

# Towards a better understanding of the role of the contractile skin

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**ABSTRACT:** Various properties of the contractile skin have been measured by numerous researchers in disciplines outside of civil engineering. The findings are pertinent to research in unsaturated soil mechanics, and assist in the interpretation of the behavior of unsaturated soils. This paper provides an insightful review into the nature of the contractile skin, including its molecular structures, physical and chemical properties, and related theories associated with soil suction. The reviews show that there is a distinction between the properties of the bulk water and water within the contractile skin. These findings further confirm that the contractile skin is appropriately considered as the fourth phase of unsaturated soils. In addition, the behavior of contractile skin is relevant to the interpretation of thixotropy phenomenon, changing the friction coefficient and the attenuation in wave propagation in fine-grained soils.

## 1 INTRODUCTION

The capillary phenomena have been known since 16 century when Leonardo da Vinci observed the liquid rise in narrow, wetted capillaries, bores and plugs (Lyklema, 1991). The importance of capillary forces on soil behavior was indicated by Terzaghi (1943) and Taylor (1948) in the early development of soil mechanics. Capillarity was observed to increase intergranular forces and produce higher strength of soils, prevent expansion of a clay sample after the overburden pressure was removed, and produce a siphon effect for water to flow above the phreatic line in an earth dam.

Not surprisingly, the framework and the importance of unsaturated soil mechanics can be readily seen in the early studies of soil behavior (Terzaghi, 1943; Taylor, 1948). However, much of the importance about the role of the contractile skin has been largely missed in most present-day presentations of soil mechanics. In addition, an understanding of the role of the contractile skin in unsaturated soils has also been given little attention. The purpose of this paper is to provide an insightful review of the properties of contractile skin and related theories associated with soil suction with the aim of providing a better understanding its role and importance in soil mechanics.

## 2 AIR-WATER INTERFACE AND SURFACE TENSION

The surface tension of water arises from unbalanced molecular interactions on the air-water interface. The associated contractile tendency of the interface can function like an “elastic membrane” which makes water drops rebound from a super-hydrophobic surface just like a solid ball (Figure 1). A serial image of the impact process captured by a high-speed camera is shown in Figure 2. Apparently the properties of the contractile skin are quite different from those of ordinary water as Terzaghi inferred, and therefore the contractile skin can be considered as the fourth phase in the soil matrix. The energy dissipation of the bouncing water drop comes from the viscous loss associated with the vibrating fluid. The similar energy loss mechanism can also be applied to unsaturated and moist fine-grained soils (Wang, 2001).

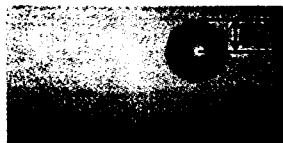
The surface tension can be interpreted thermodynamically and mechanically. Most of the surface-tension measurements are implemented based on mechanical equilibrium in terms of force (per unit length) required to enlarge the interfacial surface (Adamson and Gaster, 1997; Lyklema, 2000). However, the thermodynamic description can better capture the temperature dependence of surface tension via the entropic contribution (Lyklema,

2000). The thermodynamic definition of surface tension is,

$$T_s = (\partial F / \partial A)_{V,T,n} \quad (1)$$

$$T_s = (\partial G / \partial A)_{P,T,n} \quad (2)$$

where  $T_s$  is the surface tension,  $A$  is the area, and  $F$  and  $G$  are the Helmholtz and Gibbs energy, respectively. The subscripts represent fixed variables where  $P$  is pressure,  $T$  is temperature, and  $n$  represents the amount of composition in the system. In general, the units of surface tension is force/length, which is equivalent to energy/area. Equations (1) and (2) explicitly indicate that surface tension,  $T_s$ , is also a function of states.



Radius = 0.4 mm

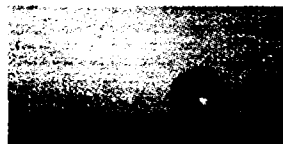


Figure 1 (upper). Water drop falling on a superhydrophobic surface (Richard et al., 2000).



Figure 2 (left). Millimetric drop (radius is 0.4 mm) impacting a superhydrophobic surface. The snapshots are obtained from a high-speed camera (9000 frames per second) (Richard et al., 2000).

The available surface energy tends to be a minimum so that the measured surface tension will be larger when thermodynamic equilibrium is not attained. Fortunately, the surface tension in general can be established within a millisecond (Lyklema, 2000). That is, time effects on the development of surface tension can be ignored from a practical standpoint for unsaturated soils. However, suction homogenization among soil particles cannot be completed within a short time, and therefore time-

dependent recovery of stiffness in unsaturated soils (fine-grained) can be observed - thixotropy (Cho and Santamarina, 2001).

Note that the surface tension not only increases soil strength but also changes soil volume. The test for the shrinkage limit and the desiccation cracks observed in field are of evidence of this phenomenon.

### 3 CAPILLARY PRESSURE

The Young-Laplace equation and Kelvin equation are introduced, followed by a discussion of the limitations and anomalies of these equations.

#### 3.1 Equations

The pressure difference,  $\Delta P$  across the air-water interface can be obtained through the Young-Laplace equation,

$$\Delta P = T_s \left( \frac{1}{R_1} + \frac{1}{R_2} \right) = T_s \frac{1}{R_m} \quad (3)$$

where  $R_1$  and  $R_2$  are the principal radii of curvature of the interface (Figure 3), and  $(R_1^{-1} + R_2^{-1})^{-1}$  is defined as the first or mean radius of curvature,  $R_m$ . Ignoring the influence of gravity,  $\Delta P$  and the mean radius  $R_m$  are all the same throughout the whole curved interface. As the interface is a sphere, Equation 3 can be reduced to the following form,

$$\Delta P = T_s \frac{2}{R} \quad (4)$$

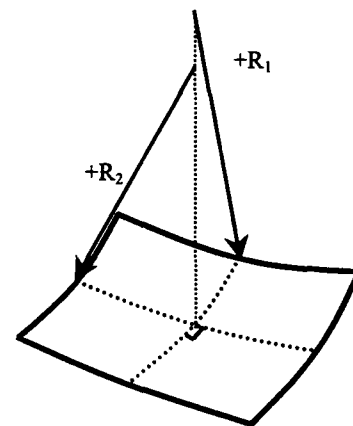


Figure 3. Schematic diagram of principal radii of the contractile skin.

Figure 4 illustrates some simplified geometries for the air-water interface that might form in an unsaturated soil matrix. The associated pressure difference,  $\Delta P$ , across the interface based on the Young-Laplace equation is also indicated for each case. Note that  $R_1$  is equal to  $-R_2$  for the case of a saddle-type meniscus (Figure 4d).

Combining Gibbs free energy with the capillary equation gives the well-known Kelvin equation,

$$R_v T \ln \frac{P}{P_{sat}} = T_s V \left( \frac{1}{R_1} + \frac{1}{R_2} \right) = T_s V \frac{1}{R_k} \quad (5)$$

where  $P$  is the equilibrium vapor pressure of the liquid,  $P_{sat}$  is the saturated vapor pressure for a flat surface,  $R_v$  is the Avogadro's number,  $V$  is the molar volume ( $18 \text{ cm}^3/\text{mole}$ ),  $R_k$  is the Kelvin radius (mean radius), and  $T$  is the absolute temperature. The more exact formulation of the Kelvin equation is given by Equation (6) (Fisher and Israelachvili, 1981),

$$RT \ln \frac{P}{P_{sat}} = T_s V \left( \frac{1}{R_k} - (P - P_{sat}) \right) \quad (6)$$

"The Kelvin equation can be used to calculate the enhanced vapor pressure of a liquid drop ( $R_k$  is positive) and the lowered vapor pressures in bubbles and above capillary held wetting liquid ( $R_k$  is negative)" (Fisher and Israelachvili, 1981). For the latter case, the ratio,  $P/P_{sat}$ , can be considered as the relative humidity  $RH$  and therefore a unique relationship exists between the Kelvin radius and relative humidity can be constructed.

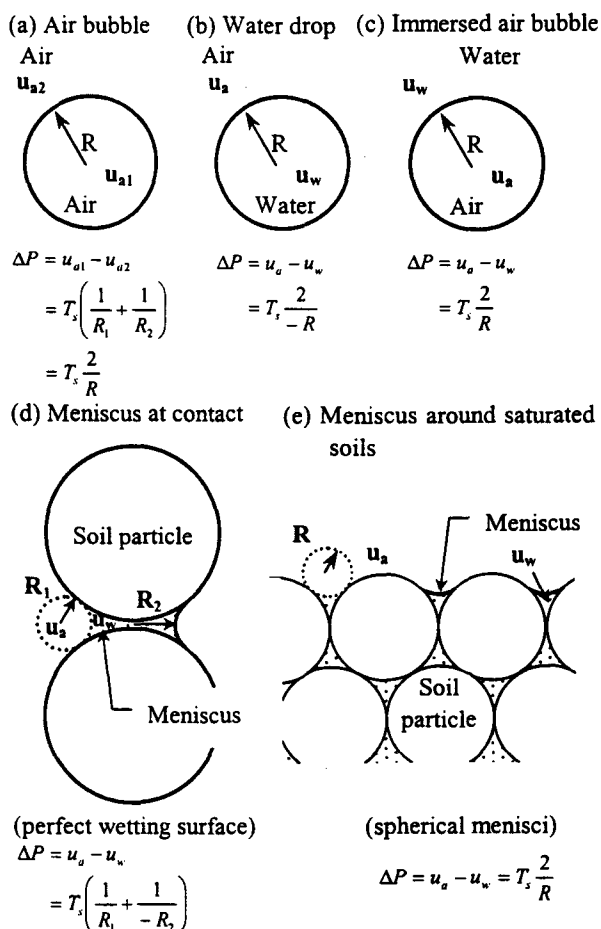


Figure 4. Schematic diagram of simplified geometry of the air-water interface and associated pressure difference  $\Delta P$  across the interface based on the Young-Laplace equation.

The above two equations are the fundamental relationships of surface chemistry (Adamson and Gast, 1997). These equations are also important in quantifying the matric suction of soils under different degrees of saturation.

### 3.2 Anomaly and limitation

Both equations do not appear to always be valid and have some limitations, as discussed below.

#### 3.2.1 The Young and Laplace equation

For a spherical air-bubble immersed in water, its volume decrement should be associated with a higher pressure-difference,  $\Delta P$ , across the interface (refer to Equation 4). This observation infers that the Young-Laplace equation is not able to explain why the air bubble can gradually dissolve in water without any apparent difference between the air and water pressures (Fredlund and Rahardjo, 1993).

#### 3.2.2 The Kelvin equation

The macroscale Kelvin equation applies when the value of curvature  $R_k$  (Equation 5) exceeds  $30 \text{ \AA}$  (Adamson and Gast, 1997). Christenson (1988) concluded that the surface tension of water is equal to the value of bulk water when the relative humidity is above 70%, based on experimental observations made using a Surface Force Apparatus (SFA). If the Kelvin equation is valid at a relative humidity of 70%, the corresponding radius of curvature,  $R_k$ , is equal to  $15 \text{ \AA}$ , and the suction pressure is  $4.83 \times 10^4 \text{ kPa}$  based on the Young-Laplace equation. This value is much higher than the cavitation pressure of  $100 \text{ kPa}$ . Note that it is plausible to suspect the validity of the Kelvin equation as the radii of curvature reduces to the molecular scale.

The other uncertainty in using the Kelvin equation is the time required for thermodynamic equilibrium (Melrose, 1989). Experimental results show that the capillary condensation can give rise to an ageing phenomenon in sand, resulting in an increase in the friction coefficient with time (Bocquet, 1998).

#### 3.2.3 The influence of a curved surface on surface tension

The surface tension can also be affected by a highly curved interface (i.e., very small radii) as indicated by Equation (7) (Melrose, 1968),

$$T_s = T_s^0 \left( 1 - \frac{t}{R_k} \right) \quad (7)$$

where  $T_s^0$  is the surface tension without an influence from a curved interface and  $t$  is the thickness of interfacial region.

### 3.3 Stress state variables

Fung (1965) describes the state of a system as that "information required for a complete characterization of the system for the purpose at hand." The state variables must be independent of the physical properties of the material. The Young-Laplace equation indicates that the suction coming from the contractile skin is determined by the characteristics of menisci and not affected by the soil properties. Consequently, the pressure difference,  $\Delta P$ , across the fourth phase (i.e. the contractile skin) can be considered as a stress state variable which is a tensor (Li, 2002).

## 4 CHARACTERISTICS OF THE CONTRACTILE SKIN

The air-water interfacial region is in fact in an extremely turbulent state (Adamson and Gast, 1997). At room temperature and at the saturated vapor pressure, each square centimeter above the interface contains  $1.2 \times 10^{22}$  arrivals and departure of water molecules in a second. The lifetime of a water molecule staying on the interface is in the order of  $1 \times 10^{-7}$  second. In addition, below the interface the water molecules can also diffuse from the liquid. The diffusion time is about  $1 \times 10^{-6}$  second for a travel distance of  $100 \text{ \AA}$  based on Einstein's equation (Adamson and Gast, 1997). In summary, water molecules are in a state of violent agitation within the interfacial region.

The unbalanced molecular interactions on the air-water interface give rise to surface tension and the associated capillary phenomena. The next question of interest is: "how deep can the unbalanced force extend and what are the properties of the contractile skin?" Definite answers to the above questions still appear to be an uncertainty. Following is a brief summary of information related to molecular dynamic simulation and experimental observations.

### 4.1 Density distribution

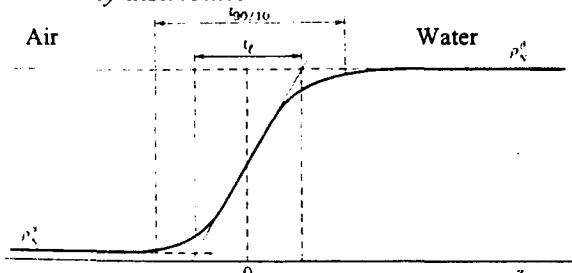


Figure 5. Schematic diagram of a possible water-molecule distribution across the air-water interface (Lyklema, 2000).

Figure 5 is a schematic diagram of the possible water-molecule distribution across the air-water interface. The density distribution is close to a hyperbolic tangent function which can be observed from the results of molecular dynamic simulation. In

Figure 5, the term,  $\rho_N^\alpha$ , represents the density of vapor water (i.e.,  $z = -\infty$ ) and  $\rho_N^\beta$  represents the density of liquid water (i.e.,  $z = \infty$ ). Most of the density variation takes place within the thickness,  $t_s$ , which can be obtained from the extrapolation of the linear part of the density distribution. However, the 90 - 10 thickness,  $t_{90/10}$ , has been generally adopted to represent the interfacial thickness (i.e., thickness of the contractile skin). The 90 - 10 thickness covers the density range from 90% below  $\rho_N^\beta$  to 10% above  $\rho_N^\alpha$  (Figure 5).

### 4.2 Thickness of the contractile skin

There is no definite conclusion as to the interfacial thickness due to different model assumptions used in the molecular dynamic simulations and different experimental interpretations. Most of the simulated and experimental results agree with that the interfacial thickness ( $t_{90/10}$ ) ranges within several molecular diameters. For instance, the effective diameter of a water molecule is  $2.8 \text{ \AA}$  (Israelachvili, 1991), and a thickness around  $5 \text{ \AA}$  is approximately equivalent to 1.5~2 molecule diameters. Figure 6 summarizes the simulated and experimental results of the 90 - 10 thickness. The thin contractile skin is primarily owing to the presence of hydrogen bonding (Townsend and Rice, 1991). Molecular dynamics simulations also indicate that the thickness,  $t_{90/10}$ , increases with temperature as the dotted line indicates in Figure 6 (Matsumoto and Kataoka, 1988; Alejandre et al., 1995). Note that this thickness is much smaller than Terzaghi (1943) anticipated (i.e.,  $100 \text{ \AA}$ ).

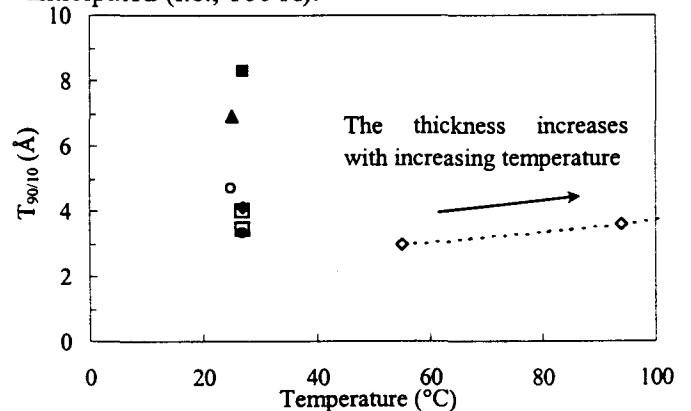


Figure 6. The thickness of the air-water interface,  $t_{90/10}$ . Results are from both molecular dynamic simulations and experiments.

Results of Molecular dynamic simulation			
Sy.	°C	Thickness, $t_{90/10}$ (Å)	References
◇	55	2.99	Alejandre et al., 1995
◇	94	3.62	
○	25	4.7	Lie et al., 1993
□	27	3.45	Townsend and Rice, 1991
□	27	4	
Experimental Results			
■	27	8.3 (X-ray reflectivity experiment)	Matsumoto and Kataoka (1988)
◆	27	4.1 (Ellipsometric experiment)	
▲	25	6.91 (X-ray reflectivity experiment)	Schwartz et al. (1990)
●	27	3.3 (X-ray reflectivity experiment)	Braslaw et al. (1988)

### 4.3 Tensile stress

The equivalent tensile stress in the contractile skin can be estimated as 140,000 kPa based on the assumption that the surface tension is 71.99 mN/m and the thickness of  $t_{90/10}$  is 5 Å at 25 °C. Therefore, the contractile skin is under a high tensile stress.

### 4.4 Structure

Lowering the surface excess entropy of water gives rise to a structural change near the interface, ordered orientation and maximized density, which is quite different from the randomly oriented liquid water molecules (Matsumoto and Kataoka, 1988). The origin of ordering arises from the influence of dipoles and hydrogen bonding (Chacón et al., 1985; Eggebrecht et al., 1987). The structure of a water molecule near the interface is: "in the vapor side of the surface, a water molecule has its one H atom projecting towards the vapor phase. In the liquid side, a molecule tends to lie down on the surface with its both H atoms slightly directed toward the liquid phase" (from Matsumoto and Kataoka, 1988). Similar results were also concluded by Townsend and Rice (1991).

The ordered structure of water molecules can be explained as it is similar to the formation of the structure of ice (Matsumoto and Kataoka, 1988). This is similar to the boundary layer structure close to a hydrophilic surface (Derjaguin and Churaev, 1981). The orientational preferences of water molecules and the tendency towards a decreasing density favor the decrease in the average number of hydrogen-bonded neighbors per water molecule (Pohorille and Wilson, 1993). In addition, the ordered structure will be destructed at high temperatures (Matsumoto and Kataoka, 1988). This is similar to that the high temperature will destruct the modified structure and the high viscosity of the boundary layer (Derjaguin and Churaev, 1981).

### 4.5 Physical and Chemical Properties

Since the thickness of the contractile skin is extremely small, it is hard to measure its properties and available data is rare. Results of molecular dynamic simulation show that the diffusion coefficient in the interfacial region is 58% greater than that in the bulk water, which is consistent with its decreasing density (Townsend and Rice, 1991). The characteristics of molecular structure of polar liquids is reflected in permittivity. The permittivity of a thin layer of water between hydrophilic surfaces of clay particles shows a marked difference when compared with that of bulk value (Derjaguin and Churaev, 1981). Therefore, the permittivity of the contractile skin is expected to be different from that

of bulk water. However, further experimental evidence is needed.

## 5 INFLUENCE OF TEMPERATURE AND PRESSURE ON SURFACE TENSION

The surface tension of water is a well-studied property. Although there exists some discrepancies between different measurements, the data is essentially the same from a practical standpoint (Lyklema, 2000).

Measured results of surface tension show a downward trend with increasing temperature. A comprehensive review also can be found in Lyklema (2000). Figure 7 shows that the data suggested by Terzaghi (1943) is identical to the values proposed by Vargaftik et al. (1983) (Note: the data is also reproduced in the CRC handbook of chemistry and physics).

A power law was suggested to fit the downward trend (Kayser, 1976; Lyklema, 2000),

$$T_s(T) = T_s(T_m) + aT + bT^2 \quad (8)$$

where  $T_s(T_m)$  is the surface tension at the melting point (i.e., 0 °C),  $a$  and  $b$  are constant, and  $T$  is temperature in Celsius. Lyklema (2000) suggest that  $T_s(T_m) = 75.83$  mN/m,  $a = -0.141$  mN/m·T,  $b = -0.29 \times 10^{-3}$  mN/m·T<sup>2</sup>, which are average values from collected data. Note that the linearization of Equation (8) causes noticeable error at higher temperature (i.e., the dot line indicated in Figure 7). Therefore, the constants in Equation (8) are not without physical meaning. The value of  $a$  can be considered as the surface excess entropy per unit area,  $S_a^\sigma$ , which can be interpreted as follows:

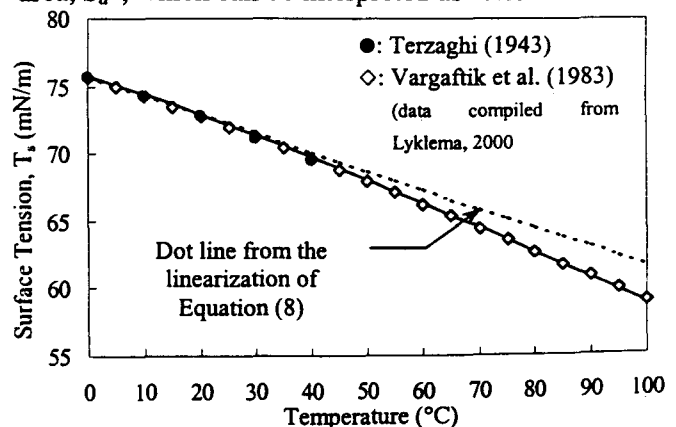


Figure 7. The surface tension  $T_s$  versus temperature  $T$  (°C). Note that the solid line is based on Equation (8).

For a pure liquid, the surface tension,  $T_s$ , also can be given as

$$T_s = U_a^\sigma - TS_a^\sigma \quad (9)$$

where  $U_a^\sigma$  and  $S_a^\sigma$  are the surface excess energy and entropy per unit area, respectively. The differentiation of Equation (9) makes both  $S_a^\sigma$  and  $a$  equivalent.

Theoretically, the surface tension has an upward trend with respect to the pressure (Adamson and Gast, 1997). However, in reality the influence from pressure is relatively irrelevant so this effect can be practically ignored (Lyklema, 2000).

## 6 DISCUSSION AND SUMMARY

- (1) The properties and behavior of the contractile skin are quite different from those of bulk liquid and therefore it can be considered as the fourth phase of an unsaturated soil matrix. In addition, the associated suction is independent to the soil properties and can be a stress state variable.
- (2) The behavior of the contractile skin is associated with soil strength and volume change. Also, it is relevant to the interpretation of thixotropy phenomena, friction coefficient change and attenuation in wave propagation, in fine-grained soils.
- (3) The Young-Laplace and Kelvin equations are two fundamental relationships that can be used to quantify soil suction. However, both equations have limitations.
- (4) In the air-water interfacial region, water molecules tend to be ordered and prefer to maximize density. The thickness of the interfacial region is about 1.5~2 water molecular diameters at room temperature. Increasing temperature will disrupt the ordered orientation and enlarge the thickness. The tensile stress in the contractile skin is in the order of  $10^5$  kPa at room temperature.
- (5) Surface tension reduces with temperature but the influence from pressure is insignificant.

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