Capillary Processes in Porous Media
(An introduction to Soil Physics)

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Cargèse Summer School - 2018
Capillary processes in soil, the *vadose and critical zones*

- The **vadose zone** (also the *unsaturated zone*) is the subsurface domain extending between land surface and saturated groundwater (*vadosus* = shallow in Latin)

- Within the vadose zone, the **biosphere** meets the **atmosphere**, the **lithosphere** and the **hydrosphere** (life flourishes where solid-liquid- and gaseous phases coexist)

- Often, soil and the vadose zone are synonymous (in humid regions) – but not always (arid regions with deep water tables)

- The "critical zone" extends the vadose zone to consider exchange from the top plant canopies and often involves larger scales and soil formation time scales
Provisioning and regulating services by soil

- Soil provides anchoring and growth media for plants (food & fiber) supports >95% global biomass stocks (forests)
- Serves as water reservoir and functions as a water purification system
- Nature’s recycling system – supporting global biogeochemical cycles (C, N)
- Provides habitats to the largest number of species in the biosphere
- Used as building material and provides foundation for engineered systems

The economic value of soil services is estimated at $100 Trillion (10^{12}) per year exceeding annual global GNP of $72 Trillion (Costanza et al. 1997; Young 2006)
Soil Water Potential - *definitions and expressions*

- Liquid in porous media, or water in soil is subject to several forces, their combined effects define the potential energy state of liquid (water) relative to a reference state.

- **Total Soil Water Potential** $\psi_T$ is expressed as the sum of a few potential components (commonly present and affect soil water energy status):

$$\psi_T = \psi_z + \psi_m + \psi_p + \psi_s + \ldots$$

- Soil water potential energy can be expressed in terms of chemical potential $\mu$ (energy/mass), soil water potential $\psi$ (energy/volume), or soil water head $h$ (energy/weight).

*Definition* - The amount of work that an infinitesimal amount of water at equilibrium is capable of doing when it moves to a standard (reference) state.

These are linked via relations between volume, mass and weight (of water):

$$\mu = \frac{\psi}{\rho_w} = g \cdot h$$

<table>
<thead>
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<th>Units</th>
<th>Symbol</th>
<th>Name</th>
<th>Dimensions</th>
<th>SI Units</th>
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<td>Energy/Mass</td>
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<td>Chemical Potential</td>
<td>$L^2/t^2$</td>
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<td>Energy/Volume</td>
<td>$\psi$</td>
<td>Soil Water Potential Suction/</td>
<td>$M/(L^2t^2)$</td>
<td>N/m² (Pa)</td>
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<td>Tension</td>
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<tr>
<td>Energy/Weight</td>
<td>$h$</td>
<td>Soil Water Head</td>
<td>$L$</td>
<td>m</td>
</tr>
</tbody>
</table>
The matric (capillary) potential

$$\psi_T = \psi_z + \psi_m + \psi_p + \psi_s + ...$$

- The matric/capillary potential results from capillary phenomena and adsorptive forces between water and the soil solid matrix; the spontaneous solid-liquid interactions bind water and lower its potential energy relative to that of “free” water.

- $\psi_m$ ranges from zero for saturated soil to large negative values for dry soil (still expressed in terms of pressure!)
Factors affecting the *matric potential/capillary pressure*

- **Interfacial processes:**
  - Liquid-gas surface tension
  - Contact angle and surface wettability
  - Surface roughness

- **Geometrical factors:**
  - Curved interfaces and capillarity
  - Capillary rise
  - Capillarity in angular pores

- **More interfacial processes:**
  - Surface forces and liquid film adsorption
Surface tension

- Polar water molecules ($\delta^-$ near O; and $\delta^+$ near H) are mutually attracted and form short-lived hydrogen bonds (HB) with neighboring molecules in the liquid (a “flickering crystal”)

- At the liquid-gas interface, molecules are exposed to different forces than molecules within bulk liquid (4 HB in bulk but only 3 HB on average at the interface)

- The surface imbalance in HB formation makes it energetically unfavorable to bring new molecules to the interface, thus creating “skin-like” interface that tends to minimize its area and give rise to surface tension

Water surface acts like a membrane with tendency to contract to minimize its interfacial energy thus giving rise to surface tension
Surface tension is expressed as energy per unit area (or force per unit length) \( \text{J/m}^2 \) or \( \text{N/m} \).

There is a direct link between the surface tension of various liquids and their enthalpy of vaporization (latent heat of vaporization) – both phenomena must overcome intermolecular forces.

**Water at 20\(^\circ\)C = 0.0727 N/m**

**Ethyl Alcohol = 0.022 N/m**

**Mercury = 0.43 N/m**

<table>
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<tr>
<th>Liquid</th>
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<th>Surface tension (mN/m(^{-1}))</th>
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<td>20.14</td>
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<tr>
<td>Perfluoromethylcyclohexane</td>
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<td>Hydrogen sulfide</td>
<td>20</td>
<td>12.3</td>
</tr>
<tr>
<td>Perfluoropentane</td>
<td>20</td>
<td>9.89</td>
</tr>
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</table>

Direct measurement of surface tension

The Ring Method (du Noüy 1919)

\[ W_{\text{tot}} = W_{\text{ring}} + 4\pi R \sigma \]

- The method is simple and measures the detachment force (the surface tension multiplied by the periphery \(2 \times 2\pi R\))
- A platinum ring with torsion wire (force) are used
- Errors due to internal and planar curvatures require some modifications

Wilhelmy plate (1863)

\[ W_{\text{tot}} = W_{\text{plate}} + p \sigma \cos \theta \]

- \(p=2(l+b)\) is the perimeter of a thin slide (glass or platinum); for wettable surfaces no corrections are needed (the contact angle \(\theta\) is known)
Contact angle and wettablity

• When liquid is placed on a solid surface in the presence of gas, the interfaces between the three phases form a **contact angle** $\gamma$ measured between solid-liquid (S-L) interface and liquid-gas interfaces (L-G).

• For a liquid drop resting on a solid surface under equilibrium (e.g., when spreading stops), the sum of forces acting to spread the drop is equal to the opposing forces and the resulting force balance expressed by the **Young equation** (1805) for the contact angle:

$$\Delta E = \Delta A (\sigma_{SL} - \sigma_{GS}) + \Delta A \cos(\gamma) \sigma_{LG}$$

At equilibrium:

$$\frac{\Delta E}{\Delta A} = 0 = \sigma_{LG} \cos(\gamma) + \sigma_{SL} - \sigma_{GS}$$

$$\cos \gamma = \frac{\sigma_{GS} - \sigma_{SL}}{\sigma_{LG}}$$

$$\frac{dA_{LG}}{dA_{SL}} = \cos(\gamma)$$
**Contact angle and wettablity**

- When adhesion of a liquid drop to the solid surface is stronger than cohesion among neighboring liquid molecules - the resulting contact angle is small (< 90°) and the surface is said to be wettable (hydrophilic)

- When the cohesive forces dominate adhesion to the surface, the contact angle may become > 90° indicating the solid “repels” the liquid hence the designation nonwettable (hydrophobic)

\[ \gamma \]

\[ \gamma \text{ for water on glass is often taken as } 0^\circ \text{ (in practice it is in the range of } 20^\circ-30^\circ) \]

\[ \gamma \text{ for mercury on glass is } 148^\circ \]
Wettability - heterogeneous and rough surfaces

- The contact angle formed at equilibrium on flat and homogeneous surfaces, may exhibit a range of behaviors for inclined, chemically heterogeneous, and rough surfaces.

- For chemically heterogeneous surfaces made of patches with two contact angles $\gamma_a$ and $\gamma_b$ covering fractions $f$ and $1-f$, a drop may form an apparent contact angle ($\gamma_e$) given by the Cassie equation:

$$\cos(\gamma_e) = f \cos(\gamma_a) + (1 - f) \cos(\gamma_b)$$

- For rough surfaces where roughness ($r=A/A_{\text{smooth}}$) affects the solid–liquid and solid–vapor interfacial areas only, minimization of surface free energy results in an apparent contact angle expressed by the Wenzel equation:

$$\cos(\gamma_e) = r \cos(\gamma)$$

Cassie eq. for porous surface with porosity or entrapped air fraction $\phi$

$$\cos \gamma^* = \frac{(1-\phi)(\sigma_{GS} - \sigma_{SL}) + \phi\sigma_{LG}}{\sigma_{LG}}$$
Partial wettability – *Cassie* and *Wenzel* regimes

**Cassie’s regime with partially wettable sand grains**

Contact angle hysteresis and roughness

The pinning of a moving contact line on an edge; the Young condition stipulates that liquid form a contact angle $\theta$ with solid hence the angle may have any value between $\theta$ (flat surface) and $\pi - \phi + \theta$ (colored region)

**Superhydrophobic rough surfaces**

Exploiting wettability
Wettability of biological surfaces

- Plant surfaces exhibit a wide range of microstructures and variations in surface properties aimed at controlling wettability of these surfaces.

Progress in Materials Science 54 (2009) 137-178
Multifunctional surface structures of plants: An inspiration for biomimetics
The Young-Laplace equation links interfacial curvature to the pressure jump across the curved interface.

\[ \Delta P = \frac{2\sigma}{r} \]

Consider an air bubble of radius $r$ in water, the air pressure required to increase its volume by $dV$ is resisted by the surface tension with a force proportional to the increase in bubble surface area $dA$:

$$\Delta P dV = \sigma dA$$

$$\Delta P \left[ \frac{4\pi}{3} ([r + dr]^3 - r^3) \right] = 4\pi\sigma \left[ (r + dr)^2 - r^2 \right]$$

A simple force balance (neglecting terms of $dr^2$ and higher) yields the **Young-Laplace equation**:

$$\Delta P \frac{4}{3} \pi (3r^2 dr) = 4\pi\sigma (2rdr)$$

$$\Delta P = \frac{2\sigma}{r}$$

The **Young-Laplace eq.** links interfacial curvature to the pressure jump across curved interfaces (of any shape!)
Interface shapes and capillary pressures

- For pendular bridges between spherical particles (sand grains) the pressure difference (liquid-gas) is given as:

\[ \Delta P = \sigma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \]

A useful convention: interface curvature to liquid: \textit{-sign}; curvature towards air: \textit{+sign})

- For simple volume and force calculations the exact bridge shape with mean curvature: \( H = \frac{\Delta P}{\sigma} \) is approximated by an arc of a circle with radius \( R_2 \) (the \textit{toroidal approximation} of \textit{Fisher 1926}) – the exact axisymmetric shape is described by:

\[
\frac{1}{R_1} = \frac{1}{y(x)\sqrt{1+y'(x)^2}} \quad \frac{1}{R_2} = \frac{y''(x)}{(1+y'(x)^2)^{3/2}}
\]

\[
H \left(1+y'(x)^2\right)^{3/2} + \frac{1+y'(x)^2}{y(x)} - y''(x) = 0
\]
The challenge of perpetual capillary flow...

• “Some days ago a method was proposed to me by an ingenious friend, for making a perpetual motion, which seemed so plausible, and indeed so easily demonstrable from an observation by the late Mr. Hawksbee, said to be grounded upon experiment that, thou I am far from having any opinion of attempts of this nature, yet, I confess, I could not see why it should not succeed.

• “But as searches after things impossible in themselves are frequently observed to produce other discoveries unexpected by the inventor”

James Jurin (1684-1750)
The capillary rise model *(cylindrical capillary)*

Vertical force balance:  

\[ F_C = Mg \]

\[ 2\pi r \sigma \cos \gamma = \pi r^2 h \rho_w g \]

Upward force (capillary force)  

Downward force (weight of water)

Rise of water in a glass capillary:  

\[ h = \frac{2\sigma \cos \gamma}{\rho_w g R} \]

\[ h(m) \approx \frac{15}{R(\mu m)} \]
Models for capillarity in porous media

- Common conceptual models for capillary water retention in porous media rely on a simplified picture of soil pore space as a “bundle-of-capillaries”

- The key conceptual step is converting behavior in a complex pore to an equivalent (idealized) cylindrical capillary

- Capillary rise or “capillary forces” that determine the matric potential are higher in soils with smaller pores

Assuming mean pore radius \( r_p = \frac{d}{6} \) particle diameter

Sand, \( d = 0.5 \text{mm}, \ r_p \approx 80 \ \mu\text{m} \rightarrow h=190 \ \text{mm} \)

Silt, \( d = 0.025 \text{mm}, \ r_p \approx 4 \ \mu\text{m} \rightarrow h=3750 \ \text{mm} \)

Clay, \( d = 1 \mu\text{m}, \ r_p \approx 0.17 \ \mu\text{m} \rightarrow h=90 \ \text{m}! \)
Capillarity rise in angular pores

\[ h = \frac{2\sigma \cos \gamma}{\rho_w g r} \]

Why the focus on cylindrical capillaries?
The process of filling or emptying of angular pores involves abrupt interface reconfiguration at certain states (snap-off or snap-on).

These interfacial instabilities are important for residual phase entrapment (liquid retention, oil recovery), time scales of drainage, and many aspects of fluid displacement front physics.
Capillary interfaces in angular pores

- When angular pores drain, a fraction of wetting phase remains in pore corners resulting in ‘dual occupancy’ of water and air not possible in cylindrical tubes.

- Water filled area \( (A_w) \) at matric head \( h \) for polygons with \( n \) corners is the sum of water area in each corner behind an interface with curvature \( r(h) \):

\[
A_w = r(h)^2 F(\gamma) = \frac{\sigma^2}{(g \rho w h)^2} F(\gamma)
\]

- For pore cross-sectional area \( A_{\text{pore}} \) the value of saturation \( (S_w) \) is:

\[
S_w = \frac{r(h)^2 F(\gamma)}{A_{\text{pore}}}
\]

<table>
<thead>
<tr>
<th>Edges</th>
<th>Angle</th>
<th>Angularity Factor ( F_n )</th>
<th>Area factor ( A_n )</th>
<th>Pore Shapes</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n )</td>
<td>( \gamma )</td>
<td>( \sum_{i=1}^{n} \left( \frac{1}{\tan\left(\frac{\gamma_i}{2}\right)} - \frac{\pi(180 - \gamma_i)}{360} \right) )</td>
<td>( \frac{n}{4 \cot\left(\frac{\pi}{n}\right)} )</td>
<td>( )</td>
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<td>3</td>
<td>60°</td>
<td>( 3\sqrt{3} - \pi )</td>
<td>( \sqrt{3}/4 )</td>
<td>( \triangle )</td>
</tr>
<tr>
<td>4</td>
<td>90°</td>
<td>( 4 - \pi )</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>150°</td>
<td>( \frac{12}{2+\sqrt{3}} - \pi )</td>
<td>( 3\left(2+\sqrt{3}\right) )</td>
<td></td>
</tr>
</tbody>
</table>
Example – *saturation in (cross-section) triangular pore*

**•** Find the relative saturation at matric head of **-0.45 m** in a cross-section of an equilateral triangle pore of length **100 µm**?

1) The angularity factor $F(60^\circ) = 3\sqrt{3} - \pi = 2.054$

2) The interfacial curvature $r(\psi) = \sigma / (\psi)$ or $r(h) = \sigma / (\rho_w gh) = 16.3 \mu m$

\[ A_w = r(h)^2 F(\gamma) = \frac{\sigma^2}{(\rho_w gh)^2} F(\gamma) = 16.3^2 \times 2.054 = 547 \mu m^2 \]

**•** For pore cross-sectional area $A_{pore}$, the relative saturation ($S_w$) is simply:

\[ S_w = \frac{r(\psi)^2 F(\gamma)}{A_{pore}} = \frac{4 \times 547}{100^2 \sqrt{3}} = 0.126 \]

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<table>
<thead>
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<th>Area factor $A_n$</th>
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<td>$n$</td>
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<td>$\frac{\sqrt{3}}{4}$</td>
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Capillarity rise in angular pores (Bico and Quere 2002 JCIS)

- For wettable liquid entering a square capillary of sides $a$, we may balance capillary force:

$$F_c = p\sigma \cos(\theta)$$

$p$ is the perimeter ($4a$ for square tube), with gravity ($W$=weight of liquid):

$$W = \rho gh a^2 + 4 \rho g \int_0^h (1 - \pi/4) r^2(z) \, dz$$

- The resulting capillary rise height (w/corners)

$$h = \frac{(2 + \sqrt{\pi}) \sigma \cos(\theta)}{\rho ga} \approx \frac{3.77\sigma}{\rho ga}$$

the “finger” interface curvature $r(z)$ obeys:

$$r(z) = \frac{\sigma}{\rho g z}$$
Capillarity rise in angular pores \((Bico and Quere 2002 JCIS)\)

\[ h \approx \frac{4\sigma \cos(\theta)}{\rho ga} \quad (w/o \text{ fingers}) \]

**FIG. 3.** Height \(h\) of the central meniscus (defined in Fig. 2) in a square tube of inner size \(a\). The liquid used is cyclohexane, of surface tension \(\gamma = 25.5\) mN/m and density \(\rho = 820\) kg/m\(^3\). The straight line is a fit to Eq. [7].

\[ h = \frac{11.32\sigma}{\rho gb} \]

\[ h = \frac{4.49\sigma}{\rho gb} \]

**FIG. 5.** Height of the central meniscus inside an assembly of close-packed cylinders of radius \(b\). The lattice can be either triangular (maximum packing) or square, the corresponding data being respectively symbolized by triangles and squares. The full line is a fit to Eq. [11] and the dotted one Eq. [14].
Capillary rise dynamics – *rates and inertia*

- We have seen that equilibrium height of capillary rise is inversely proportional to pore radius, but how fast a meniscus rises in a capillary?

- The dynamics of capillary rise are discussed next - the sketch on the right depicts rapid capillary rise in sand relative to loam and clay – why is that?
Dynamics of capillary rise – **Washburn-Lucas equation**

- **Lucas (1918)** and **Washburn (1921)** independently proposed models for capillary rise dynamics, starting from simplified momentum balance in a cylindrical capillary (expressed as pressures):

\[
\frac{2\sigma \cos \theta}{R} = \rho gh \sin \psi + \frac{8\mu h}{R^2} \dot{h} + \rho \frac{d(h\dot{h})}{dt}.
\]

- Note that the “standard” capillary rise equation balances only first two terms in the force balance (capillary and gravitational forces – no dynamics!):

\[
F_g = \rho_w g r \pi r^2 = F_c = 2\pi r \sigma \cos \gamma \quad \Rightarrow \quad h = \frac{2\sigma \cos(\gamma)}{\rho_w g r}
\]

- **Lucas** and **Washburn** considered balancing capillary and viscous forces in absence of gravity (liquid length in a horizontal capillary is marked by \(x(t)\) – reserving \(h\) for cases w/ gravity)

\[
F_c = 2\pi r \sigma \cos(\gamma) = F_v = 8\pi \eta x \frac{dx}{dt}
\]

- Separation of variables and integration yields the **Washburn-Lucas** equation:

\[
x(t) = \sqrt{\frac{r \sigma \cos(\gamma)}{4\eta} t}
\]
Interface motion in short capillaries

- The forces and velocities governing interfacial flows into short capillaries (soil pores) are vastly different than the familiar equilibrium capillary rise.

- **Inertial forces** dominate interfacial motions in short capillaries of the order of pore throats.

- At early times:

  \[
  \frac{2\sigma \cos \theta}{\rho R} = \frac{d(h\dot{h})}{dt} = \dot{h}^2 + h\ddot{h}.
  \]

  \[
  h = t \sqrt{\frac{2\sigma \cos \theta}{\rho R}}.
  \]

  \[
  \nu \approx \sqrt{\frac{2\sigma \cos(\gamma)}{\rho r}}
  \]

  \(v=0.38 \text{ to } 3.8 \text{ m/s}
  \]

  \(r=1 \text{ mm to } 10 \text{ µm}
  \]

- (Fries and Dreyer, 2008, JCIS)
Observations in model porous medium (4 mm sintered glass beads) show details of drainage front motion and enable direct links between interfacial jumps and associated capillary pressure fluctuations (+ AE generation).

As mean flow rate increases multiple pores are invaded simultaneously resulting in complex and cooperative pressure fluctuations.

Inertial effects are evident by the oscillating interfaces.
Not all is quiet at displacement fronts...

- The motion of imbibition and drainage fluid fronts are common in many porous media applications (hydrology, petroleum, building materials, paper)

- **Advance of a front** - the seemingly smooth macroscopic motion of a front is a result of numerous pore scale rapid interfacial jumps and pressure bursts

- This pore scale picture challenges the continuum Buckingham-Darcy representation of fluid front motions (and postulated dissipation mechanisms)

- **Passage of a front** – rapid interfacial processes (**Haines jumps**) have been linked to residual phase entrapment and macroscopic transport properties; and proposed as potential mechanisms for **hysteresis** and **dynamic capillary pressure** - yet these are often dismissed as “peculiarities”
The macro (front) and micro (pore) velocities exhibit radically different behaviors.

- Front motion is composed of numerous local *interfacial jumps* at significantly higher velocities than mean front speed \( \rightarrow \) **inertial regime**

- Pore jump velocity is only slightly affected by the macroscopic front velocity

**(Moebius and Or, JCIS 2012)**

**(Moebius and Or, PRE 2014)**
Modeling interfacial front motion – *pore throat network*

\[ 0 = \sum_n \frac{r_i^2}{8\eta} \cdot \frac{A_{i,n}}{d_{i,n}} \cdot \{p_n - p_i + p_{hn} - p_{hi}\} - \sum_j \frac{dh_{ij}}{dt} \cdot \pi r_i^2 (h_{ij})^2 - \frac{Q}{N} \]

volume exchange between nodes and in throats - global flow rate

with the pressure \( p_i \) at node \( i \)

\[ p_i = -\frac{2\sigma \cos \theta}{r(h_{ij})} + \rho g \cdot (\pm \sin(\frac{\pi}{4}) h_{ij}) + \frac{8\eta}{r_{eff}^2} h_{ij} \frac{dh_{ij}}{dt} + \rho \left( h_{ij} \frac{d^2 h_{ij}}{dt^2} + \left( \frac{dh_{ij}}{dt} \right)^2 \right) \]

capillary \hspace{1cm} \text{hydrostatic} \hspace{1cm} \text{viscous inertial term}

\[ \downarrow \text{ air invading } \]

\[ \downarrow \text{ water withdrawn } \]

(Moebius and Or, PRE 2014)
- Inertia broadens distribution of interfacial jump velocities (slower & faster jumps)
- Consideration of inertial forces modifies throat invasion sequence (smaller throats may be invaded with inertia)
- Surprisingly, inertia exerted a negligible effect on liquid phase entrapment

*(Moebius and Or, PRE 2014)*
Inertial effects – *minor influence on total phase entrapment*

- Surprisingly, inertia had a negligible effect on total liquid phase entrapment.
- Consideration of inertial forces modified throat invasion sequence - smaller throats may be invaded and the resulting phase entrapment pattern is modified.
The soil water characteristic curve \textit{(back to hydrostatics)}

- The soil water characteristics (\textit{SWC}) or water retention curve (WRC) describes the functional relationships between soil water content (\(\theta_v\) or \(\theta_m\)) and the (capillary) matric potential under equilibrium.

- The SWC is related to pore space distribution (sizes, connectivity), and is strongly affected by texture, structure and other factors including organic matter.

- The SWC is an important hydraulic property required for modeling water flow in unsaturated soils and other porous media.

- The SWC function is highly nonlinear and relatively difficult to obtain accurately.
• The parameters of BC and VG models are linked to features of the SWC
The idealization of soil pores as a bundle of capillaries provides a link between the (experimentally determined) SWC shape and idealized soil pore size distribution based on capillary rise (how much pressure must be applied to drain a “capillary” of a of certain size? How will saturation vary?)

\[ h_i = \frac{2 \sigma \cos \gamma}{\rho_w g r_i} \]

\[ A_i = r_i^2 \pi n_i \]
Conceptual steps in estimating $K(h)$ from SWC

1. Extraction of radii distribution of capillary radii of the BCC (from SWC)

2. Hydrodynamics: the volumetric discharge in full cylindrical tubes according to Poiseuille’s law ($Q \propto r^4$)

3. Integration of surviving (full) tubes at a potential; performed analytically (closed-form models) or numerically

\[ Q = \frac{\pi r^4}{8 \eta_0} \left( \frac{\Delta P}{L} \right) \]

\[ n_i = \frac{\Delta \theta_i r_i^2}{\pi \Delta} \]

\[ \bar{r}_i = -\frac{2\sigma}{\rho g \mu} \]

\[ \Delta \theta_i \]

\[ \mu_i \]

\[ \text{Water Content} - \theta - [m^3 m^{-3}] \]

\[ \text{Matric potential} \mu - [m] \]

[van Genuchten, 1980]

[Mualem, 1976]

Figure 25. Serial type model.

[van Genuchten, 1980]
Adsorption and capillarity in soils

• Another complication to the “cylindrical capillary” picture of water retention in soil is the role of adsorptive surface forces (van der Waals forces, water held by electrical forces associated with DDL, and more)

• Generally, soil water is held within the soil complex geometry by capillary and by adsorptive surface forces

• Due to practical limitations of present measurement methods no distinction is made between adsorptive and capillary forces - all contributions are lumped into the matric potential (capillary pressure...)
Adsorption and capillarity: decomposing the SWC

- Considering *van der Waals* forces only, thin liquid films (<100 nm) form under equilibrium in which the thickness of flat adsorbed water film \( h \) as a function of matric potential is:

\[
h = \frac{3 A_{svl}}{6\pi g \rho_w \psi}
\]

- For known specific surface area (SA) we may decompose a SWC curve into capillary and adsorptive contributions:
  - Dominance of capillarity near saturation
  - Adsorption dominates at SWC dry end
- Consequently, the soil specific surface area is expected to control water retention at the SWC dry end

\( A_{svl} \) ... Hamaker Constant [J] \( \sim 10^{-20} \) J

\( g \) ... Acceleration of Gravity [m/s²]

\( \rho_w \) ... Density of Water [kg/m³]

\( \psi \) ... Matric Potential [m]
Dry-end of SWC scales with surface area (SA)

- Expressing the “dry end” of SWC in terms of thickness of adsorbed water film (i.e., scaling by soil specific surface area) shows remarkable similarity among many soils.

- The scaling behavior is in good agreement with theoretical predictions based on van der Waals adsorption isotherm [Iwamatsu and Horii, 1996]

\[
h = \frac{\theta_m}{SA \cdot \rho_w}
\]

Adsorption isotherm

\[
h = 3 \sqrt[3]{\frac{A_{svl}}{6\pi g \rho_w \psi}}
\]
The “inverse problem” – surface area from SWC?

Advanced psychrometric methods (e.g., Decagon WP4) allow fast and reliable measurement of matric potential at low water contents (the dry end of SWC).

Promising results for a wide range of soil textures

<table>
<thead>
<tr>
<th>Soil</th>
<th>Surface Area in m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Determined - WP4</td>
</tr>
<tr>
<td>Ca⁺ Montmorillonite</td>
<td>690</td>
</tr>
<tr>
<td>Palouse B</td>
<td>170</td>
</tr>
<tr>
<td>Salkum</td>
<td>99</td>
</tr>
<tr>
<td>Walla Walla</td>
<td>70</td>
</tr>
<tr>
<td>Royal</td>
<td>52</td>
</tr>
<tr>
<td>L-Soil</td>
<td>21</td>
</tr>
</tbody>
</table>
Capillarity and (unsaturated) porous media mechanics

- Capillary forces exerted by liquid bridges impart strength onto assemblies of granular media affecting the mechanics of unsaturated soils (soil strength, aggregates, sand castles)
- The force exerted by a liquid bridge at the contact between equal size spheres of radius $R$

\[
F_{\text{Cap}} = 2\pi R\sigma \sin \phi \sin(\phi + \theta) - \Delta P \cdot \pi R^2 \sin^2 \phi
\]

- For soft aggregates, capillary forces deform and “sinter” contacts (wet-dry cycles)

(Ghezzehei and Or, WRR 2000)
Summary – Capillary processes in porous media

- Fundamentals of surface tension and liquid-solid interfacial interactions
- Wettability on surfaces with different chemical and geometrical properties (Cassie and Wenzel regimes)
- Aspects of capillarity in angular pores (multiphase occupancy and snap-off)
- Capillary rise in angular pores – simple to derive
- Dynamics of capillary rise - Washburn-Lucas equation and inertial regimes
- The role of inertia in pore invasion
- Pore size distribution from SWC
- Adsorption processes at the SWC dry end – decomposing SWC and soil SA
- Capillary forces and unsaturated soil mechanics
Extra Slides
• Fries, N. and M. Dreyer (2008) The transition from inertial to viscous flow in capillary rise , J. Colloid Interface Sci. 327, 125
Capillary evacuation and air entry

- The largest continuous pore within the pore size distribution defines the first pore to drain
- The pressure required to drain the largest pore in a sample is called *bubbling pressure* or *air entry value* marking onset of air invading a saturated soil
- This is the elevated air pressure at the atmospheric side necessary to offset the negative pressure at the liquid side of the meniscus formed in the largest pore
- The *bubbling pressure* is important for designing porous materials that must remain saturated to a specific pressure (e.g., tensiometer porous cups)
- Emptying of more complex sequence of capillaries and pore throats is illustrated in the figure

\[ \rho_w g h^* = \frac{2 \sigma \cos \gamma}{r^*} \]

Fig. 4. Cylindrical pores with radii \( r_L \) and \( r_S \); the larger pore has a constriction with radius \( r'_L \). (a) when radius of meniscus equals \( r_L - \delta \), large pore drains down to constriction; (b) meniscus passes restriction only when \( |r_m| = r'_L - \delta \); (c) if \( r'_L - \delta < r_S - \delta \), the small pore drains while the large pore remains partially full.
Air entry – *the two menisci problem*... (Chatterjee, 2008)

- For design of pressure plate and other capillary barriers one must consider displacement of two menisci.
- The force balance for a liquid column of length $h$ is:

$$\frac{2\sigma \cos(\theta_T)}{R} = \rho gh + \frac{2\sigma \cos(\theta_B)}{R}$$

- Application of air pressure $P_a = \rho gh_a$ would modify the shape of the menisci according to (bottom now assists top meniscus):

$$\rho g (h + h_a) = \frac{2\sigma (\cos(\theta_T) + \cos(180 - \theta_B))}{R}$$

- Defining $\beta = \cos(\theta_T) + \cos(180 - \theta_B)$
- Experiments with water and glass capillaries yield $\beta = 1.63$ (with $\theta_T \sim 100^0$ and $\theta_B \sim 130^0$ at bubbling)
- We thus need to apply a factor of 1.63 to correct for the second meniscus in estimation of critical pressure or pore radius.
Liquid retention in angular pores

- An important aspect of imbibition and drainage in angular pores (in addition to unstable states) is dual phase occupancy not present in cylindrical geometry
- Pores with higher angularity $F(\gamma)$ retain more liquid at a given potential than those with low angularity (obtuse angles or higher polygons)
- At a critical potential, liquid spontaneously fills up a pore (snap-off) at an interfacial radius of inscribed circle in the pore cross-section (different than invasion by NW phase)

\[ r_{\text{imb}} = \frac{2 \cdot A}{P} = \frac{P}{4[F(\gamma) + \pi]} \]

\[ r_d = \frac{P}{2 \cdot [(F(\gamma) + \pi) + \sqrt{\pi \cdot (F(\gamma) + \pi)}]} \]
Shrink-swell affects soil pores at all scales

Microscale (clay fabric)

Mesoscale (texture)

Macroscale (cracks)
Clay shrink/swell damage to structures & roads

- Changes in soil water content or solution chemistry of clayey soils induce swelling pressures sufficiently large to fracture and damage structures & roads
- Estimated damage in excess of $7 billion/yr in the US
Simplest interfacial front model – **two connected capillaries**

- A pair of hydraulically connected capillaries representing neighboring pores
- Considering capillary, hydrostatic, viscous, and **inertial** forces

\[ -\frac{2\sigma}{r_1(h_1)} \cos(\theta) + \frac{8\eta}{r_v^2} h_1 \dot{h}_1 + \rho(h_1 \ddot{h}_1 + \dot{h}_1^2) + \rho g h_1 \]

\[ = -\frac{2\sigma}{r_2(h_2)} \cos(\theta) + \frac{8\eta}{r_v^2} h_2 \dot{h}_2 + \rho(h_2 \ddot{h}_2 + \dot{h}_2^2) + \rho g h_2 \]

- **Force balance**
  - Capillary term
  - Viscous term
  - Inertial term
  - Gravitational term

\[ Q = \pi r_1^2 (h_1)^2 \dot{h}_1 + \pi r_2^2 (h_2)^2 \dot{h}_2 \]

(Moebius and Or, 2012 JCIS)
The pair of hydraulically-connected (sinusoidal) capillaries reproduces characteristics of observed dynamic interfacial jumps.

Extension to pore throat network → next
Dynamics of capillary rise with gravity

- Gravity could be introduced to the force balance (capillary pull is balanced by viscous and gravity forces):

\[ 2\pi r\sigma \cos(\gamma) = 8\pi \eta h \frac{dh}{dt} + \rho_w gh \pi r^2 \]

- A simplifying transformation reduces the differential equation to the form:

\[
\frac{dh}{dt} = \frac{a}{h} - b
\]

with:

\[
\frac{a}{4\eta} = \frac{r\sigma \cos(\gamma)}{4\eta}, \quad \frac{b}{8\eta} = \frac{\rho gr^2}{8\eta}
\]

- The implicit analytic solution with gravity of Washburn(1921):

\[
t = -\frac{h}{b} - \frac{a}{b^2} \ln \left( 1 - \frac{bh}{a} \right)
\]

- This has recently been transformed to an explicit solution $h(t)$, is given (using the $W(x)$ function also known as ProductLog) as:

\[
h(t) = \frac{a}{b} \left[ 1 + W(-e^{-1-\frac{b^2t}{a}}) \right]
\]


An analytic solution of capillary rise restrained by gravity

N. Fries, M. Dreyer
Dynamics of capillary rise with gravity

- The implicit solution with gravity of Washburn (1921) was recently transformed to an explicit solution $h(t)$, is given (using the $W(x)$ function also known as ProductLog or Lambert W function) as:

$$h(t) = \frac{a}{b} \left[ 1 + W\left( -e^{-1} \frac{b^2 t}{a} \right) \right], \quad x = W(x) e^{W(x)}$$
The number of capillaries with radius $R_j$ per unit area at each water content interval is: $n_j = \frac{\Delta \theta_v}{pR_j^2}$ (where $\Delta \theta_v$ is interpreted as the fraction of water-filled cross sectional area reduced when all capillaries of radius of $R_j$ drain)

SWC is linked with pore size distribution
Linking SWC and soil pore size distribution

\[ \frac{d\theta}{dh} = C_w(\theta) = \frac{(\theta_s - \theta_r)(n-1)\alpha^n h^{n-1}}{[1+(\alpha h)^n]^{2-1/n}} \]

where

- \( \frac{2\sigma}{h} \) is a parameter related to the pore size distribution.
- \( \theta_s \) and \( \theta_r \) are the saturation and residual water content, respectively.
- \( n \) is a shape parameter.
- \( \alpha \) is a proportionality constant.
- \( h \) is the head (m).
Fixed volume liquid bridge – *force/distance relations*

- Measurements of force-distance

\[
F_{\text{cap}} = 2\pi \cdot \sigma \cdot R \cdot \frac{\cos(\theta + \beta) + \cos(\theta)}{2} \cdot \left(1 - \frac{D}{\sqrt{\frac{V}{\pi \cdot R} + D^2}}\right)
\]

- The critical rupture distance is a function of liquid volume, radius and contact angle

\[
D_{\text{rupt}} = \sqrt[3]{\frac{V}{R^2}} \left(1 + \frac{\theta}{2}\right)
\]

- \(D = \text{distance between spheres}\)
- \(V = \text{liquid bridge volume}\)
- \(\theta = \text{effective contact angle}\)
- \(\beta = \text{half filling angle}\)
- \(\sigma = \text{surface tension}\)
- \(R = \text{sphere radius}\)
Variable bridge volume - fixed distance *(evaporation)*

\[ V = \pi \frac{R}{2} \left[ 4r^2 \left( \frac{\cos(\theta + \beta) + \cos(\theta)}{2} \right)^2 - D^2 \right] \]

- "Corrected" force measurements with constant filling angle of 40°
Liquid bridges during shearing of granular media

- Contrary to “conventional wisdom” (pore volume expansion with dilation attract more liquid), the shearing of unsaturated granular media depletes the shear zone...

\[ D_{\text{rupt}} = \sqrt[3]{V} \left( 1 + \frac{\theta}{2} \right) \]
Outlook - *Capillary processes in porous media*

- Energy state of water in porous media – the water potential
- Water-solid properties (surface tension, wettability, capillarity)
- Wetting of rough and heterogeneous surfaces
- Capillarity in angular pores
- Dynamics of capillary rise
- The role of inertia in capillary processes (oscillations and Haines jumps)
- Linking pore size distribution and capillary water retention
- Adsorption and water films
- Capillary forces and liquid bridges – rupture distance and force
- Summary
Ecological functions of soil (top layer of the vadose zone)

- Soil is the most biologically active compartment of the biosphere hosting the largest pool of biodiversity

- Soil is a giant recycling and water filtration system; it provides most of our needs for food, feed, fiber and wood, and supports most stocks of global biomass

- **Earth life support system** - soil functions as Earth's life support body, a thin film of life covering much of terrestrial surfaces

- **A natural body** - soil is a functioning complex natural body with unique characteristics that cannot be deduced from a collection of its constituents or individual processes
Specific SA determination from measured SWC data

- SWC “dry-end” is dominated by adsorbed vDW water films, reflects dominance of specific surface area

- A wide range of soil textures shows consistent scaling based on soil SA leading to “universal” SWC slope

\[
\frac{d\theta}{d\psi} = -\frac{1}{3} \sqrt[3]{\frac{A_{svl}}{6\pi \rho_w g}} \cdot SA \cdot \rho_w \cdot \psi^{-\frac{4}{3}}
\]

\[
\frac{d\theta}{d\psi} = -C \cdot SA \cdot \psi^{-\frac{4}{3}}
\]

- Capillary condensation within roughness or nanopores may affect SWC slope

\[\text{Table 2. Comparison of Specific Surface Area Measurements Obtained With a Psychrometric Method and EGME Adsorption}^a\]

<table>
<thead>
<tr>
<th>Soil Series</th>
<th>Psychrometric Surface Area, m²/g</th>
<th>EGME Surface Area, m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-soil</td>
<td>24 (26)</td>
<td>25</td>
</tr>
<tr>
<td>Royal</td>
<td>58 (63)</td>
<td>45</td>
</tr>
<tr>
<td>Walla Walla</td>
<td>71 (74)</td>
<td>70</td>
</tr>
<tr>
<td>Millville</td>
<td>72 (81)</td>
<td>73^b</td>
</tr>
<tr>
<td>Salkum</td>
<td>84 (87)</td>
<td>51</td>
</tr>
<tr>
<td>Palouse B</td>
<td>181 (184)</td>
<td>203</td>
</tr>
<tr>
<td>Ca²⁺ Montmorillonite</td>
<td>597 (602)</td>
<td>760^c</td>
</tr>
</tbody>
</table>

^aValues in parentheses represent SA estimates using a single point, driest, (Tuller and Or, WRR 2005)
Defining pores – *geometry, pressure and invasion volumes*

**Geometrical pores**

**Imaged invasion event volumes**

**Pressure deduced pore volumes**

Pore volume = waiting time x flow rate

(Moebius and Or, WRR 2014)