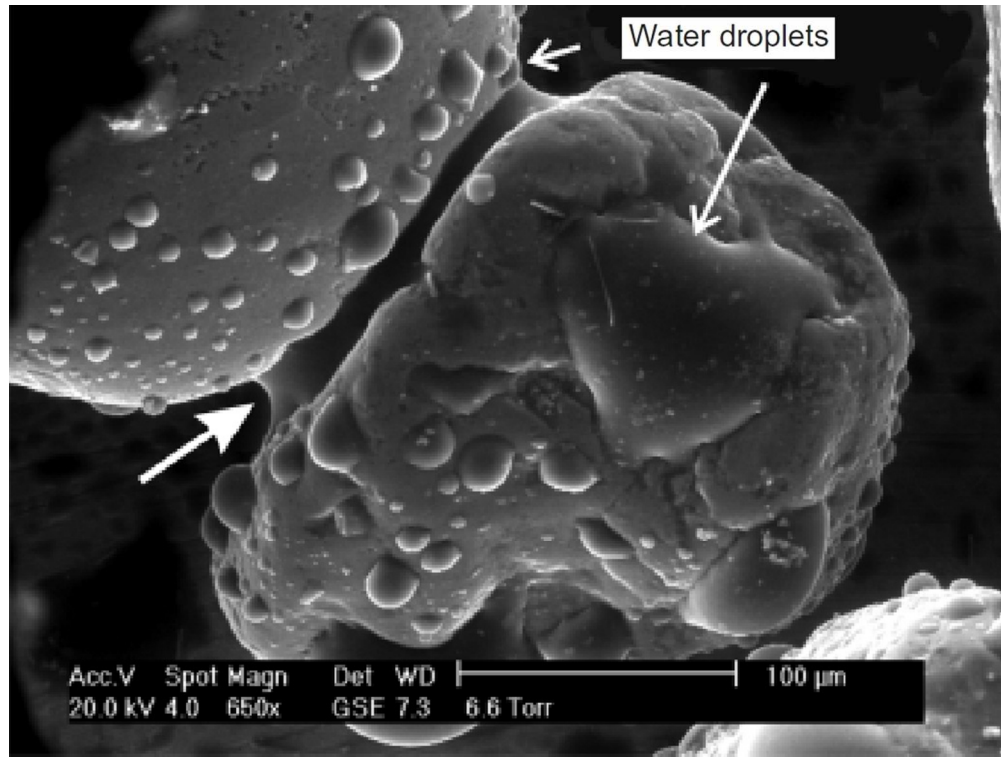




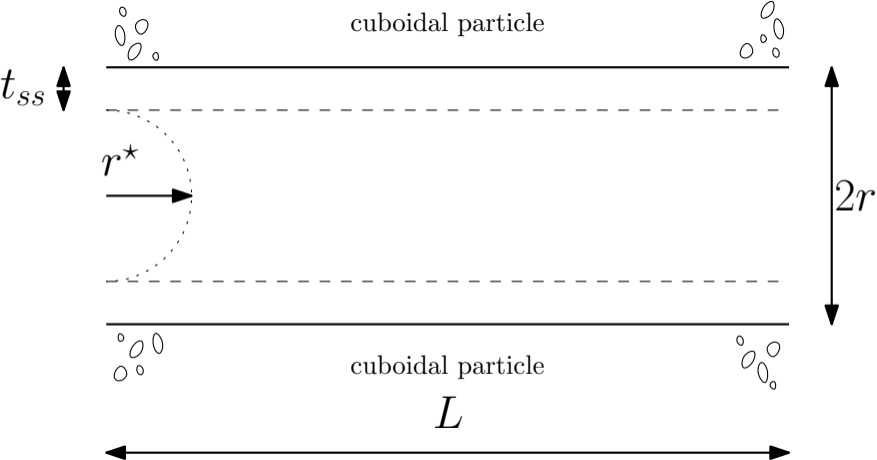


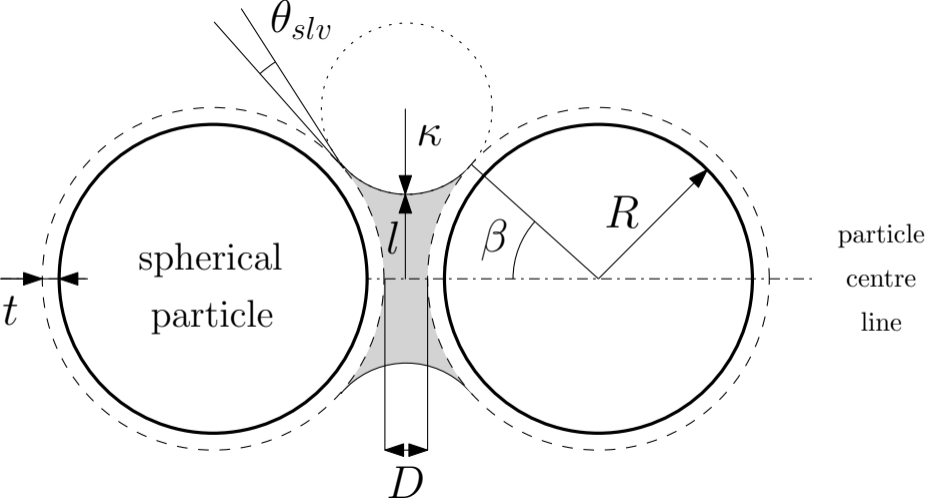


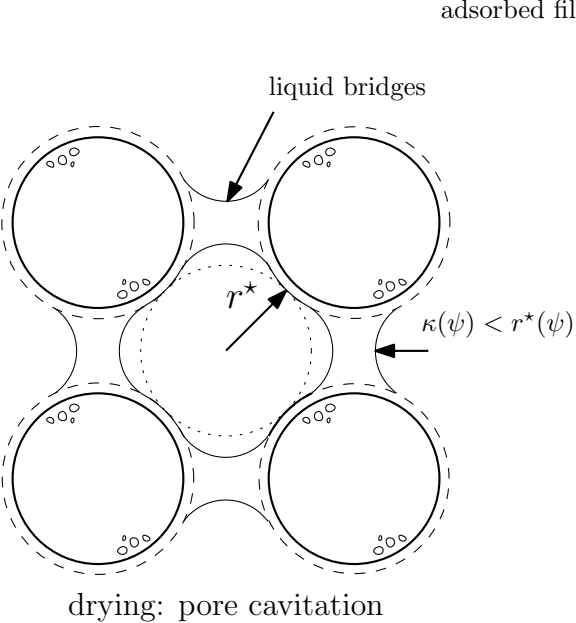




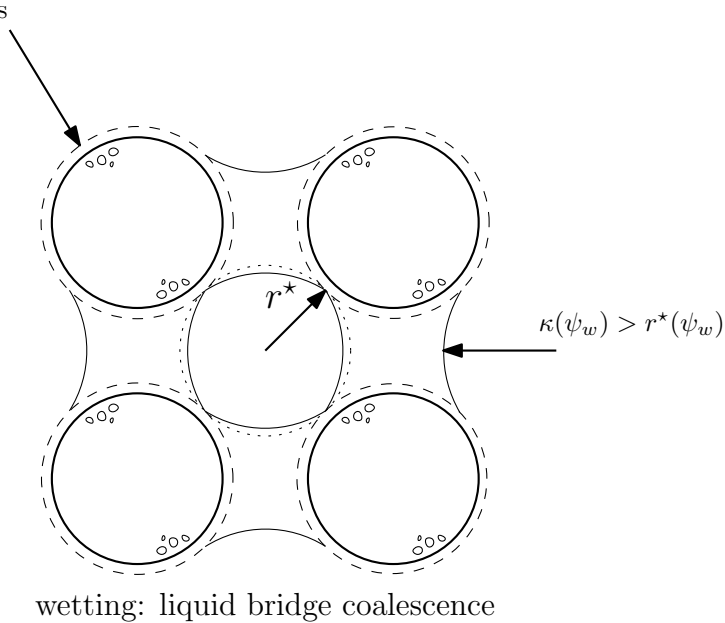
274x206mm (96 x 96 DPI)







(a)



(b)

