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REVIEWS AND ANALYSES

Soil water potential: A historical perspective and recent breakthroughs

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Abstract

Soil water potential is a cornerstone in defining the thermodynamic state of soil water required to quantify phenomena such as water phase change, water movement, heat transfer, electric current, chemical transport, and mechanical stress and deformation in the earth's shallow subsurface environment. This potential has historically been conceptualized as free energy stored in a until volume of soil water. Though the concept of soil water potential has been evolving over the past 120 yr, a consensual definition is still lacking, and answers to some fundamental questions remain controversial and elusive. What are the origins and mechanisms for the free energy of soil water? Can the common mathematical expression of soil water potential as superposition of gravitational, osmotic, and matric potentials be used to define water phase transitions in soil? Are these major components of soil water potential independent or coupled? Is pore water pressure always tensile under unsaturated conditions? If so, how can soil water density be as high as 1.7 g cm^{-3}? How do adsorptive soil–water interactions originating from the electromagnetic field around and within soil particles transfer to mechanical pore pressure? In this review, the authors (a) provide critical analysis of historical definitions of soil water potential to identify their strengths, limitations, and flaws; (b) synthesize the origins of electromagnetic energies in soil to clarify the fundamental differences between adsorptive and capillary soil water potential mechanisms; (c) introduce a recently emerging concept of soil matric potential that unifies contributions of adsorption and capillarity to soil water potential; and (d) illustrate the generality and promise of the unified definition of soil water potential for answering some of the fundamental questions that remain elusive to the hydrology, geoengineering, and geoscience communities.

Abbreviations: BOS, Bureau of Soils; CEC, cation exchange capacity; EDL, electrical double layer; EMF, elastic modulus function; FX, Fredlund and Xing; ISSS, International Society of Soil Science; REV, representative elementary volume; SFC, soil freezing curve; SSA, specific surface area; SSP, soil sorptive potential; SWI, soil water isotherm; SWR, soil water retention; SWRC, soil water retention curve; TCF, thermal conductivity function; VG, van Genuchten; YL, Young–Laplace.

1 | INTRODUCTION

Soil water potential quantifies the change in energy for a unit volume of water retained by soil relative to the energy of free water, which is generally designated as zero under standard temperature and ambient air pressure. By convention, total soil water potential is the collective sum of three potential functions, namely, gravitational potential, osmotic potential, and matric potential (Or et al., 2005). Gravitational potential can be either positive or negative depending on the selection of a global or local reference elevation. Osmotic potential arises from interactions among soil water and dissolved solutes and is generally negative to reflect the reduction in energy resulting from these interactions. Matric potential of soil water is also generally negative because soil–water interactions tend to reduce the energy level of free water (Iwata et al., 1995). Soil water potential is the cornerstone for understanding numerous aspects of soil behavior, including soil water retention (SWR) (e.g., Lu, 2016), suction stress evolution (Lu & Likos, 2006; Lu et al., 2010), hydraulic conductivity (e.g., van Genuchten, 1980), thermal conductivity (Lu & Dong, 2015), freezing suppression (Zhang & Lu, 2021), and biological activities (Charra-Vaskou et al., 2016), among others. Comprehensive understanding and robust definition of soil water potential, therefore, is required to advance understanding of these and many other phenomena in the soil–water environment and the implications toward a variety of practical problems and applications in hydrology, geoengineering, and geoscience.

All current definitions for soil water potential can be dated back to Edgar Buckingham's seminal work published at the beginning of the 20th century (Buckingham, 1907). Buckingham introduced the concept of potential from physics to study water flow in unsaturated soil and first defined matric potential as a capillary potential. The idea to treat soil water potential (particularly matric potential) by thermodynamic reasoning did not prosper until 1943 when N. E. Edlefsen and Alfred B. C. Anderson published a comprehensive review on the topic (Edlefsen & Anderson, 1943). Due to lack of consensus, however, different terminologies were often used for the matric potential and caused great confusion in the literature. Matric potential was referred to as many names by different researchers to emphasize specific but poorly defined mechanisms governing the soil water matric potential, including capillary potential (Buckingham, 1907; Gardner, 1920), pressure potential (Day et al., 1967; Richards, 1928), and moisture potential (Philip, 1969b, 1969c; Veihmeyer & Edlefsen, 1937).

Until recently, matric potential has been universally defined as the difference between the bulk pore water pressure and pore air pressure ($P_w - P_{air}$) for the entire range of SWR (e.g., Aslyng et al., 1963; Day et al., 1967; Fredlund & Rahardjo, 1993; Hilf, 1956; von Fay, 1985). Fundamentally, $P_w - P_{air}$ is the capillary potential, and the validity of solely treating capillary potential as the equivalent of matric potential is questionable because capillary water and adsorbed water can coexist at soil water contents higher than a certain value (e.g., Lu, 2016; Luo & Lu, 2021). In fact, capillary water under negative pressure (i.e., tension) is in a metastable state and prone to undergo phase change through cavitation (Luo et al., 2021). When water pressure drops below a physical limit (i.e., cavitation pressure), capillary pore water can disappear, and the soil–water interaction (potential) is dictated by adsorption. Any complete definition of matric potential, therefore, must consider energy contributions from both capillarity and adsorption at different stages over the entire range of SWR, including the disparities in physical scale within which each mechanism operates.

Core Ideas

- A historical perspective and recent breakthroughs on soil water potential is provided.
- Critical analysis of historical definitions of soil water potential is provided to identify their strength and flaws.
- Fundamental differences between adsorptive and capillarity soil water potentials are clarified.
- A general soil water potential definition unifying both adsorption and capillarity mechanisms is provided.
- Practical implications of unified soil water potential definition to fundamental soil properties are illustrated.

Iwata et al. (1995) and Nitao and Bear (1996) recognized the disparities in physical scale and magnitude of free energy where capillary water and adsorptive water operate in soils, identified a few specific adsorptive forces (e.g., electric field and van der Waals forces) and reviewed their respective contributions to soil water potential, thus paving the way for better definition of matric potential. More than two decades have passed since then and additional knowledge of soil–water interaction has emerged. Recent theoretical breakthroughs in synthesizing the concept of soil sorptive potential (SSP) now enable soil matric potential to be uniquely defined within a given representative elementary volume (REV) of the soil–water–air system under the thermodynamic equilibrium condition (Lu & Zhang, 2019; Zhang & Lu, 2019b). In a departure from the former augmented Young–Laplace (YL) equation, which considers homogeneous soil water properties throughout the entire adsorbed water film (Philip, 1977; Tuller et al., 1999), the SSP explicitly quantifies the variation of adsorption strength with respect to a distance from the soil particle surface. New frameworks based on the SSP theory have been developed to explain long-standing puzzles in unsaturated soils including abnormally high water density (Zhang & Lu, 2020a), adsorption-induced effective stress (Zhang & Lu, 2020b), cavitation suppression (Luo et al., 2021), and freezing point depression (Zhang & Lu, 2021).

Below, the authors review previous definitions of soil water potential following the free energy concept from a historical perspective starting from the time of Buckingham at the first half of 20th century. Basic thermodynamic principles and their applications toward soil water potential are then critically assessed to reveal the limitations and misconceptions in these historical concepts. A unitary definition of soil water potential is synthesized from all soil–water interactions identified in the comprehensive review and used to resolve some fundamental limitations inherent in the previous definitions. Examples are provided to validate the capability of the proposed definition as a cornerstone for studying soil physical, hydrological, thermal, and mechanical properties, including soil water density, soil water freezing, thermal conductivity, suction stress, and elastic modulus.

2 | ENERGY CONCEPT OF SOIL WATER

2.1 | Buckingham's capillary potential

At the turn of the 20th century, Milton Whitney, who believed that soil physical properties affected crop productivity more profoundly than soil fertility (Nimmo & Landa, 2005), was appointed head of the U.S. Department of Agriculture (USDA) Division of Soils, and later the Bureau of Soils (BOS) (Gardner, 1986). Under the lead of Whitney, Lyman Briggs investigated the ability of soil to retain water through experiments with vertical soil columns predicated on the basis of interactions between capillarity and gravitational forces (Briggs, 1897; Landa & Nimmo, 2003). The significance of water movement in soil had also drawn Briggs' attention during this period but he certainly did not emphasize it as much as what was stated (Briggs, 1897): "to present the application of certain dynamical principles to problems attending the movement and retention of soil moisture." Instead, in Briggs' later work with his collaborators, empirical equations relating a series of soil moisture constants (moisture equivalent, hygroscopic coefficient, and moisture-holding capacity) with the wilting coefficient (i.e., water content corresponding to wilting point of plants) were established for different soil types by conducting centrifuge experiments (Briggs & McLane, 1907; Briggs & Shantz, 1912). Edgar Buckingham, a physicist and a colleague of Lyman Briggs, introduced the term "capillary potential" (denoted ψ) to study the dynamic problem of water flow in unsaturated soil (Buckingham, 1907). In his "Studies on the Movement of Soil Moisture" published in 1907 as Bulletin 38 of the BOS, USDA, Buckingham defined the capillary potential as analog to thermal and electrical potentials. He stated:

> Let a small mass of water δθ be pulled away from the soil, so as to reduce its water content by δθ. Let ψδθ be the work that we have to do to pull this water away. Then we may define ψ as the work required per centigram to pull water away from the mass of soil. We shall call ψ the capillary potential of the soil. (Buckingham, 1907, p. 29)

With this statement Buckingham has been recognized as the person who first introduced the energy concept to the community of soil physics (e.g., Narasimhan, 2005, 2007).

Because there was no instrument available at that time for direct measurement of capillary potential, but building on the preliminary work done by Briggs (Briggs, 1897), Buckingham also conducted vertical soil column experiments (as shown in Figure 1a), in conjunction with the proposed concept of capillary potential, to estimate ψ for different types of soils. Evaporation on the top of soil column was prevented, and the bottom was immersed in a large container with a constant-elevation free water surface (i.e., water table) where air pressure is equal to the pore water pressure. Due to the capillary effect, water gradually advanced upward against gravity into the dry soil. If it is assumed that the entire soil–water system reaches its isothermal equilibrium after a period of time, the downward pull of the gravitational force for water is balanced by the upward capillary attractive force originating from soil–water interaction. Therefore, Buckingham indirectly determined the capillary potential using the relationship as follows (Buckingham, 1907):

$$\psi = A_{\mathrm{g}} h \tag{1}$$

where h is height of the location of interest above the free-water surface and A_{g} is a constant depending on the gravitational acceleration. By taking water content (θ) measurements at various elevations within the vertical soil column after presumptive equilibrium, Buckingham obtained the very first experimental measurements of soil water retention curves (SWRCs) capturing capillary potential as a function of soil water content (Figure 1b). He stated "The value of ψ, for a given state of packing, temperature, etc., depends only on the water content, decreasing as θ increases" (Buckingham, 1907, p. 29).

The difference in water potential, specifically the capillary potential, within unsaturated soil was originally proposed and used in the third section of Buckingham's work as the driving mechanism that caused water flow in the vertical soil columns (Buckingham, 1907). He stated:

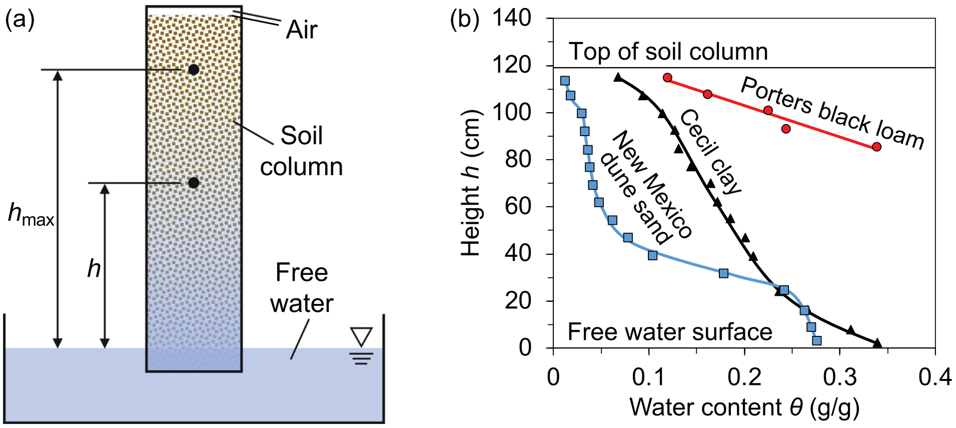

FIGURE 1 (a) Vertical soil column used by Buckingham (1907) for measurements of capillary potential (adapted from Russell, 1943); (b) representative soil water retention curves (SWRCs) determined from vertical column experiments for three selected soils (adapted from Buckingham, 1907)

> Let ψ be a quantity which measures the attraction of the soil at any given point for water. Then the gradient of attraction, which we may denote by S, is the amount by which ψ increases per centimeter in the direction of the current, by reason of the fact that the water content of the soil decreases in that direction. (Buckingham, 1907, p. 27)

This in fact was a revolutionary concept in Buckingham's time. Inspired by observations in fully saturated soil, in which water flow depends on the gradient of hydrostatic pressure, Gardner (1919) correctly recognized the capillary potential as capillary pressure (i.e., pressure difference between air and water immediately below the curved meniscus). Furthermore, Gardner (1920) pointed out that to be consistent with the definitions of other well-known potential functions, the capillary potential, previously defined by Buckingham as the work required to move a unit mass of water from a point in soil to a free water surface, should be redefined as "the work done by the field forces in bringing unit mass from the point in question to infinity." These two definitions are actually equal in value but opposite in sign, meaning that the capillary potential has a negative value at any location above the free-water surface.

Gardner's redefinition naturally correlated the capillary pressure at any point in a soil–water system to the hydrostatic pressure at the same point in soil via the density of water, leading to numerical equivalence between these two quantities if unity is assumed for water density. Gardner and Widtsoe (1921) later added gravitational potential to capillary pressure and used the concept of total potential to describe capillary water movement in a linear differential equation. This is in accordance with modern understanding that the gradient of total potential, but not that of soil water content, should be the actual driving mechanism for upward water flow in Buckingham's vertical soil column experiment (e.g., Nassar & Horton, 1989; Philip & De Vries, 1957; Russell, 1943). Once equilibrium is reached in a soil–water system, the gradient of total potential would be zero between any two locations therein. Shortly after this recognition, a porous cup apparatus (a predecessor of the modern tensiometer) was invented in 1922 for direct measurement of the soil water potential (specifically the capillary pressure) at any location of interest by means of inserting a probe into soil and subsequently recording gauge pressure after equilibrium (Gardner et al., 1922). In fact, a similar experimental setup was already used by Burton Edward Livingston in 1908 for auto-irrigation of potted plants (Livingston, 1908; Or, 2011). Further details about the tensiometer will be discussed in subsequent sections of this review. Since then, the meaning of soil water potential had been gradually improved and extended by follow-up studies from the early to mid-20th century.

2.2 | Deficiencies of Buckingham's capillary potential

The capillary potential considered by Buckingham has certain drawbacks and is questionable. First, this capillary potential does not exist intrinsically, although its magnitude can be converted from the gravitational potential when the soil–water system reaches equilibrium. According to current understanding, the actual capillary potential (or capillary pressure) should be defined as the ratio of surface tension to the mean principal radius of a meniscus occurring at the air–water interface (e.g., Lu & Likos, 2004), which depends neither on the gravitational field (supposing negligible distortion of meniscus) nor on the distance to the free water surface. For instance, let's consider an infinitely long horizontal soil column with constant supply of water at its right end. The water would continuously flow from right to left and the soil–water system in such an experimental setup can never come to an equilibrium state without the effect of gravity. In such a case, the capillary potential is not measurable or simply does not exist in the system, as also pointed out by Iwata et al. (1995).

Second, it was found that the heights of capillary rise were not consistent for soil columns with different cross-sectional diameters, and a greater rise generally was observed in soil columns with larger diameter (Wadsworth & Smith, 1926). Gravitational potential was considered as the only counterpart to capillary potential in these experiments. Ideally, the upward movement of water at equilibrium ceases at the height (e.g., $h_{\max}$ in Figure 1a) where the capillary force at the wetting front is balanced against the gravitational force acting on the continuous water fringes (Lu & Likos, 2004), similar to the rise of water in a capillary tube. Even for the same soil, however, the capillary potential measured from a soil column experiment is largely affected by many factors other than the gravity, such as grain size, spatial distribution of pore size, and solid–liquid contact angle. Moreover, the accuracy of capillary potential measured from a soil column test is dictated by the actual equilibrium condition, which highly depends on the liquid connectivity at the wetting front. The upward movement of water is greatly slowed down at locales with poor liquid connectivity. Water will thus follow preferential pathways above the water table and form capillary fingers in soil, leading to nonuniform distribution at the same height of the soil column. In other words, the true "capillary potential" that Buckingham refers to (i.e., Equation 1) may take a much longer time than days, or perhaps years, to reach equilibrium.

Third, the term "capillary" generally invokes notions of surface tension or curved air–water interfaces. Robert Kenworthy Schofield in his 1935 paper deliberately referred to the capillary potential as Buckingham's potential (Schofield, 1935) because the former might not always reflect the real circumstance of soil water. When the water content is low (e.g., the top layer of a vertical soil column), water is tightly adsorbed and distributes in thin films over the surfaces of soil particles (e.g., Lu & Khorshidi, 2015) indicating that adsorption, rather than capillarity, is the dominant mechanism controlling the soil–water retention under those circumstances.

2.3 | Inconsistency in terminology

The water potential concept as discussed above, starting from Buckingham, solely assumed pure water (or very dilute solution) for which the effect of electrolytes was negligible, likely because Whitney (chief of BOS at the time) considered soil physical conditions as more decisive in plant growth. Franklin Hiram King, who joined the USDA as a physicist in 1901, disagreed with Whitney and believed that nutrient supply (i.e., water-soluble salts) in soil was crucial for crop yield (King, 1904, 1905). Linford (1926) later proposed inclusion of osmotic potential produced by solutes in soil water as part of the aforementioned total potential, thus interpreting the energy state of soil water from both mechanical and chemical perspectives. Richards and Weaver (1944) also stressed the importance of taking into account osmotic potential in the total soil water potential for semiarid soils.

More extensive discussion was subsequently motivated by the uncertain nomenclature and meaning of capillary potential (Veihmeyer & Edlefsen, 1937). Various names were used as an equivalent substitution of total potential by different researchers in the context of moisture movement, purely as a matter of convenience for analyzing a specific problem. Different components were sometimes even included under the same nomenclature, yet without explicit explanation, and resulted in unnecessary confusion from the vague definition. For instance, as mentioned above, the capillary potential defined by Buckingham had been interchangeably called pressure potential (i.e., capillary pressure) (Bodman & Edlefsen, 1934; Gardner, 1920; Gardner et al., 1922; Richards, 1928, 1931). Linford (1926), as well as Remson and Randolph (1962), further interpreted Buckingham's capillary potential as the negative sum of pressure and osmotic potentials to account for the effect of solutes. Veihmeyer and Edlefsen (1937) were in favor of using "moisture potential," "potential function," or simply "potential" to refer to the capillary potential and pressure potential, because they thought "it is clear that it refers to soil-moisture." In the subsequent discussion section of the same report, however, Lorenzo A. Richards pointed out that the moisture potential defined by Veihmeyer and Edlefsen was meant to represent total potential (i.e., all energy changes in soil water), and not merely the capillary potential.

2.4 | Formal definition of total soil water potential from a mechanical perspective

The general lack of unanimity in terminology rendered difficulties in fully and correctly understanding the literature at the time, and was seen to hinder progress in the field. To tackle this issue, the Terminology Committee of Commission I of the International Society of Soil Science (ISSS) first provided a terminology report in 1963, in which total water potential was formally defined to express the energy state of water in soil as follows:

> The amount of work that must be done per unit quantity of pure water in order to transport reversibly and isothermally an infinitesimal quantity of water from a pool of pure water at a specified elevation at atmospheric pressure to the soil water (at the point under consideration). (Aslyng et al., 1963, p. 7)

Accordingly, the total potential ψ_t of soil water expressed using the notation and terminology of mechanics is as follows (e.g., Bolt & Miller, 1958):

$$\begin{aligned}\psi_t &= -\int \mathbf{F}_g \cdot d\mathbf{l} - \int \mathbf{F}_{op} \cdot d\mathbf{l} - \int \mathbf{F}_p \cdot d\mathbf{l} - \int \mathbf{F}_{ad} \cdot d\mathbf{l} \\ &= -g \int dh - \upsilon \int d\Pi - \upsilon \int dp - \tfrac{\varepsilon-1}{8\pi}\upsilon \int d\,(\nabla\phi)^2\end{aligned} \tag{2}$$

where d**l** is a displacement vector; $\mathbf{F}_g$, $\mathbf{F}_{op}$, $\mathbf{F}_p$, and $\mathbf{F}_{ad}$ represent the force vectors corresponding to four components of total potential (gravitational, osmotic, pressure, and adsorptive potentials, respectively); g is gravitational acceleration; h is the direction pointing to the center of the Earth; υ is specific volume (i.e., reciprocal density) of water; Π and p are osmotic and gauge pressures, respectively; ε is the dielectric constant of water; and ϕ is electric potential within the electrical double layer (EDL) formed at external surfaces of the soil particles.

The total potential defined from such a mechanical perspective is a scalar negative quantity, which can be determined by the algebraic sum of various components corresponding to different mechanisms altering the water potential in soil (Day et al., 1967). In the most recent literature, the last two terms in Equation 2 (i.e., capillary pressure and adsorptive potential) are generally combined into a single term such that ψ_t is divided into three major components (e.g., Hillel, 1998; Iwata et al., 1995; Lu, 2019a; Or et al., 2005; Osman, 2013):

$$\psi_t = \psi_g + \psi_o + \psi_m \tag{3}$$

where ψ_g is gravitational potential due to the gravitational force field; ψ_o is osmotic potential caused by electrolytes dissolved in the water; and ψ_m is matric potential stemming from the soil–water interactions. Additional terms may also be added to the total potential expression in some particular situations, such as the so-called "overburden potential" specifically implemented for expansive soils (Iwata et al., 1995; Philip, 1969a, 1969b).

Despite these advances, there are still issues to resolve in the above definitions and interpretations of total soil water potential. First of all, comparing Equation 2 with Equation 3, adsorptive potential should be included as a component of matric potential, whereas the latter has been universally defined in literature as the negative capillary pressure, having a magnitude that can be well captured by the YL equation:

$$\psi_m = P_w - P_{air} = \frac{2T_S \cos\alpha}{r} \tag{4}$$

where P_w and P_{air} are pore water and air pressures (Pa), respectively; T_s is surface tension of water (N m^{-1}); α is soil–water contact angle (°); and r is mean principal radius of curvature at the air–water interface (m). Strictly speaking, capillary pressure equal to the pressure difference between pore water and ambient air is only valid under equilibrium conditions, yet nonequilibrium situations that alter such relationship are also found in the field (e.g., Hassanizadeh et al., 2002).

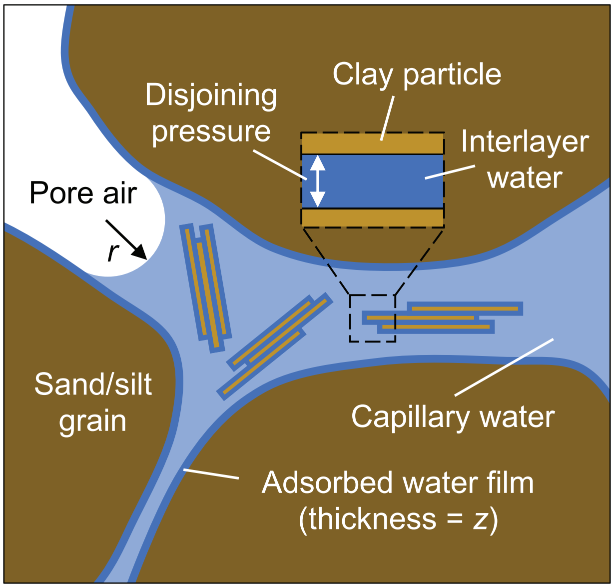

FIGURE 2 Schematic of an unsaturated pore space showing the coexistence of capillary water and adsorbed water films

This common definition of matric potential (i.e., Equation 4) is incomplete (e.g., Or & Tuller, 1999; Tuller et al., 1999) because the adsorptive component is incorrectly excluded, or deliberately ignored by oversimplification. The coexistence of capillary water and adsorbed water films in unsaturated soil has been long recognized (Figure 2), even dating back to Buckingham's 1907 paper in which film water was explicitly distinguished from the capillary water (Buckingham, 1907). Any situation where matric potential can be approximated by capillary pressure (i.e., the difference between pore water pressure and pore air pressure) with precision only occurs in unsaturated soil above the soil–water cavitation pressure (Lu, 2016, 2019b) when capillarity is dominant over adsorption.

Second, although the adsorptive potential presented in Equation 2 considers the effect of the EDL, this is just one of the several adsorptive mechanisms occurring during the process of soil–water interaction. Theoretical calculations and experimental evidence have indicated that other adsorptive forces such as van der Waals attraction and hydration forces can also make important contributions to reducing the soil water potential (Khorshidi et al., 2016; Lu & Zhang, 2019; Tuller & Or, 2005a; Zhang et al., 2017). For this reason, another widely used expression of matric potential, known as the augmented YL equation, was developed to take additional adsorptive mechanisms into account (e.g., Lu & Khorshidi, 2015; Philip, 1977; Tuller et al., 1999):

$$\psi_{\mathrm{m}} = -\frac{2T_{\mathrm{S}}\cos\alpha}{r} + A(z) \tag{5}$$

where the adsorptive component A of matric potential is only a function of thickness z of the adsorbed water film and can be recognized as equivalent to the disjoining pressure termed by Derjaguin et al. (1987). The disjoining pressure has been commonly quantified only by the attractive van der Waals interaction (i.e., the molecular or dispersion component of surface forces), which can be expressed as follows (Derjaguin et al., 1987; Frydman & Baker, 2009; Iwamatsu & Horii, 1996; Tuller et al., 1999; Starov et al., 2007):

$$A(z) = \frac{A_{\mathrm{H}}}{6\pi z^3} \tag{6}$$

where A_{H} is the Hamaker constant between soil and water. Typical values of A_{H} for representative clay minerals range from -3.1×10^{-20} J for kaolinite to -2.2×10^{-20} J for montmorillonite (Lu et al., 2008; Novich & Ring, 1984). Based on the above equation, however, the water pressure is considered as a constant within the entire water film, which is a highly disputable approximation (water pressure profile in the pore space of soil will be discussed in detail in later sections).

Third, the simple superposition of different components of soil water potential, as exhibited in Equations 2 and 3, implies an assumption of independence between individual components, the validity of which remains questionable (e.g., Bolt & Frissel, 1960; Gardner et al., 1951). Direct evidence for this concern is that a higher solute concentration will simultaneously reduce both the osmotic potential of bulk water in soil (i.e., the second term in Equation 2) and the electric potential of the EDL (i.e., the fourth term in Equation 2) (Israelachvili, 2011; Mitchell & Soga, 2005), indicating that the components of total potential defined by either Equation 2 or Equation 3 may be coupled instead of being practically independent of each other.

Furthermore, Iwata (1972a) argued that the concept of mechanical work used in the above definition is inaccurate because the total potential is not always equal in value to the amount of work done upon the water transferred. For instance, if water is considered incompressible (i.e., constant volume with pressure change) for practical purposes, zero mechanical work will be done by increasing the external pressure applied to the soil–water system, whereas during this process the energy state of water (i.e., pressure potential) has actually been changed by compression. With the growing understanding of the energy concept initiated from Buckingham, soil science researchers realized that soil water potential can be better defined using thermodynamic functions to express the energy changes of water over the entire range of conditions found in soil.

3 | THERMODYNAMIC TREATMENT OF SOIL WATER POTENTIAL

The soil water potential concept (e.g., capillary and pressure potentials) defined as above was treated purely in a mechanical sense. Iwata (1972a) criticized the definition of total soil water potential by the ISSS (Aslyng et al., 1963), which considered water potential as the amount of work done on pure water because the pressure potential of confined water can be increased by elevating the external pressure while the external work is zero, considering that water is generally assumed incompressible. He further argued that such potential should essentially stem from a change in the thermodynamic state of water in soil rather than relating to a mechanical concept. Although Buckingham pointed out in his 1907 paper, with much foresight, that the concept of thermodynamic potential or free energy should be used to deal with more complex situations (e.g., effects of solutes) in the soil–water system, the importance of Buckingham's notion was unrealized until almost two decades later. During the interim period there was no follow up for further development in applying the energy concept to study the water flow in soil (or soil–water distribution). The value of this idea had been gradually appreciated and eventually became widespread after 1943, when Edlefsen and Anderson provided a comprehensive summary and detailed introduction to the treatment of thermodynamics of soil water (Edlefsen & Anderson, 1943).

Below, the basic concepts of thermodynamics are first reviewed to underpin the development and evolution of the thermodynamic treatment of soil water. Previous research efforts in using thermodynamic principles to the study of soil water potential are then critically evaluated with an aim to reconcile the controversies among these research efforts.

3.1 | The first and second laws of thermodynamics

A closed thermodynamic system represents a region enclosed in an envelope that allows energy transfer (e.g., heat and work) inside and out but is impermeable to exchange of substance with the surroundings. If no chemical reaction is considered in a closed system (i.e., no change in composition), then the change in the internal energy ΔU of the system can be quantified via the First Law of thermodynamics:

$$\Delta U = \Delta Q - \Delta W \tag{7}$$

where ΔQ is the amount of heat absorbed by the system from the surroundings and ΔW refers to the total work done by the system on the surrounding environment (positive value by convention).

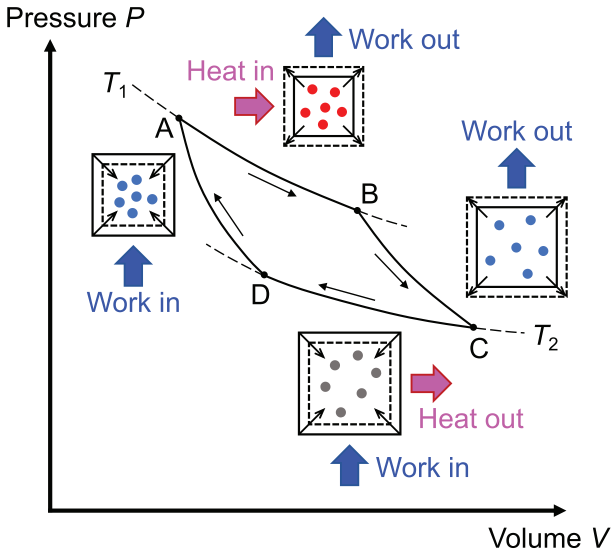

FIGURE 3 Schematic illustration of the relationship between heat flow and useful work in a Carnot cycle, which includes four reversible processes: isothermal expansion at a higher temperature T_1 (A→B), adiabatic expansion (B→C), isothermal compression at a lower temperature T_2 (C→D), and adiabatic compression (D→A)

A Carnot cycle for ideal gas (Figure 3) can be used as an example to intuitively understand the First Law. As shown, heat exchange and work between the gas molecules and their surrounding environment happen throughout the cycle. Along the path from Point A to Point B, a certain quantity of heat enters the system from a hotter environment, during which the gas expands to do work on the environment at constant T_1. Following an adiabatic process from Point B to Point C, the system continues to expand its volume and do work due to inertia, causing the temperature of gas molecules to drop from T_1 to T_2. The system then starts to undergo an isothermal compression (i.e., work done by the surrounding environment) from Point C to Point D and releases heat to a colder environment (T_2). In the last step of the Carnot cycle, the surrounding environment returns the system to its initial state via adiabatic compression, accompanied by rise of the system's temperature from T_2 to T_1. Heat flow between the two heat reservoirs (i.e., hot and cold environments) in a complete Carnot cycle allows the system to output work to the surrounding environment, and the net work done by the system ΔW is calculated by the area enclosed in the four curves (Figure 3):

$$\Delta W = \int P(V)\mathrm{d}V \tag{8}$$

where P is environmental pressure exerted on the system, V is the volume of system, and $\mathrm{d}V$ thus represents the infinitesimal change in its volume.

The work mentioned in the previous paragraph means all types of work and may include both pressure-volume (compression–expansion) work PV and any other work W_m (e.g., mechanical, electrical, magnetic, etc.). Thus, the infinitesimal total work done $\mathrm{d}W$ by a system in a constant-pressure environment is expressed as

$$\mathrm{d}W = P\mathrm{d}V + \mathrm{d}W_\mathrm{m} \tag{9}$$

In addition, the Second Law of thermodynamics infers that for a thermodynamically reversible process, the infinitesimal amount of heat intake $\mathrm{d}Q$ at constant temperature T can be expressed as

$$\mathrm{d}Q = T\mathrm{d}S \tag{10}$$

where S is the entropy of the system. As such, a new form of Equation 7 may be written as

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V - \mathrm{d}W_\mathrm{m} \tag{11}$$

3.2 | Thermodynamic potentials

As early as 1873, American physicist Josiah Willard Gibbs published two important papers in Transactions of the Connecticut Academy of Arts and Sciences (Gibbs, 1873a, 1873b), where he presented a geometrical approach to construct the thermodynamic model with an assumption: "The leading thermodynamic properties of a fluid are determined by the relations which exist between the volume, pressure, temperature, energy, and entropy of a given mass of the fluid in a state of thermodynamic equilibrium" (Gibbs, 1873b, p. 382).

To determine the spontaneity of a chemical reaction at different thermodynamic conditions (e.g., temperature, pressure, volume, etc.), later in 1875, Gibbs followed the idea established by F. Massieu in 1869 and further defined three important and profound thermodynamic functions, namely enthalpy H, Helmholtz's function F, and Gibbs function G (Gibbs, 1875). For a detailed introduction to their motivations and assumptions, interested readers can refer to many thermodynamics textbooks and related references (e.g., Edlefsen & Anderson, 1943; Partington, 1913; Schroeder, 2000).

Below are mathematical expressions of these three functions using the current thermodynamic notation:

$$H = U + PV \tag{12}$$

$$F = U - TS \tag{13}$$

$$G = H - TS = U + PV - TS \tag{14}$$

Each of the above functions is a single equation that condenses all the abovementioned characteristic properties of a fluid (liquid or gas), and the logical reasoning behind such mathematical formulations can be found in Schroeder (2000). In fact, these thermodynamic functions can be switched from one to another or can be directly derived from the internal energy U, by performing Legendre transformations with respect to various state variables (e.g., Epstein, 1937; Pellegrino et al., 2016; Silbey et al., 2004).

The above three thermodynamic functions, together with the internal energy U, are also called the thermodynamic potentials. In most cases, only the infinitesimal changes in these quantities are of practical interest, rather than their absolute values. As such, expressions can be derived by differentiating the above three thermodynamic functions and combining the First and Second Laws of thermodynamics (e.g., Edlefsen & Anderson, 1943; Gardner & Chatelain, 1947; Schroeder, 2000). These are

$$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}P - \mathrm{d}W_{\mathrm{m}} \tag{15}$$

$$\mathrm{d}F = -S\mathrm{d}T - P\mathrm{d}V - \mathrm{d}W_{\mathrm{m}} \tag{16}$$

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P - \mathrm{d}W_{\mathrm{m}} \tag{17}$$

Specifically, enthalpy is a thermodynamic quantity related to the concept of total energy and is captured by the following metaphor:

> To create a rabbit out of nothing and place it on the table, the magician must summon up not only the energy U of the rabbit, but also some additional energy, equal to PV, to push the atmosphere out of the way to make room. (Schroeder, 2000, p. 33)

If the only work done is the pressure–volume work used to expand against the atmosphere, enthalpy then directly quantifies exactly how much heat has been added during such a process.

Similarly, both the Helmholtz function F and the Gibbs function G represent a certain amount of energy that can be recovered from (or must be provided to) the system, provided isothermal/isochoric and isothermal/isobaric conditions, respectively. For instance, based on the partial derivative of Gibbs function (i.e., Equation 17), the nonexpansion work being done by the system during a process with constant temperature and pressure (i.e., $\mathrm{d}T = \mathrm{d}P = 0$) can be calculated as

$$\Delta G = \int \mathrm{d}G = \int -\mathrm{d}W_{\mathrm{m}} = -\Delta W_{\mathrm{m}} \tag{18}$$

In other words, any decrease in value of the Gibbs function (i.e., ΔG) during a reversible process is numerically equal to the useful work (i.e., $-\Delta W_{\mathrm{m}}$) that the system can perform to serve useful purpose, such as in the case of mechanical engines (Epstein, 1937), fuel cells (Schroeder, 2000), biological activities (Levine, 2009), and changes in surface energy (Lewis & Randall, 1923). If the only work performed by a system to its surroundings is the pressure–volume work for expansion or contraction, ΔG would be zero for a reversible process carried out at constant temperature and external pressure (e.g., isothermal phase transformation).

However, most thermodynamic processes in reality are irreversible, during which new entropy is created and hence $\mathrm{d}Q < T\mathrm{d}S$. Then Equation 18 becomes

$$-\Delta G > \Delta W_{\mathrm{m}} \tag{19}$$

which illustrates that the decrease in value of Gibbs function represents the maximum nonexpansion work obtainable from a system in a process under constant T and P. Consequently, the Gibbs function is also commonly called Gibbs free energy or free energy in the literature (same for the Helmholtz function), mainly due to its historical origin with conversion between heat and mechanical work in steam engines (Chatelain, 1949; Epstein, 1937). Nevertheless, although all quantities in Equation 17 have the dimension of energy, the Gibbs function itself is not conserved during an irreversible process, rendering the word “free energy” inappropriate and causing great confusion in practical applications adopted by different research fields (Bazhin, 2012; Schroeder, 2000).

The abovementioned three thermodynamic potentials defined by Gibbs [i.e., $H(S, P)$, $F(T, V)$, and $G(T, P)$] are so-called state functions that use a series of state variables (e.g., U, S, T, P, and V) to describe the state of a thermodynamic system in equilibrium. As such, the change in state function for a process depends only on the initial and final states of system and is independent of the path between any two states. Because the temperature and external pressure generally are two easily measurable macroscopic quantities for a thermodynamic system, the total derivative of the Gibbs function, for example, can be given as

$$\mathrm{d}G = \left(\frac{\partial G}{\partial T}\right)_P \mathrm{d}T + \left(\frac{\partial G}{\partial P}\right)_T \mathrm{d}P \tag{20}$$

and comparison with Equation 17 leads to

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \tag{21a}$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V \tag{21b}$$

where the subscript outside the parenthesis indicates that the other property should be kept constant during the partial differentiation of a specific property, and also signifies the independence between these state variables (Takagi, 1954).

A closed system with no composition change is largely assumed in above derivations for simplicity. When it comes to matter exchange between a system and its surroundings (i.e., an open system), or involving chemical reaction in a closed system, the internal energy of the system should not be only a function of S and V, but also of the amounts of substances contained [i.e., U (S, V, $\{m_i\}$)] (McKay, 1935). Neglecting the entropy change produced by exchange of matter between system and surroundings (Knuiman et al., 2012) and assuming the pressure–volume work for total work done by the system to the surroundings, the differential of U thus becomes

$$\begin{aligned} \mathrm{d}U = \left(\frac{\partial U}{\partial S}\right)_{V,\{m_i\}}\mathrm{d}S + \left(\frac{\partial U}{\partial V}\right)_{S,\{m_i\}}\mathrm{d}V \\ +\sum\nolimits_i \left(\frac{\partial U}{\partial m_i}\right)_{S,V,\{m_{j\neq i}\}}\mathrm{d}m_i \end{aligned} \tag{22}$$

where m_i is the amount (e.g., mass, volume, or mole) of ith substance in the system. Comparing with Equation 11 results in

$$\left(\frac{\partial U}{\partial S}\right)_{V,\{m_i\}} = T \tag{23a}$$

$$\left(\frac{\partial U}{\partial V}\right)_{S,\{m_i\}} = -P \tag{23b}$$

The partial differential coefficient with respect to m_i in the last term on the right side of Equation 22 is defined as chemical potential (denoted by μ_i), representing the internal energy per unit amount of a substance in the system (i.e., an intensive state variable independent of the system size):

$$\mu_i = \left(\frac{\partial U}{\partial m_i}\right)_{S,V,\{m_{j\neq i}\}} \tag{24}$$

According to different thermodynamic conditions and their corresponding potential functions, a family of expressions can be obtained for the chemical potential through Legendre transformations (Day, 1942; Gibbs, 1875; Takagi, 1954):

$$\begin{aligned} \mu_i = \left(\frac{\partial U}{\partial m_i}\right)_{S,V,\{m_{j\neq i}\}} = \left(\frac{\partial H}{\partial m_i}\right)_{S,P,\{m_{j\neq i}\}} \\ = \left(\frac{\partial F}{\partial m_i}\right)_{T,V,\{m_{j\neq i}\}} = \left(\frac{\partial G}{\partial m_i}\right)_{T,P,\{m_{j\neq i}\}} \end{aligned} \tag{25}$$

Chemical potential μ_i at constant T, P, and m_j is thus equal to the partial specific value of Gibbs function G. Likewise, chemical potential is recognized as a state function that can be described by using the state quantities (e.g., T, P, and $\{m_\mathrm{i}\}$) of the system (e.g., Iwata et al., 1995).

3.3 | Previous interpretations of soil water potential using thermodynamic concepts

The preceding thermodynamic principles reveal a unique advantage of the Gibbs function in studying soil water potential over other thermodynamic potentials (e.g., Edlefsen & Anderson, 1943; Slatyer & Taylor, 1960), because temperature and external pressure (usually atmosphere) in Equation 17 are generally easy to determine or control for soil systems (e.g., Gardner & Chatelain, 1947). A decade after the first formal definition of soil water potential by the ISSS in 1963 (Aslyng et al., 1963), this concept was updated again by the second Terminology Committee of Commission I with further detail, and more thoroughly from the perspective of thermodynamics:

> The total potential, ψ_t, of the constituent water in soil at temperature T_0, is the amount of useful work per unit mass of pure water, in J/kg, that must be done by means of externally applied forces to transfer reversibly and isothermally an infinitesimal amount of water from the state S_0 to the soil liquid phase at the point under consideration. (Bolt et al., 1976, p. 18)

The total potential in this later definition specifically represents the energy state of a unit amount of water at a point in soil, with respect to a standard state S_0 under the condition of constant temperature (i.e., the same internal kinetic energy). Although this standard state of water can be arbitrarily selected, the most commonly used definition is as follows:

> …pure (i.e., water not influenced by dissolved salts, or, in other words, water whose osmotic pressure, π, is zero), free (i.e., water not influenced by the solid phase) water at temperature T_0, height h_0 and atmospheric pressure P_0… (Bolt et al., 1976, p. 18)

Based on Equation 18, the concept of useful work used in the 1976 ISSS definition for total potential of soil water clearly follows the framework of the Gibbs function. The total soil water potential, defined as the "amount of useful work per unit mass of pure water" (Bolt et al., 1976), can thus be regarded as the chemical potential of water in soil (Iwata, 1972a, 1972b, 1972c), captured by Equation 25. In light of the important work of Edlefsen and Anderson (1943), various research efforts have been made to revise the formulation and to expand the scope of chemical potential of soil water, mainly for investigating fluid flow problems, swelling behavior, and the phase transition of water in unsaturated soil.

3.3.1 | Selection of thermodynamic state variables

Various thermodynamic state variables have been customized for addressing different practical problems and for accommodating the measurability of state variables. For instance, Babcock and Overstreet (1955) selected water content θ of soil as an additional thermodynamic state variable along with the existing ones (i.e., temperature T, external pressure P, and chemical composition m_i) and wrote the expression for chemical potential $\mu_\mathrm{w}(T, P, \{m_i\}, \theta)$ of water in soil as

$$\begin{aligned} \mathrm{d}\mu_\mathrm{w} &= \left(\frac{\partial U}{\partial T}\right)_{P,\{m_i\},\theta} \mathrm{d}T + \left(\frac{\partial \mu}{\partial P}\right)_{T,\{m_i\},\theta} \mathrm{d}P \\ &\quad + \sum_i \left(\frac{\partial \mu}{\partial m_i}\right)_{T,P,\{m_{j\neq i}\},\theta} \mathrm{d}m_i + \left(\frac{\partial \mu}{\partial \theta}\right)_{T,P,\{m_i\}} \mathrm{d}\theta \end{aligned} \tag{26}$$

where partial specific entropy $\bar{S}$ and partial specific volume $\bar{V}$ can be defined for the first two partial differentials in a similar way to Equation 21a. The third term is known as the osmotic potential dω (Day, 1942; Low & Deming, 1953), but no rigorous thermodynamic relation is available for the last differential. Consequently, Equation 26 may also be rewritten as

$$\mathrm{d}\mu_\mathrm{w} = -\overline{S}\mathrm{d}T + \overline{V}\mathrm{d}P + \mathrm{d}\omega + \left(\frac{\partial \mu}{\partial \theta}\right)_{T,P,\{m_i\}} \mathrm{d}\theta \tag{27}$$

Here, the potentials produced by external force fields (e.g., gravity) were ignored. When gravitational force field is imposed upon an isothermal, solute-free soil system, the same expression as Buckingham's capillary potential can be deduced from Equation 27, provided that the atmospheric pressure gradient is absent (i.e., limited elevation difference) (Babcock & Overstreet, 1957) or the soil is rigid (i.e., $\overline{V} = 0$) (Sposito, 1981). The combined soil–water interactions including capillary effect, van der Waals attraction, and electrical interactions were all lumped into one water content term by Babcock and Overstreet (1955), because they thought that the state variables used for thermodynamic formulations should always be macroscopic properties of the system that were directly measurable. For an isothermal process in a solute-free soil under constant atmospheric pressure (i.e., $\mathrm{d}T = \mathrm{d}P = \mathrm{d}\omega = 0$), an infinitesimal change of chemical potential for the soil–water system would only be affected by the soil's water content, as indicated by Equation 27. However, a change in water content of soil will certainly induce a corresponding change in concentration (i.e., osmotic potential) if the liquid phase is an electrolyte solution, making this treatment generally nonapplicable.

Moreover, hysteresis evident in the SWRC demonstrates that the chemical potential of soil water is not a single-valued function of the water content (or degree of saturation), but rather depends on the path (i.e., wetting or drying) that soil has taken to reach its state (e.g., Bear et al., 1968; Childs, 1957; Haines, 1930; Miller & Miller, 1956; Philip, 1964; Topp, 1971). For nonequilibrium situations, Hassanizadeh and Gray (1993) proposed a rigorous definition of capillary potential to describe the capillary hysteresis observed for the multiphase flow in porous media, and they suggested to also consider the capillary potential as a function of the specific area of fluid–fluid interface besides the degree of saturation. Nonetheless, Tuller et al. (1999) later argued that completely neglecting the surface adsorptive forces made these derivations thermodynamically incomplete.

Iwata also insisted that the total potential of soil water is equivalent to its chemical potential at the same temperature and pressure (Bolt et al., 1976; Iwata, 1972a), while he was serving as a member of the second Terminology Committee of ISSS. However, Iwata pinpointed the issue inherent with the popular treatment in the literature that introduced the water content as a thermodynamic state variable to study the change in chemical potential of soil water. According to his 1972 paper:

> … because water in soil has been dealt with as a homogeneous system. In the author's opinion, water in soil must be a heterogeneous system being influenced by an electric field and Van der Waal's force field. In other words, at equilibrium, though chemical potential shows constant value at any point, the other thermodynamic quantities, including partial internal energy, would give different values depending on the distance from the surface of the soil particles. (Iwata, 1972b, p. 165)

The above conception is consistent with the later theoretical and experimental findings that water density in soil is not always the same as the free water density (i.e., a constant of 0.997 g cm^{-3}) but rather can vary greatly within the range of 0.995–1.872 g cm^{-3} depending on the distance from soil particle surface to location in question (Martin, 1962; Zhang & Lu, 2018, 2020a).

As a result, Iwata et al. (1995) considered using seven different state variables, including temperature, external pressure, solute concentration, surface tension, adsorptive forces, electrical field, and gravitational field, to describe the chemical potential of soil water. He proposed

$$\mathrm{d}\mu_{\mathrm{w}} = -\bar{S}\mathrm{d}T + \bar{V}\mathrm{d}P_i + \sum_i \left(\frac{\partial \mu_{\mathrm{w}}}{\partial C_i}\right)\mathrm{d}C_i + \frac{\partial}{\partial r}\left(\frac{2T_{\mathrm{S}}}{r}\bar{V}\right)\mathrm{d}r + \frac{\partial \varphi}{\partial x}\mathrm{d}x + \frac{\bar{V}}{4\pi}\left(\frac{1}{\bar{\varepsilon}} - 1\right)\mathrm{d}D + g\mathrm{d}h \tag{28}$$

where P_i refers specifically to the water pressure of the ith local system and is the sum of external pressure and internal pressure; C_i is the concentration of ith substance in the system; T_{s} is the surface tension of water defined by energy per unit area; φ is the potential energy of van der Waals force field between soil particle surface and water molecules; x is the distance away from the soil particle surface; $\bar{\varepsilon}$ is the partial dielectric constant; D is the electric displacement; g is the gravitational acceleration; and h is the height above a reference surface. The subscripts for each partial differentiation are eliminated for simplicity.

There are both merits and limitations in Iwata's theoretical construction of chemical potential of soil water. Although a similar strategy to Equations 26 and 28 (i.e., expanding the expression of chemical potential by considering different factors as the state variables) was widely adopted by many researchers (e.g., Babcock, 1963; Babcock et al., 1951; Bolt & Frissel, 1960; Groenevelt & Bolt, 1972; Iwata, 1972b; Iwata et al., 1995; Slatyer & Taylor, 1960), continuously extending the original meaning of chemical potential from Gibbs or chemical engineering community (Equation 25) to cover all effects in soil is in the authors' opinion a misconstruction of the potential function referenced from thermodynamics. Generally, the potential energies of a system as a whole do not affect the internal energy that the system possesses. It is thus more appropriate to not consider the potentials due to the existence of external force fields (e.g., most commonly gravitational force) as part of the traditional chemical potential defined in thermodynamics (Babcock & Overstreet, 1955; Chatelain, 1949). For situations where external force fields X are considered, Bolt and Frissel (1960) defined a quantity called partial specific free energy $\bar{G}_i$ for the ith constituent of the system as

$$\bar{G}_i = \left(\frac{\partial G}{\partial m_i}\right)_{T,P,\{m_{j\neq i}\},X} \neq \left(\frac{\partial G}{\partial m_i}\right)_{T,P,\{m_{j\neq i}\}} = \mu_i \tag{29}$$

where the partial specific free energy $\bar{G}_i$ was clearly distinguished from the concept of chemical potential due to the inconsistency in fundamental definition. A similar argument was also raised by Babcock (1963).

Iwata's treatment of chemical potential of water in soil also double counts the same effect through different parameters. In fact, a constant surface tension T_{s} independent of the radius of air–water interface and the temperature is implicitly assumed in Equation 28. Although the former is generally tenable because most soil pores have much larger radii than the size of a water molecule, experimental data in the literature have revealed the dependence of surface tension (also contact angle) on temperature and hence the capillary potential (e.g., Grant & Bachmann, 2002; Grant & Salehzadeh, 1996). Moreover, the local water pressure term in Equation 28 is determined by the sum of external and internal water pressures (Iwata et al., 1995). Specifically the atmospheric pressure is usually adopted as the external pressure, based upon which the internal pressure is recognized as the increment that develops when soil water is affected by one or multiple external force fields (Gilpin, 1980; Iwata, 1980). However, as will be discussed later in Section 4 in greater detail, this local water pressure is not an independent state quantity for the soil water potential. Changes in any adsorptive components, including but not limited to the van der Waals force field (φ) and electric field (D) of Equation 28, will lead to a corresponding alteration in the water pressure term.

3.3.2 | Selection of thermodynamic system

Due to the compositional heterogeneity intrinsic to unsaturated soil as a three-phase material (i.e., soil solid, water, and gas), different selections of the thermodynamic system have been designated for different thermodynamic state variables, further complicating the definition of soil water potential. For example, if water content is adopted as one of the state variables, as demonstrated in Equation 27, then the soil–water–air system can be regarded as one homogeneous system (Takagi, 1959). The same thermodynamic treatment can also be found in the analysis of clay swelling behavior, in which the entire swelling clay–water system is assumed to be macroscopically homogeneous and its volume is chosen as a state variable (Sposito, 1972, 1973). Alternatively, the water phase or water containing dissolved solutes is more often treated as a system by itself, for which soil particles and gaseous phases are considered as the boundaries.

Bolt and Frissel (1960) conducted a review on the implementation of thermodynamic analysis to the study of soil water potential and summarized that each of the two categories mentioned above for system selection can be further divided into two subsets termed macro- and micro-approaches. The micro-approach, as its name implies, focuses on a local infinitesimal point inside a larger water body, whereas the latter is the object selected by the macro-approach. In other words, the approaches are separated mainly in terms of the scale of the test body. Because these four means of system selection are prone to use diverse state variables to suit their own needs on the thermodynamic treatment, different meanings may sometimes be imposed to the same variable, most commonly appearing on the pressure term. For example, Babcock and Overstreet (1955) follow a macro-approach in analyzing a homogeneous soil–water–air system, because they considered water content of the soil as a state variable and defined the pressure term in Equation 27 as the external atmospheric pressure. On the contrary, Iwata et al. (1995) treated the water phase as one system by itself and adopted a micro-approach in Equation 28 to emphasize water adsorption occurring near the soil–water interface.

Beyond the selection of thermodynamic system, Arthur T. Corey and his collaborators criticized the previously defined concept of total water potential for not making clear distinction between state variables used for the soil water solution and those solely used for water, considering that water is only one of the multiple constituents in a water solution (Corey & Kemper, 1961a, 1961b; Corey & Klute, 1985; Corey et al., 1967). Corey and Kemper (1961a) classified water movement in soil into convection (motion of bulk solution including all constituents) and diffusion (motion of water only). Because osmotic pressure only develops in the presence of a rigid semipermeable membrane, which constrains the movement of ions but not water molecules, they hypothesized that the potential function used for prediction of water flow direction should also include the properties of porous medium in addition to the state of the water. They further presented an idealized thought experiment and demonstrated that the gradient of total potential did not always indicate the direction of net transport of water. Critiques on this opinion were written by Philip F. Low, who noted that Corey and Kemper's hypothesis that "challenges the basic tenets of thermodynamics" (Low, 1961a, 1961b).

4 | UNITARY DEFINITION OF SOIL WATER POTENTIAL

Though the Gibbs free energy has been widely used to represent the energy stored in soil water available for physical interactions with its surrounding environment, there is still not a consensus definition for soil water potential. As summarized above, previous interpretations of the origins or mechanisms of soil water potential are elusive, selective, controversial, or even contradictory. With the aid of recent breakthroughs in theorizing the SSP, an unambiguous definition of soil water potential is presented in this section, via a generalized thermodynamic treatment and inclusive identification of all fundamental elements that alter the soil water potential. Although some of these elements have been introduced in the existing literature, it is important not to misinterpret, overlook, or duplicate the effects of all factors involved.

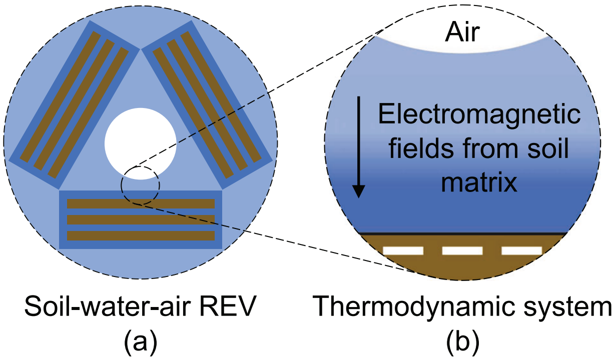

FIGURE 4 Conceptual illustration of (a) soil–water–air representative elementary volume (REV) and (b) thermodynamic system selected for unitary definition of soil water potential

4.1 | A generalized thermodynamic treatment of soil water potential

The REV selected for the unitary soil water potential contains all three phases of the soil system, including soil solids, water, and air (Figure 4a). In this soil–water–air REV, capillarity relates to the "interfacial free energy" that encompasses all the dynamic and kinematic effects (intermolecular tension among water molecules) along the air–water interface (Lu & Zhang, 2019; Schwartz, 2002). Therefore, extending Equation 22 renders the following formulation for the infinitesimal change in internal energy of the water phase:

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + \sum_i \mu_i \mathrm{d}m_i + \gamma \mathrm{d}A_{\mathrm{aw}} \tag{30}$$

where P is the external air pressure (Pa); γ is the specific interfacial free energy of water (J m^{-2}), numerically equal to the surface tension T_{s} (N m^{-1}); and A_{aw} is area of the air–water interface (m^2). To avoid the issue of double counting and maintain simplicity, an isothermal condition (i.e., $\mathrm{d}T = 0$) is assumed for the derivations below. Considering the total derivative of Equation 14, the infinitesimal change in Gibbs function is then written as

$$\begin{aligned}\mathrm{d}G &= \mathrm{d}U - T\mathrm{d}S + V\mathrm{d}P + P\mathrm{d}V \\ &= V\mathrm{d}P + \sum_i \mu_i \mathrm{d}m_i + \gamma \mathrm{d}A_{\mathrm{aw}}\end{aligned} \tag{31}$$

As previously mentioned, potential energies possessed by a system placed in external force fields should not be considered as part of the internal energy of the system. In the derivation below, the infinitesimal change in potential energy (denoted as $\mathrm{d}\Phi$) of the soil–water system will be used in lieu of the nonexpansion work $\mathrm{d}W_{\mathrm{m}}$ in Equation 9, and the electromagnetic fields generated by soil are thus isolated from the thermodynamic system to act as the external force fields like gravity (Dinulescu, 1979). Two major potential energies are commonly identified in soil: gravitational potential energy $\mathrm{d}W_{\mathrm{g}}$ and electromagnetic potential energy $\mathrm{d}W_{\mathrm{em}}$, according to the types of interactions between water molecules and the external force fields. Consequently, the total static energy of a soil–water–air REV can be described by a general characteristic function $\mathrm{d}\Psi$ defined as the sum of Gibbs function $\mathrm{d}G$ (internal) and potential energy function $\mathrm{d}\Phi$ (external) due to energy conservation (e.g., Chatelain, 1949; Groenevelt & Bolt, 1969; Iwata, 1972b; Low, 1951):

$$\mathrm{d}\psi = \mathrm{d}G + \mathrm{d}\Phi = V\mathrm{d}P + \sum_i \mu_i \mathrm{d}m_i + \gamma \mathrm{d}A_{\mathrm{aw}} + \mathrm{d}W_{\mathrm{g}} + \mathrm{d}W_{\mathrm{em}} \tag{32}$$

Referenced to the pure water at standard state (i.e., $\Psi_0 = 0$), the infinitesimal change in Ψ for the soil water (i.e., $\mathrm{d}\Psi$) represents the current energy state of the soil–water–air REV. Consequently, the total soil water potential ψ_{t}, which can be recognized as the intensive form of the characteristic function Ψ, is derived in a similar way to the definition of chemical potential (Equation 25) as

$$\psi_{\mathrm{t}} = \mu_{\mathrm{w}} + \varphi_{\mathrm{w}} = \bar{V}\mathrm{d}P + \sum_{i=1}^{k-1} \left(\frac{\partial \mu_{\mathrm{w}}}{\partial C_i}\right)_{P,T,\{C_{j\neq i}\},W} \mathrm{d}C_i + \frac{\partial}{\partial r}\left(\frac{2\gamma}{r}\bar{V}\right)\mathrm{d}r + w_{\mathrm{g}} + w_{\mathrm{em}} \tag{33a}$$

where φ_{w} refers to the sum of various types of potentials (e.g., gravitational potential w_{g} and electromagnetic potential w_{em}) that unit quantity of soil water possesses; and C_i is the concentration of the ith component of the system having k components, among which only $k-1$ are independent. Rearranging Equation 33a leads to:

$$\psi_{\mathrm{t}} = w_{\mathrm{g}} + \sum_{i=1}^{k-1} \left(\frac{\partial \mu_{\mathrm{w}}}{\partial C_i}\right)_{P,T,\{C_{j\neq i}\},W} \mathrm{d}C_i + \bar{V}\mathrm{d}P + \frac{\partial}{\partial r}\left(\frac{2\gamma}{r}\bar{V}\right)\mathrm{d}r + w_{\mathrm{em}} \tag{33b}$$

The fifth term on the righthand side of Equation 33b represents the change in chemical potential of soil water due to the change in principal radius of curvature r at the air–water interface (Iwata et al., 1995). Comparing with Equation 3, the last three terms of Equation 33b are collectively called the matric potential, whose unitary definition will be given in a later section after first identifying all of the physicochemical mechanisms of soil–water interaction.

It is worth pointing out that the total potential ψ_{t} of soil water will only be equal to its chemical potential μ_{w} in the absence of external force fields (i.e., $\varphi_{\mathrm{w}} = 0$), according to Equation 33a. The so-called chemical potential (or the specific Gibbs free energy) that is defined through a continuously extended way no longer has the same meaning as the one originally used by Gibbs. Instead, the thermodynamic potential functions defined as such are completely new characteristic functions customized for solving specific problems, as has been pointed out by many researchers (Babcock, 1963; Bear & Nitao, 1995; Bolt & Frissel, 1960; Chatelain, 1949; Low, 1951; Low & Deming, 1953; Sposito, 1975). Therefore, misuse of the concept of chemical potential should be avoided to prevent confusion in future studies of soil–water potential for unsaturated soil. Motivated by the same reasoning, Lu and Zhang (2019) suggested to decompose the "total chemical potential" into external and internal chemical potentials. Similar to Equation 33a, the former describes the thermodynamic energy state associated with the internal interactions inside the system and the latter is induced by the interactions with external force fields.

4.2 | Environmental factors

For pure water in a large enough open container at some reference datum (Figure 5a), if the flat air–water surface is under standard atmospheric pressure (i.e., $P_{\mathrm{atm}} = 101$ kPa), then the water pressure in a REV of water right underneath the water surface is equal to the atmospheric pressure. Once the reference level of gravity is chosen at the center of the REV, the total water potential ψ_{t} therein is commonly defined as zero (i.e., equivalent to the free water) (e.g., Or et al., 2005):

$$\psi_{\mathrm{t}} = 0 \tag{34}$$

As demonstrated in both Equations 3 and 33b, the total water potential in unsaturated soil will be altered from the reference state by many factors, including external air pressure, solutes, and matric effects. The previous two are classified as environmental factors that can affect the water potential for all occasions, whereas the last one (i.e., matric potential) only occurs in the presence of the soil matrix. Environmental factors that can potentially affect the water potential in soil will be first summarized here.

4.2.1 | Gravitational force field

Gravity is the most common force field on the earth that universally affects substance having mass. Considering the same REV as that in Figure 5a, the REV starts to possess gravitational potential ψ_{g} if the container is lifted to a height of Δh above the datum (Figure 5b):

$$\psi_{\mathrm{g}} = \rho_{\mathrm{w}} g \Delta h \tag{35}$$

where ρ_{w} is water density (0.997 g cm^{-3} for free water at 25 °C); and g is gravitational acceleration (9.81 m s^{-2}). The datum is an artificially selected reference level, such as h_0 shown in Figure 5a. For soil water, as long as a datum is chosen, the gravitational potential will be determined by the work performed against gravity to move a unit amount of

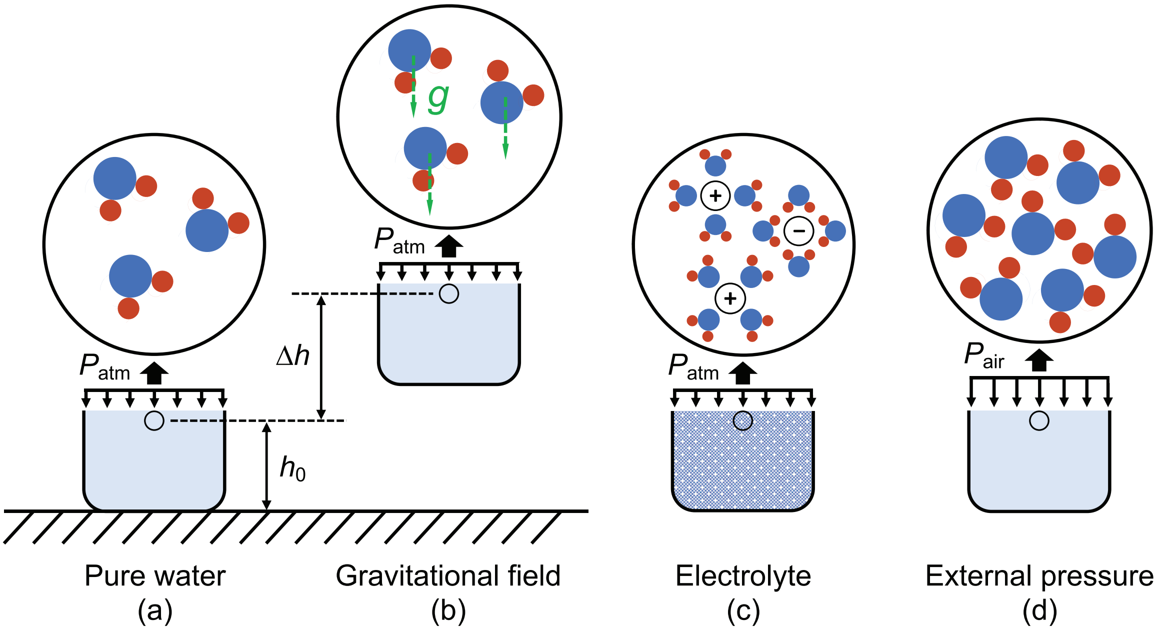

FIGURE 5 (a) Reference state of water and (b–d) three environmental factors affecting the total potential of soil water, without the involvement of soil particles

water from its original position to the reference level. Thus, an absolute magnitude of gravitational potential is meaningless. Also, the gravitational potential is usually unimportant in many cases unless dealing with a large-scale problem atypical for many applications in soil systems. For example, the gravitational potential of soil water at 1-m height is only ∼10 kPa, which is far less than the other components of soil water potential discussed below and is negligible in unsaturated soil.

4.2.2 | Electrolytes (osmosis)

Most of the earth surface is covered by soils that contain electrolytes to different extents. Practical problems of interest include the soil salinization problem commonly encountered near coastlines (e.g., Daliakopoulos et al., 2016), road salt (i.e., a deicing agent) contamination frequently occurring in regions with annual snowfall (e.g., Robinson & Hasenmueller, 2017), among many others. When charged solute is dissolved in water, the polar water molecules will be attracted to the electrolyte cations and anions due to the hydration force, which reduces the water potential in the electrolyte solution and produces the osmotic potential.

A U-shaped tube with two sides separated by a semipermeable membrane (permeable to water molecules but not ions) has been widely used to illustrate the osmotic potential (e.g., Stillwell, 2016). Considering a U-shaped tube with equal diameter throughout, filling the tube with pure water will produce the same water levels on both sides of the tube at equilibrium. If solute is only added to one side of the membrane, water molecules driven by the osmotic potential gradient will move from the side of pure water (higher water concentration or lower solute concentration) to that of electrolyte solution (lower water concentration or higher solute concentration), causing the level of the tube containing the salt solution to rise. Because a difference in water level will also generate a hydrostatic pressure gradient acting opposite to the osmotic gradient at the membrane, the osmotically driven flow will continue until the two sides have the same water potential. The magnitude of osmotic potential ψ_o for the REV presented in Figure 5c, for dilute solution, can be approximated by the van't Hoff equation (e.g., Lachish, 2007):

$$\psi_o = -\upsilon_i CRT \tag{36}$$

where υ_i is the van't Hoff factor of electrolyte (e.g., $\upsilon_i = 2$ for NaCl crystals completely dissolved in water); C is the concentration of solute (mol m^{-3}); R is the universal gas constant (8.3145 J mol^{-1} K^{-1}); and T is the absolute temperature (K). The negative sign indicates that the presence of solute will lower the water potential in an electrolyte solution.

4.2.3 | External pressure

The osmotic-induced flow can be reversed by increasing the external pressure, either through air pressure or other physical contacts (e.g., piston force), acting on the side of the tube containing electrolyte solution. The external pressure will be identical in magnitude to the osmotic pressure when the water levels on both sides of the U-shaped tube are brought back to the same height by pressure-driven flow (Baumgarten & Feher, 2012). The air pressure applied to the water surface in soil can often deviate (either increase or decrease) from the standard atmospheric pressure. For instance, air pressure can be higher than atmosphere in a confined pore space, whereas it decreases with increasing altitude. Therefore, the water potential ψ_{Pe} in the same REV (Figure 5d) is determined by the difference between the ambient air pressure (or pore air pressure) P_{air} and the standard atmospheric pressure P_{atm}:

$$\psi_{\mathrm{pe}} = P_{\mathrm{air}} - P_{\mathrm{atm}} \tag{37}$$

where in Figure 5d $P_{\mathrm{air}} \geq 0$.

4.3 | Physicochemical mechanisms for matric potential

Based on a designated reference state (e.g., without the involvement of environmental factors), matric potential ψ_{m} quantifies the change in energy state of water in soil due to physicochemical interactions between soil particles and water molecules. The matric potential can vary over six orders of magnitude from 0 kPa (for full saturation below water table) to -1.6×10^6 kPa (for approximate oven dryness) under natural and laboratory conditions, rendering it the most prominent factor that dominates the soil water potential. As such, the total soil water potential ψ_{t} is conventionally reducible to the matric potential ψ_{m} when the environmental factors are ignored. Once the soil–water system is in equilibrium with water vapor of the ambient environment, the soil water potential can be expressed as a function of relative humidity (RH) (i.e., the ratio of water vapor pressure to air pressure) via Kelvin's equation (e.g., Lu & Likos, 2004):

$$\psi_{\mathrm{t}} = \psi_{\mathrm{m}}(\theta) = \frac{RT}{\upsilon_{\mathrm{w}}} \ln\left[\mathrm{RH}(\theta)\right] \tag{38}$$

where υ_{w} is the molar volume of water (1.8×10^{-5} m^3 mol^{-1} at standard temperature and pressure).

It is generally accepted that three regimes can be conceptualized on a SWRC (i.e., matric potential vs. soil water content) in the order of decreasing soil water content: namely, capillary, adsorbed film, and tightly adsorbed regimes (Lu & Khorshidi, 2015; Lu & Likos, 2004; McQueen & Miller, 1974). Each of these SWR stages are controlled by one or more mechanisms of soil–water interaction, in terms of their magnitudes of free energy change relative to free water. In this section, individual physicochemical mechanisms will be unraveled from the matric potential and will be revisited with an aim to synthesize a unitary definition of matric potential. For the purpose of illustration and visualization, a platy shape is assumed for soil particles in the following context, and an angular geometry is used to represent the macropores in unsaturated soils that contain both water and air (Tuller et al., 1999).

4.3.1 | Capillarity

Capillarity describes phenomena in which a curved gas–liquid interface (i.e., meniscus) is present among the three phases of solid, liquid, and gas (van Honschoten et al., 2010). The angle measured inside the liquid phase from the solid surface to the gas–liquid interface is called the contact angle and reflects the surface energy of the solid macroscopically. The surface of a solid with higher surface energy is generally hydrophilic, corresponding to a smaller contact angle, or less than 90°, and vice versa.

Specifically for unsaturated soil, water menisci are often formed at the corners of micrometer-sized pores, showing a curvature convex towards the air phase. Unlike the flat air–water surface observed in an open container (Figure 5a), the curved air–water interface formed in this case produces a sudden pressure drop from air to soil water due to the existence of surface tension. The magnitude of this pressure deficiency can be determined from the YL equation:

$$P_{\mathrm{air}} - P_{\mathrm{w}} = 2T_{\mathrm{S}}\kappa_{\mathrm{aw}} \tag{39}$$

where κ_{aw} is mean curvature of the meniscus. For a two-particle system with toroidal approximation to the meniscus curvature, $2\kappa_{\mathrm{aw}}$ can be well defined using cylindrical coordinates with polar axis a and longitudinal axis b (e.g., Lechman & Lu, 2008):

$$2\kappa_{\mathrm{aw}} = \frac{1}{a\left(1+\dot{a}^2\right)^{1/2}} - \frac{\ddot{a}}{\left(1+\dot{a}^2\right)^{3/2}} \tag{40}$$

where $\dot{a} = \mathrm{d}a/\mathrm{d}b$ and $\ddot{a} = \mathrm{d}^2a/\mathrm{d}b^2$. Based on a two-dimensional double-curvature concept idealized from the saddle-like geometry of capillary water, Equation 39 can be written as (e.g., Lu & Likos, 2004)

$$P_{\mathrm{air}} - P_{\mathrm{w}} = T_{\mathrm{S}}\left(\frac{1}{R_1} - \frac{1}{R_2}\right) \tag{41}$$

where R_1 and R_2 are the two principal radii of curvature of the air–water–soil interface, and they depend on soil's pore size and shape distribution. To aid the physical interpretation of the above relationship, the geometry of air–water–soil interface is approximated by a spherical meniscus (Figure 6a), as commonly conceptualized in the bundled capillary tube model (Tuller & Or, 2005b). Then Equation 39 can be

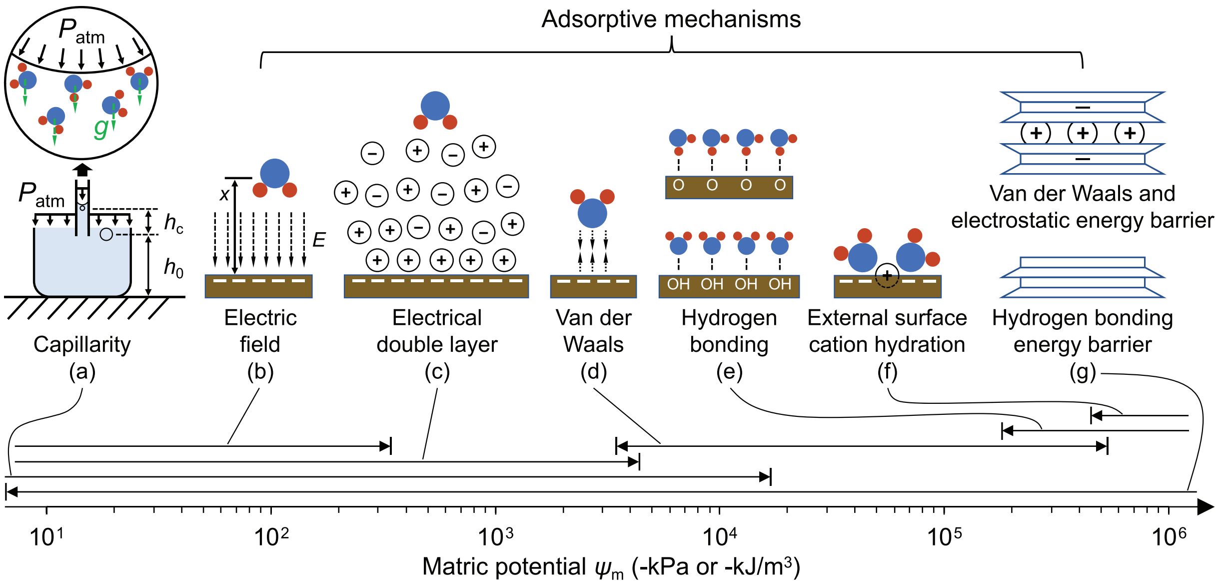

FIGURE 6 Change of matric potential due to the physicochemical interactions between water molecules and negatively charged clay particles: (a) pressure drop across the air-water interface caused by capillarity; (b–f) independent mechanisms mainly contributing to the water adsorption and soil sorptive potential; and (g) energy barrier provided by attractive forces between adjacent 2:1 (top) and 1:1 (bottom) clay layers

simplified as

$$P_{\mathrm{air}} - P_{\mathrm{w}} = \frac{2T_{\mathrm{S}} \cos \alpha}{r} \tag{42}$$

where r is radius of the capillary tube analogous to the mean pore radius in soil; and α is contact angle between the water and the tube. Hence, the capillary potential (or capillary pressure) ψ_{cap} is obtained by

$$\psi_{\mathrm{cap}} = P_{\mathrm{w}} - P_{\mathrm{air}} = -\frac{2T_{\mathrm{S}} \cos \alpha}{r} \tag{43}$$

The capillary water pressure calculated above is also widely called the negative pressure in the literature (e.g., Frydman & Baker, 2009; Mendes et al., 2019; Tarantino & Mongiovì, 2001), because for soil particles with hydrophilic surfaces, the intermolecular tension developed along the air–water interface always reduces the water pressure below the pore air pressure.

According to the water phase diagram and nucleation theories, liquid water is in the metastable state if the water pressure is lower than the prevailing vapor pressure, rendering phase transition from liquid to vapor energetically favorable (Caupin & Herbert, 2006; Debenedetti, 1996; Maris & Balibar, 2000). Such an isothermal phase change due to tension is known as cavitation, which has been recognized as an important mechanism for SWR (Lu, 2016; Luo & Lu, 2021). During the desaturation of soil, the entrapped bubbles on rough surfaces of soil particles are mostly responsible for the soil water cavitation occurring in relatively large pores with sizes of at least sub-micrometer (Luo et al., 2021). A wide range of cavitation pressures, ranging from −7 to −28 MPa, has been experimentally measured in different studies (Briggs, 1950; Caupin & Herbert, 2006; Duan et al., 2012), depending on the experimental techniques (e.g., acoustic burst and centrifugation) and the purity of water. The practical consequence is that capillarity will only be the dominant mechanism of soil–water interaction at matric potential much greater than −20 MPa (e.g., Luo & Lu, 2021; Tuller & Or, 2005a), in which the capillary potential ψ_{cap} can be considered as equal to the matric potential ψ_{m} with sufficient accuracy.

4.3.2 | Adsorption on external mineral surfaces

Adsorptive mechanisms become significant or even dominate soil–water interactions at the medium to low matric potential range (−10 to −1,000 MPa) (Bolt & Miller, 1958; Edlefsen & Anderson, 1943; Philip, 1977). Fine-grained soils, and especially clays, generally have a much larger specific surface area (SSA) than coarse-grained soils, which favors water retention by adsorption. In addition to the presence of fine particle sizes (<2 μm), clay minerals are also negatively charged at the mineral surface as the result of isomorphous substitution, which is a structural defect naturally occurring in the tetrahedral sheet and octahedral sheet (Moore & Reynolds, 1997; Tournassat et al., 2015). Net negative charges in the crystal structure attract positive cations to the clay surface (or interlayer space) to compensate for the charge deficiency such that an overall electric neutrality can be achieved for the clay–water–ion system. Most of these cations are loosely bonded to the clay surface and are exchangeable with the pore fluid, giving most fine-grained soils a so-called cation exchange capacity (CEC) and resulting in an even higher water adsorption capacity.

Water adsorption on soil particle surfaces is dictated in the broadest sense by five independent physicochemical mechanisms, including electrical field polarization, EDL, van der Waals attraction, cation hydration, and hydrogen bonding. The sections below explain how the soil water potential is altered by each individual mechanism, with magnitudes theoretically quantified by considering a parallel-plate configuration commonly assumed for clays (i.e. the pore space is formed by two semi-infinite [length > > width] platy clay particles parallel to each other).

Electric field

Neglecting the small edge (pH dependent) charges due to breakage or discontinuity of mineral crystals, the net negative charges on surfaces of clay particles will produce a local electric field that attracts not only cations but also water molecules due to their polar nature (Figure 6b). The electric dipole interaction enables water molecules to store an electric potential energy through electrostatic interaction with the electric field. For a water molecule located at a distance x away from the clay particle (Figure 6b), the magnitude of electrical potential ψ_{ele} can be estimated as (Lu & Zhang, 2019)

$$\psi_{\mathrm{ele}}(x) = \frac{1}{2}\varepsilon_0\left(1 - \varepsilon_{\mathrm{r}}\right)\sum\nolimits_{i=1}^{N} \mathbf{E}_i^2(x) \tag{44}$$

where ε_0 is permittivity of a vacuum (8.85×10^{-12} C^2 N^{-1} m^{-2}); ε_{r} is relative permittivity (i.e., dielectric constant) for water (78.54 at 25 °C); N is the number of clay particles; and $\mathbf{E}_{\mathrm{i}}(x)$ is a vector indicating the electric field intensity (V m^{-1}) of the ith particle, which can be calculated by

$$\mathbf{E}_i(x) = \frac{4k_{\mathrm{B}}T\kappa\xi_i}{e}\frac{\exp(\kappa x)}{\exp(2\kappa x) - \xi_i^2} \tag{45}$$

$$\kappa = \sqrt{\frac{2CN_{\mathrm{A}}e^2}{\varepsilon_0\varepsilon_{\mathrm{r}}k_{\mathrm{B}}T}} \tag{46}$$

$$\xi_i = \tanh\left(\frac{eV_{\mathrm{EDL0},i}}{4k_{\mathrm{B}}T}\right) \tag{47}$$

where $1/\kappa$ is EDL thickness (nm) and ξ_i is a function of surface potential $V_{\mathrm{EDL0},i}$ (mV) of the ith clay particle; k_{B} is the Boltzmann constant (1.38×10^{-23} m^2 kg s^{-2} K^{-1}); e is charge of an electron (1.60×10^{-19} C); C is bulk concentration of salt (mol m^{-3}); and N_{A} is Avogadro's number (6.02×10^{23} mol^{-1}).

Electrical double layer

Similar to the exchangeable cations for dry clays, a clay particle in the presence of water will also be surrounded by hydrated cations in order to achieve electric neutrality. These loosely bonded exchangeable cations will diffuse away from the particle surface and effectively become point charges drawing the anions in the water. Consequently, cations and anions will reorient their spatial distributions, forming an EDL around the clay particle (Figure 6c). This electrostatic interaction between soil and water has been conceptualized and modeled by various EDL theories (Israelachvili, 2011; van Olphen, 1977). The first layer of the EDL is called the Stern layer, in which cations orderly gather around the clay particle and cover the particle surface with low mobility. Because the cations become larger in effective size upon hydration, the negative mineral surface charge cannot be completely balanced by the Stern layer. Additional layers containing mixtures of cations and anions are thus necessary to neutralize the surface charge residual (Figure 6c). These outer layers only weakly interact with the clay particles and gradually diffuse into the bulk pore water, and thus the EDL is also commonly called a diffuse double layer.

The ionic concentration within the EDL decreases with increasing distance from the clay surface until eventually returning to the concentration in the bulk, or far-field, pore water. As such, a boundary condition is set up by the bulk pore water concentration (if solute is present) that controls the thickness of EDL. The constraint to ion movement imposed by the electric field generated by the clay particle makes the clay–water–ion system behave in a similar way to a semipermeable barrier (e.g., Malusis & Shackelford, 2002; Wei, 2014). The gradient of ionic concentration in the EDL depends on the distance x from the clay surface (i.e., being less enriched in the outer layer than the inter layer). Consequently, an osmotic water potential is created within the EDL with magnitude ψ_{osm} formulated as (Lu & Zhang, 2019)

$$\psi_{\mathrm{osm}}(x) = -CN_{\mathrm{A}}k_{\mathrm{B}}T\left\{\begin{aligned} &\exp\left[\frac{e}{k_{\mathrm{B}}T}\sum\nolimits_{i=1}^{N}V_{\mathrm{EDL},i}(x)\right] \\ &+\exp\left[-\frac{e}{k_{\mathrm{B}}T}\sum\nolimits_{i=1}^{N}V_{\mathrm{EDL},i}(x)\right] - 2\end{aligned}\right\} \tag{48}$$

where $V_{\mathrm{EDL},i}(x)$ is the electric potential at distance x from the clay particle surface. Note that the above osmotic component of matric potential ψ_{osm} is different than the osmotic potential caused by the solute dissolved in water ψ_{o}. The former always occurs in clay even if the bulk pore water contains no electrolyte, whereas the latter defines the boundary condition of the EDL.

van der Waals forces

van der Waals interaction is a collection of intermolecular attractive forces that universally exist in all substances. Molecules that are electrically neutral can have either permanent dipoles (e.g., water) or dipoles that are temporarily induced by a nearby dipole (e.g., carbon dioxide). Based on the causes of interaction, van der Waals forces can be divided into Keesom force (dipole–dipole interaction), Debye force (dipole-induced dipole interaction), and London force (instantaneous dipole-induced dipole interaction), which are all related to the fluctuation of electron orbital clouds when two objects approach a close enough distance (Israelachvili, 2011).

The van der Waals attraction for soil–water systems always exists between the atoms in the mineral crystals and adjacent water molecules (Figure 6d), leading to a reduction in water potential. The van der Waals attraction is also the major mechanism responsible for multilayer adsorption on clay surfaces. The magnitude of van der Waals attraction can be roughly estimated by the disjoining pressure using Equation 6, from which the van der Waals component of matric potential for the first layer ($h = 0.14$ nm) of adsorbed water is calculated as around −599 MPa (Figure 6d). It should be noted, however, that the above formulation of disjoining pressure only calculates the water potential caused by multilayer adsorption as a quantity averaged from the entire water film. The van der Waals component of matric potential ψ_{vdW} can be calculated for a parallel-plate configuration to idealize the pore structure, based on a more realistic model that considers both the finite size of clay particle and differentiates the dependence of van der Waals attraction on the local distance x to the particle surface (Lu & Zhang, 2019):

$$\psi_{\mathrm{vdW}}(x, y) = \frac{A_{\mathrm{H}}}{24\pi}\sum_{i=1}^{N}\left[\begin{array}{l} \dfrac{2y_i^4+y_i^2(x_i+t_i)^2+2(x_i+t_i)^4}{y_i^3(x_i+t_i)^3\sqrt{y_i^2+(x_i+t_i)^2}} \\ -\dfrac{2(y_i-B_i)^4+(y_i-B_i)^2(x_i+t_i)^2+2(x_i+t_i)^4}{(y_i-B_i)^3(x_i+t_i)^3\sqrt{(y_i-B_i)^2+(x_i+t_i)^2}} \\ -\dfrac{2x_i^4+x_i^2y_i^2+2y_i^4}{x_i^3y_i^3\sqrt{x_i^2+y_i^2}}+\dfrac{2(y_i-B_i)^4+(y_i-B_i)^2x_i^2+2x_i^4}{(y_i-B_i)^3x_i^3\sqrt{(y_i-B_i)^2+x_i^2}} \end{array}\right] \tag{49}$$

where B_{i} and t_{i} are the width and thickness of the ith platy clay particle, assuming infinite length; x_i and y_i are the relative distances from the location of interest to the ith particle surface and correspondingly to the particle edge, respectively. The formulation can be further simplified if only the centerline of pore space (i.e., $y_i = 0.5B_i$) is of interest.

Hydrogen bonding

For a 1:1 clay mineral (i.e., including one tetrahedral sheet and one octahedral sheet) such as kaolinite, both the oxygen atoms in the tetrahedral sheet and the hydroxyl groups in the octahedral sheet will be exposed on the particle surface after cleavage (Sposito et al., 1999). Only the oxygen atoms will be present on the particle surface of 2:1 type (tetrahedral–octahedral–tetrahedral) clay minerals (e.g., illite and montmorillonite) by comparison. As demonstrated in Figure 6e, the oxygen atoms on the surface tend to attract the positive charge ends of water dipoles, forming the so-called hydrogen bond (Johnston, 2010). The surface hydroxyls, likewise, will form hydrogen bonds with the negative ends of water molecules. This phenomenon is herein referred to as surface hydration, having magnitude that can be determined as (e.g., Lu & Zhang, 2019):

$$\psi_{\mathrm{s-hyd}}(x) = \sum_{i=1}^{N}\psi_{\mathrm{s-hyd0}}\exp\left(-\frac{x_i}{\lambda_{\mathrm{s}}}\right) \tag{50}$$

where $\psi_{\text{s-hyd0}}$ is surface hydration component adjacent to particle surface (J m^{-3}) and λ_{s} is the decay length of surface hydration component (0.2–1.0 nm).

Reduction in water potential induced by surface hydration (Figure 6e) can be as low as −691 to −2,893 MPa (e.g., Tunega et al., 2004; Wang et al., 2006; Zhang et al., 2017), such that surface hydration is also important for adsorption in soil and can occur nearly simultaneously with the cation hydration. Therefore, despite sandy and silty soils with almost negligible CEC, the hydroxyl groups still prevail at the particle surface to accommodate the crystal instability, allowing surface hydration to play a role and make the surface hydrophilic (Zhuravlev, 2000).

Cation hydration

As mentioned previously, cations present in the Stern layer or in the hexagonal hole of the tetrahedral sheet (Figure 6f) will be surrounded by water molecules through cation–dipole (electrostatic) interaction when clay is in contact with water. The cation hydration component of matric potential $\psi_{\text{c-hyd}}$ can be determined by (e.g., Lu & Zhang, 2019):

$$\psi_{\mathrm{c-hyd}}(x) = \sum_{i=1}^{N}\left\{\begin{array}{l} \dfrac{ZeuN_{\mathrm{A}}}{4\pi\varepsilon_0\upsilon_{\mathrm{w}}}\left[\dfrac{3}{4\pi}\,\dfrac{\mathrm{SSA}\times Z(x_i-x_0)}{\mathrm{CEC}\times N_{\mathrm{A}}}+r_{\mathrm{h}}^3\right]^{-\frac{2}{3}} \\ \times\dfrac{\cos\gamma_0}{\varepsilon_{\mathrm{r0}}}\exp\left(-\dfrac{x_i}{\lambda_{\mathrm{c}}}\right) \end{array}\right\} \tag{51}$$

where Z is valence of a cation; u is dipole moment of a water molecule (6.172×10^{-30} C m); x_0 is the dimension of half of one water molecule (0.14 nm); r_{h} is the minimum distance between cation and water molecule (a sum of the radii of cation and water molecule); γ_0 and $\varepsilon_{\mathrm{r0}}$ are orientation angle and dielectric constant in the first hydration shell, respectively; and λ_{c} is decay length of structural parameter (0.1–1.0 nm).

Depending on the valence and radius of a given cation, the hydration energy can theoretically range from −250 to −1,500 kJ mol^{-1} (e.g., Marcus, 1991; Salles et al., 2007).

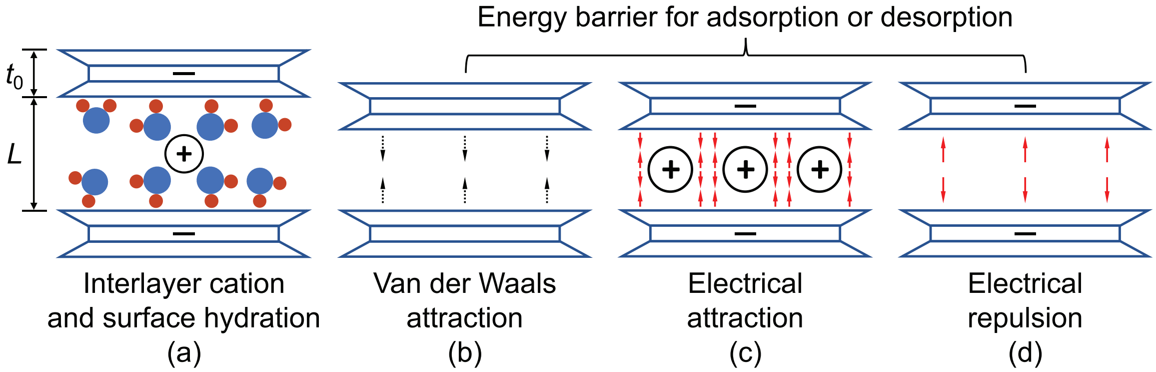

FIGURE 7 Illustrations of (a) interlayer cation hydration and internal surface hydration occurring in swelling clay minerals; and (b–d) energy barrier produced by the interlayer forces to impede crystalline swelling

Correspondingly, cation hydration significantly lowers the water potential to the magnitude of -1.383×10^4 to -8.297×10^4 MPa (Figure 6f), but it will decay rapidly with respect to distance from the particle surface and will generally persist for no more than two layers of water molecules. As a result, the sequence of soil–water interaction along a wetting path from the initially dry state always starts with the cation hydration (Zhang & Lu, 2018).

4.3.3 | Energy barrier for swelling clays

In addition to the abovementioned water adsorption occurring on external clay surfaces for all types of minerals, swelling clays (including mostly 2:1 type clay minerals such as smectites and vermiculites) can also absorb water into their expandable interlayer space (Figure 7a). This further alters the water potential via the hydration of interlayer complexes (i.e., interlayer exchangeable cations and interlayer surface). Crystalline swelling for oven-dried expansive soils will not happen immediately after exposure to water. Instead, an energy barrier (Figure 6g) stemming from the physicochemical interactions between the two adjacent 2:1 layers must be first overcome (Giese, 1978; Lu & Khorshidi, 2015; Lu & Zhang, 2020; Zhang & Lu, 2019a). Nonswelling clays such as kaolinite (a 1:1 type clay mineral), by contrast, generally have much stronger interlayer bonding (e.g., hydrogen bonding) which prevents the interlayer surface from hydration even at a very high water content.

In this section, the individual components of energy barrier in swelling clays will be examined. Swelling is the macroscopic phenomenon for interlayer hydration happening at the molecular scale (Figure 7a), meaning that the interlayer energy barrier virtually imposes a compressive pressure to the interlayer water. Based on the synthesized physicochemical mechanisms, a true intercrystalline swelling pressure can be theoretically predicted for swelling clays.

van der Waals attraction
The van der Waals forces, as previously mentioned, are intermolecular attractions ubiquitous in molecules and other condensed matter, and so will also present between two adjacent layers in a 2:1 clay mineral as part of the interlayer bonding forces. If we assume an infinite plane of finite thickness for the geometry of a clay layer, the van der Waals attraction in a parallel-plate configuration (Figure 7b) can be expressed as (Quirk & Murray, 1991):

$$\psi_{\text{vdW-ll}}(L) = \frac{A_{\text{H-c}}}{6\pi L}\left[\frac{1}{L^2} + \frac{1}{(L+2t_0)^2} - \frac{2}{(L+t_0)^2}\right] \tag{52}$$

where L is the interlayer spacing (nm); t_0 is the clay layer thickness, typically 0.95 nm for a 2:1 type layer (Moore & Reynolds, 1997); and $A_{\text{H-c}}$ is the Hamaker constant of adjacent clay layers, generally assumed as a constant value of 2.2×10^{-20} J (positive here to represent attractive forces) (Laird, 1996).

Electrical attraction
Because the clay particle surface is negatively charged, electrostatic forces are produced between the adjacent clay layers and the interlayer exchangeable cations (Figure 7c). For simplicity, cations are considered as point charges residing in a homogeneous electric field generated by a uniformly charged plane, assuming that the interlayer spacing is negligible compared with the dimensions of clay's basal plane (Nadeau, 1985). Under these conditions, the magnitude of electrical attraction from one side of cations can be estimated as

$$\psi_{\text{ele-cl}}(L) = \frac{\sigma^2}{\varepsilon_0 \times \varepsilon_r(L)} \tag{53}$$

where σ is the surface charge density (C m^{-2}) determined by soil's CEC and SSA. Here, the relative permittivity ε_r of the interlayer space is defined as a function of the interlayer spacing L (Laird, 1996), an indicator reflecting the hydration state in the interlayer space (e.g., Chipera & Bish, 2001). The value of ε_r in the interlayer space will gradually approach 78.54 (relative permittivity for free water) from 6 (relative permittivity for dry interlayer space) as the degree of interlayer hydration increases from oven dryness.

Electrical repulsion

Electrical repulsion also takes place spontaneously within the interlayer of 2:1 minerals when the two negatively charged layers are brought together by their electrical attractions with interlayer cations (Figure 7d). Similar to the above expression for electrical attraction, the magnitude of such electrical repulsion is calculated as

$$\psi_{\text{ele-ll}}\ (L) = -\frac{\sigma^2}{2 \times \varepsilon_0 \times \varepsilon_r\,(L)} \tag{54}$$

It can be observed that the magnitude of electric repulsion is half that of electrical attraction (opposite in sign), due to the fact that cations reside approximately halfway ($L/2$ in Figure 7) between the clay layers. As such, if adding the above three components of the energy barrier (Equations 52–54), the interlayer interactions are net attraction, thus holding the overall structural integrity of the clay particles.

4.4 | Unitary definition of matric potential

The total soil water potential is conventionally defined as the sum of matric potential and osmotic potential when gravitational potential is ignored (Equation 3). Matric potential is perhaps the most important but least understood component, leading to the dilemma as noted above in most previous definitions for soil water potential. Notably, adsorption is completely overlooked in the textbook definition of matric potential as the difference between bulk pore water pressure and pore air pressure. On the other hand, the influences of individual adsorptive mechanisms can also be counted twice in different components of matric potential, as discussed previously.

While the theories for all of the above physicochemical mechanisms are not new and have been well established independently in different fields, as summarized in Figure 6, a consistent definition for soil water potential that can unify a broad range of soil–water interactions went largely missing until recent breakthroughs in SSP theory (Lu & Zhang, 2019). The comprehensive review above demonstrates that the water potential components due to surface hydration and subsequent multilayer adsorption are all electromagnetic in nature (i.e., electric field, EDL, van der Waals, cation hydration, and surface hydration). As such, the SSP ψ_{sorp}, an intrinsic soil characteristic function depending only on the statistical distance x from the soil particle surface (i.e., the origin of SSP), can be conceptualized and formulated inclusively as the collective sum of these electromagnetic potentials (Lu & Zhang, 2019):

$$\begin{aligned}\psi_{\text{sorp}}\ (x) &= \psi_{\text{ele}}\ (x) + \psi_{\text{osm}}\,(x) + \psi_{\text{vdW}}\,(x)\\ &\quad+\psi_{\text{c-hyd}}\,(x) + \psi_{\text{s-hyd}}\,(x)\end{aligned} \tag{55}$$

The minimum or the most negative magnitude of the SSP function always occurs near the soil–water interface (i.e., the particle surface) and increases nonlinearly with increasing distance x. This definition of SSP is general for all soils, and there is no need in practice to distinguish or determine individual terms in Equation 55 as a prerequisite of the SSP characterization. Rather, their effects may be captured collectively in soil's total water potential or matric potential (e.g., Luo et al., 2022). A magnitude of SSP as low as −1.2 GPa has been determined (Zhang & Lu, 2020a by implementing a genetic algorithm to the measured SWRC. With the successful identification of all soil water retention mechanisms and the synthesis of SSP, a unitary definition of matric potential is achieved with the following expression for any gravimetric water content θ of soil during either the wetting or drying process (Zhang & Lu, 2019b):

$$\psi_{\text{m}}\ (\theta) = P_{\text{w}}\ (x, \theta) - P_{\text{air}} + \psi_{\text{sorp}}\,(x) \tag{56}$$

Capillarity and adsorption, which are two different mechanisms with distinct free energy levels, can coexist under the same soil water potential (i.e., here referring specifically to matric potential) considering the principle of local thermodynamic equilibrium. As such, Equation 56 can be further written as (Lu, 2020)

$$\psi_{\text{m}}\ (\theta) = \left[P_{\text{cap}}\,(\theta) - P_{\text{air}}\right]\ + \left[\psi_{\text{sorp}}\,(x) + P_{\text{sorp}}\,(x, \theta)\right] \tag{57a}$$

or

$$\psi_{\text{m}}\ (\theta) = \psi_{\text{cap}}\ (\theta) + \psi_{\text{ads}}\,(x, \theta) \tag{57b}$$

where $P_{\text{cap}} - P_{\text{air}}$ is the capillary potential, a sole function of soil water content; and P_{sorp} is the adsorption-induced water pressure. Explicitly separating the capillary and adsorptive components of matric potential (i.e., Equation 57b) provides a theoretical foundation for the development of a general SWRC model (Lu, 2016; Revil & Lu, 2013), as described subsequently.

The unitary definition of matric potential is general and also applicable to the interlayer water of swelling clays. Water molecules enter the interlayer in a stepwise manner (Hensen & Smit, 2002), and for most clays the interlayer spacing L

only expands up to 1 nm (equivalent to the thickness of three layers of water molecules). Neglecting the gel-like behavior of sodium montmorillonite (i.e., fully exfoliated 2:1 layers), such interlayer separation is usually much smaller than the dimensions of clay layer, and thus it is convenient to define the matric potential at the midplane of the interlayer space (i.e., $x = L/2$) as

$$\psi_{\mathrm{m}}(\theta) = P_{\mathrm{w-int}}\,[L(\theta)] - P_{\mathrm{air}} + \psi_{\mathrm{sorp-mid}}\left(x = \frac{L}{2}\right) \tag{58}$$

where $P_{\text{w-int}}$ is the average interlayer swelling pressure that expands the adjacent clay layers against their attractive forces; and $\psi_{\text{sorp-mid}}$ is the midplane sorptive potential including internal cation hydration and internal surface hydration. The sum of the first two terms on the righthand side of Equation 58 is numerically equivalent to the energy barrier ψ_{b}, which is calculated as (e.g., Lu et al., 2022):

$$\begin{aligned}\psi_{\mathrm{b}}(L) &= \psi_{\mathrm{vdW-ll}}(L) + \psi_{\mathrm{ele-cl}}(L) + \psi_{\mathrm{ele-ll}}(L)\\ &= \frac{A_{\mathrm{H-c}}}{6\pi L}\left[\frac{1}{L^2} + \frac{1}{(L+2t_0)^2} - \frac{2}{(L+t_0)^2}\right] + \frac{\sigma^2}{2\times\varepsilon_0\times\varepsilon_{\mathrm{r}}(L)}\end{aligned} \tag{59}$$

The energy gradient between external water and interlayer hydration gradually grows with a continuous supply of water and eventually becomes sufficiently large to overcome the energy barrier and separate the interlayer space. Pore water in swelling clay can have a different pressure between the external surface and internal space but should share the same matric potential $\psi_{\mathrm{m}}(\theta)$ at thermodynamic equilibrium. Recognizing these striking features of energy barrier and postponed hydration of interlayer complexes stimulates the recent development of augmented Brunauer–Emmett–Teller (A-BET) equation to separate the external and internal (if any) surface area for all types of soils (Lu & Zhang, 2020; Zhang & Lu, 2019a).

The synthesis of SSP enables the most up-to-date, clear, and concise definition of matric potential: the chemical potential of soil matrix that is transferrable to the unit volume of water in all three phases via multiple mechanisms of soil–water interaction, including capillarity (mechanical) and adsorption (physicochemical). The best example given by Equation 59 is that mineral's energy (i.e., the energy barrier) directly contributes to the matric potential of soil water. As such, matric potential cannot be defined logically without considering the presence of soil, which is the major limitation leading to the inabilities in previous definitions of matric potential to describe important soil phenomena and properties.

5 | IMPLICATIONS OF SOIL WATER POTENTIALS

5.1 | Coupling effect between osmotic potential and matric potential

Osmotic potential and matric potential are not independent but coupled via multiple aspects of soil–water interaction, including the five components of SSP. Both the surface and cation hydrations and the van der Waals forces essentially arise from Coulomb forces (e.g., Butt & Kappl, 2018), depending on not only the properties of soil particle but also the character of medium (i.e., relative permittivity of soil water). Dielectric decrement phenomenon (e.g., Gavish & Promislow, 2016) indicates that the relative permittivity of water generally decreases with increasing electrolyte concentration, leading to the variation in van der Waals and two hydration components. Thereby, these three components of SSP are coupled with osmotic potential.

Other two components [i.e., the electric component $\psi_{\mathrm{ele}}(x)$ and osmotic component $\psi_{\mathrm{osm}}(x)$] stem from EDL attraction. As discussed previously, fine-grained soils (especially clays) with naturally charged surface can interact with the ionic species in bulk water to form the EDL coating particles. The electric field within the EDL is the result of interaction between the charged surface and the ions as individual point charges (Israelachvili, 2011). This electric field generates Boltzmann-distributed ions in the EDL, where EDL thickness ($1/\kappa$) is a rough measure denoting the ending point of the decreasing ion density, as shown in Figure 8a. The thickness of the EDL (Equation 46) and the cation distribution therein are determined by the electrolyte concentration of bulk water (i.e., the osmotic potential). An aqueous solution with higher bulk electrolyte concentration (i.e., lower osmotic potential) will simply compress the EDL on the charged clay surface. In fact, Equation 46 has been simplified by assuming 1-1 electrolyte (e.g., NaCl). The decay of $1/\kappa$ with increasing bulk concentration of 1-1 electrolyte C is illustrated in Figure 8b. For pure water, the electrolyte concentration is fully contributed by the self-ionized H_3O^+ and OH^- [i.e., $C = C(H_3O^+) = C(OH^-) = 1 \times 10^{-7}$ mol L^{-1}], indicating a maximum $1/\kappa$ of 963 nm. An increase in C leads to highly nonlinearly decreasing of $1/\kappa$ (e.g., $1/\kappa < 1$ nm when $C > 0.1$ mol L^{-1}).

The EDL thickness controls two quantities underpinning electric component $\psi_{\mathrm{ele}}(x)$ and osmotic component $\psi_{\mathrm{osm}}(x)$, namely, the electric field intensity in Equation 45 and the electric potential in Equation 48. Therefore, the varying

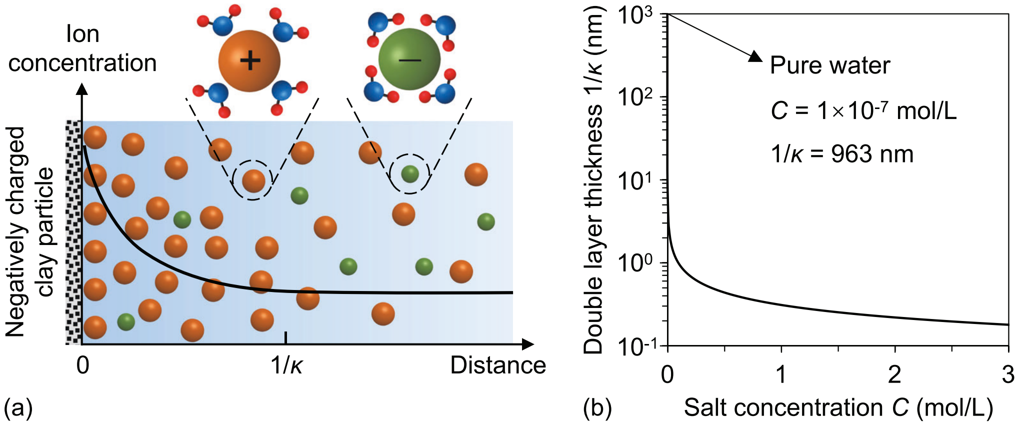

FIGURE 8 Illustrations of (a) electrical double layer (EDL) and ion density distribution; and (b) variation of EDL thickness with bulk electrolyte concentration

electrolyte concentration can notably alter SSP or matric potential via varying EDL thickness, indicating a coupling effect between the osmotic potential and the matric potential. A higher electrolyte concentration generally leads to a lower EDL thickness and hence a higher matric potential (less negative). This coupling effect can be fully captured by the proposed unified soil water potential theory.

The forgoing considerations show that all the five components of SSP depends on not only the statistical distance to soil particle surface but also the ion concentration of pore fluid. Thereby, the unitary definition of matric potential (Equation 57a) can be extended by incorporating ion concentration effects:

$$\psi_m(\theta, C) = \left[P_{cap}(\theta) - P_{air}\right] + \left[\psi_{sorp}(x, C) + P_{sorp}(x, \theta, C)\right] \tag{60}$$

Accordingly, the definition of total soil water potential should be written as

$$\psi_t(h, \theta, C) = \psi_g(h) + \psi_o(\theta, C) + \psi_m(\theta, C) \tag{61}$$

By taking into account the coupling between osmotic and matric potentials, the definition of total soil water potential in Equation 61 is distinct from the classical definition in Equation 3. The tacit assumption involved in the classical definition is that the total soil water potential can be decomposed into three independent functions of three state variables of elevation, ion concentration, and water content (i.e., gravitational, osmotic, and matric potential functions). Nonetheless, this tacit assumption is invalidated by the non-negligible coupling effect between osmotic and matric potentials. That is, the effect of ion concentration and water content is inseparable and should be included in both osmotic and matric potential functions, as stated in Equation 61.

5.2 | Soil water potential measurements

Direct measurement of soil water energy state (i.e., potential) is not available in any current sensing technology. As a result, soil water potential, whether the osmotic and matric potentials or their sum the total potential, is indirectly measured by proxy with an external substance (solid, liquid, or gas) that has reached a certain degree of equilibrium with the soil water (Campbell & Campbell, 2005). Commonly adopted experimental and in situ techniques can be classified into three categories depending on the phase of the sensing material: solid-based (e.g., filter paper), liquid-based (e.g., tensiometer and axis translation), and vapor-based (e.g., hygrometer methods). Generally, matric potential, or its opposite matric suction, is probed if the measurement is achieved via direct contact with the soil water. For example, a Whatman No. 42 (or other type of) filter paper can be brought to equilibrium with a soil sample following either a contact or a noncontact approach. Based on the measured water content of the filter paper, the matric or total potential of soil water is then estimated using a calibration function for paper either in direct contact (for matric potential) or in a closed system with the soil sample (for total potential) (ASTM, 2016). Although these methods are simple and affordable, filter paper methods in general are indirect, time consuming, and difficult to automate. In comparison, a tensiometer placed in direct contact with the soil only measures the matric potential because the porous ceramic used to isolate the solid and gas soil phases is permeable to both water molecules and solutes. Total water potential is obtained from hygrometer-based approaches, which measure the vapor pressure (i.e., relative humidity, RH) in a closed system with the soil at thermal equilibrium and convert the RH to total potential using the Kelvin's equation (Equation 38).

As described previously, the matric potential in partially saturated soil often varies significantly over six orders of magnitude from 0 to -1.6×10^6 kPa (i.e., -1.6 GPa). Each of the measurement techniques mentioned above, however, and including other approaches, are only applicable over a limited range of the matric potential (e.g., Croney et al., 1952). Rough boundaries are the following: tensiometer (0 to -1×10^2 kPa), axis translation (0 to -1.5×10^3 kPa), filter paper (-1×10^2 to -5×10^5 kPa), and hygrometer-based techniques (-1×10^2 to -5×10^5 kPa) (Lu, 2020; Lu & Likos, 2004).

The measurement range of a tensiometer is limited by the cavitation of water in the sensing system. Although high-capacity tensiometers have been developed that claim to measure matric potential as low as -7×10^3 kPa (e.g., Mendes et al., 2019), it is challenging to maintain a long-term stable reading without the occurrence of cavitation, as water is in metastable state in such pressure regime. Tiny crevices (submicron size) on the surface of porous ceramic tip and in the tensiometer body are favorable locations for bubble entrapment (Luo et al., 2021; Or & Tuller, 2003), and these bubble nuclei can later serve as sites of potential cavitation (e.g., Mendes & Buzzi, 2013). In contrast, axis translation and similar approaches suppress cavitation by artificially increasing the soil water pressure above the cavitation pressure, and then control or measure the air–water pressure difference considered equivalent to capillary potential. Experimental evidence (e.g., Bittelli & Flury, 2009; Lu, 2019b), however , has shown that SWRCs measured as such may be erroneous because measuring matric potential as the pressure deficit in soil water completely ignores the important roles of adsorption and cavitation in SWR (Luo et al., 2021). Thus, both tensiometer and the axis translation approaches can only measure matric potential when soil water retention is dominated by capillarity, and they are incapable of sensing matric potential when soil water retention is dominated by adsorption.

Dynamic dew point (hygrometer-based) methods have emerged as a powerful tool to continuously collect high-resolution soil water isotherm (SWI) data (total potential vs. water content) during wetting and drying (e.g., Likos et al., 2011). For a soil sample in powder form, a complete wetting–drying loop of isotherm measured by the vapor sorption analyzer (VSA) (Meter Group) typically includes 200 discrete data points with RH ranging from 0.95 to 0.03, corresponding to a matric potential range from -7×10^3 to -4.8×10^5 kPa. This upper limit of matric potential can be raised to -1×10^2 kPa by replacing the powder sample with a very thin oversaturated soil paste, whereas the lower limit can be expanded to -8.6×10^5 kPa by using the molecular sieve as desiccant (Dong & Lu, 2020). These and similar techniques make it possible to explore water retention behavior of soils over an extraordinarily wide range, and to obtain fundamental insight into soil properties and processes that govern soil–water interaction.

5.3 | Soil water retention curve and soil water isotherm

The SWRC and SWI are arguably the two most important soil constitutive relationships because they govern virtually all phenomena in soil such as flow, stress and deformation, and biological activities. The former describes the relationship between soil water matric potential and soil water content, while the latter describes the relationship between total water potential and soil water content. As shown in Figure 9, the overall geometry is similar between SWRC and SWI, and these two characteristic functions are almost interchangeable when the osmotic potential in soil can be ignored in a very dilute (e.g., <0.1 mol m^{-3}) soil pore water (Chang & Sposito, 1996). In the literature, matric potential down to -2×10^6 kPa has been simulated and predicted (e.g., Zhang et al., 2017), much lower than the common range of measurement offered by the currently available techniques, as summarized above. In current practice, no single measurement technique is capable of covering the entire range of matric potential from 0 kPa to theoretically -2×10^6 kPa.

Consequently, many models (e.g., Fredlund & Xing, 1994; Iden & Durner, 2014; Lu, 2016; Luo & Lu, 2021; Peters, 2013; Revil & Lu, 2013; van Genuchten, 1980) have been developed to simulate the limited and discrete SWR measurements so as to continuously characterize the SWRC or SWI over the full range of matric potential. Among these models, the van Genuchten (VG) model (van Genuchten, 1980) and the Fredlund and Xing (FX) model (Fredlund & Xing, 1994) are arguably most commonly used. Both the VG and FX models have been experimentally validated in the capillary regime (e.g., matric potential greater than -1.5×10^3 kPa), but vaguely defined model parameters for adsorption (e.g., residual moisture content and residual suction) result in their poor representation of the SWR data at matric potential lower than -1.5×10^5 kPa. For example, the VG model requires matric potential to become infinite negative at zero water content, which can be misleading and unrealistic. The FX model imposes a lower limit for matric potential below which no adsorption will occur. This minimum matric potential (or maximum matric suction) is universally set to a constant value of -10^6 kPa rather than a variable determined upon fitting. Based on Figure 6, the lowest matric potential corresponds to the strength of soil–water interaction at the very dry condition. Thus it will not be a constant throughout all soil types but should depend on the physicochemical properties of soil surface, such as the species of exchangeable cation and the surface hydroxyl groups.

Among different models, the Lu's SWRC model (Lu, 2016) and the Luo and Lu's SWI model (Luo & Lu, 2021) have demonstrated their applicability to all soil types for simulating the soil water retention process at the entire matric

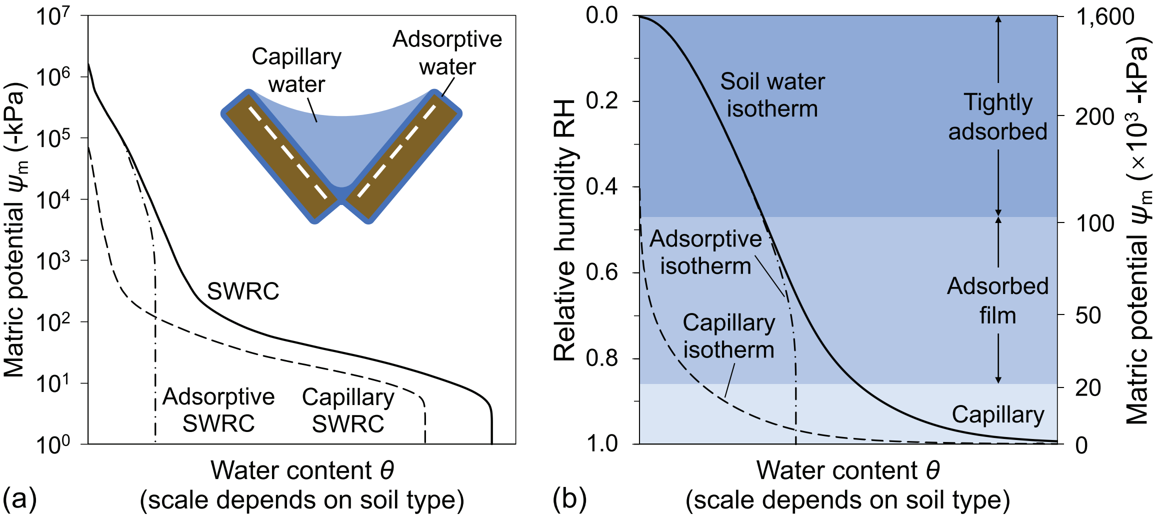

FIGURE 9 Conceptual illustrations of soil water retention regimes at different ranges of matric potential on: (a) soil water retention curve (SWRC); and (b) soil water isotherm (SWI)

potential range. These two models inclusively consider all three physical mechanisms of SWR (i.e., capillarity, adsorption, and cavitation or condensation) and clearly define the physical meaning of each model parameter. Given the local energy equilibrium in soil water, both capillary and adsorptive components of SWRC (or capillary and adsorptive isotherms) can be separated explicitly from the total SWRC (or SWI), as shown in Figure 9, and the total water content at any given matric potential (i.e., an energy state of soil water) or RH will be the mathematical sum of capillary water content and adsorptive water content.

In the capillary regime where matric potential is higher than -10^4 kPa or RH > 0.9 (Figure 9), capillary water and adsorptive water coexist under the same matric potential. The adsorption capacity of soil has been fully explored at this stage, so any further increases in the water content is only retained by capillarity. As a soil gradually dries out, the SWRC enters the adsorbed film regime, which is the transition state from capillary- to adsorptive-dominated regimes. Phase transition from liquid to vapor (i.e., cavitation) commences in the metastable capillary water (i.e., under tension), during which the curved air–water interface retreats to the corners of micrometer-size particles and a conversion from adsorptive water to capillary water may also take place. This leads to a decrease in both capillary and adsorptive water content. For most soils, capillary water disappears in the range of matric potential lower than approximately -10^5 kPa (or RH < 0.5), indicating the equivalence between the total water content and the adsorptive water content. The remaining adsorptive water is strongly attracted by the soil particle surface and the water potential is dominated by the SSP. A lower bound varying from -3.0×10^5 to -1.6×10^6 kPa for soils with different mineralogy (Jensen et al., 2015; Lu & Khorshidi, 2015; Zhang et al., 2017) has been determined and imposed to this tightly adsorbed regime such that no water adsorption will occur below the lowest matric potential (Figure 9).

5.4 | Fundamental properties of soil water

Due to the existence of SSP, water dipoles around the soil particles will experience intense electromagnetic attractions and adjust their orientation towards a high-density packing (Figure 10). Such a closely compacted and well-ordered arrangement of the water molecules always generates a positive water pressure (compression) (e.g., Lu & Zhang, 2019; Mitchell, 1962), independent of whether or not the soil is fully saturated. In addition to the spatially constant negative capillary pressure (tension), the nonlinearly decaying feature of SSP also determines the local variation in pore water pressure along the direction perpendicular to the soil particle surface (i.e., the distance x shown in Figure 10). The compressive water pressure in the first two adsorptive layers can be as high as ~1.6 GPa (e.g., Lu et al., 2021). This abnormally high water pressure will decrease quickly and nonlinearly away from the soil particle surface to the tensile pressure in capillary water (Lu & Zhang, 2019), partially compensating the spatial difference in SSP and maintaining the same matric potential everywhere within the soil–water–air REV. Conversion from SSP to either matric potential or hydromechanical water pressure is determined by the prevailing soil water content (Lu & Zhang, 2019). The local water pressure (i.e., higher at locations near the soil particles than farther away) is considered as the true intermolecular pressure that determines the fundamental physical properties of soil water (e.g., density and viscosity) and governs the water phase transition (e.g., liquid to ice and liquid to vapor) on a water phase diagram, as elaborated upon in the sections below.

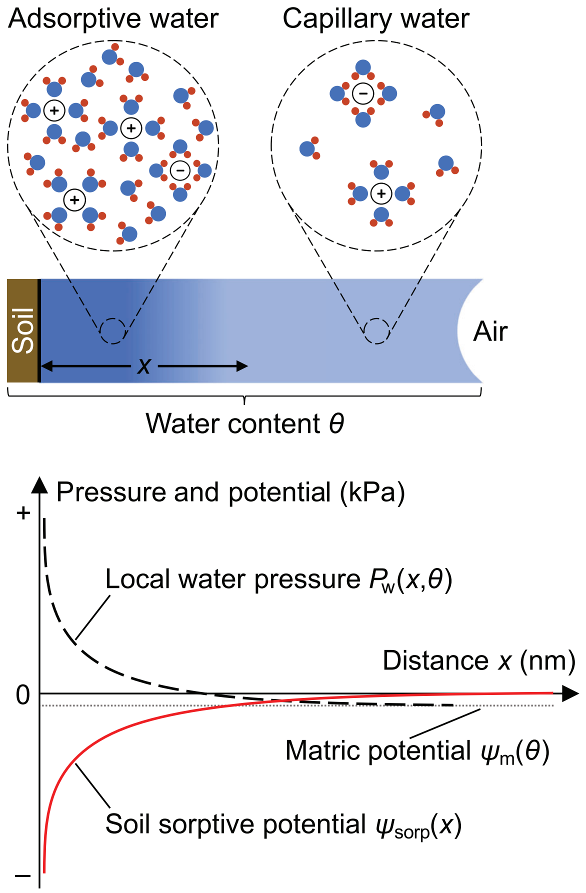

FIGURE 10 Schematic illustrations of the unitary definition of matric potential and its effect on local water distribution in the direction away from the soil particle surface

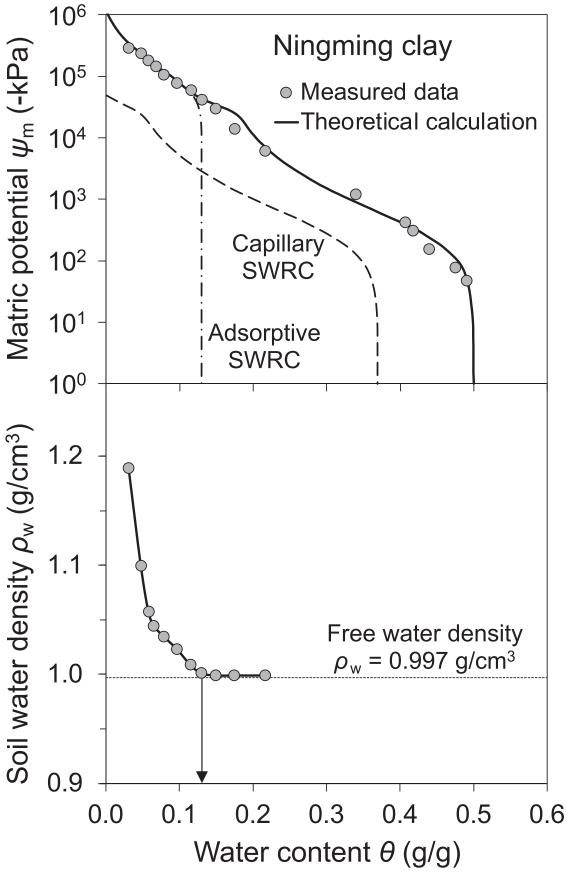

FIGURE 11 Soil water retention curve (top) and soil water density curve (bottom) measured for Ningming clay, demonstrating the importance of the specific surface area and adsorptive water in increasing soil water density, hence the need for the unitary definition of matric potential (data from Dong et al., 2020)

5.4.1 | Soil water density

In most practical situations, water density has been considered as unity (i.e., the free water density), regardless of the state conditions. As a matter of fact, however, water density as high as 1.7 g cm^{-3} has been measured in soils by various experimental techniques (Martin, 1962; Zhang & Lu, 2018). Neglecting the structural change in water molecules during surface hydration, water density much higher than unity (1.0 g cm^{-3}) is the result of the abnormally high compressive water pressure (up to a few gigapascals) occurring near soil particle surface or within swelling clay's interlayer space. On the contrary, surface tension at the air–water interface produces a negative (tensile) water pressure, which stretches the water molecule bonds and thereby slightly decreases the water density (0.995 g cm^{-3}) compared with unity (Zhang & Lu, 2018).

As a consequence, adsorption and capillarity are recognized as two fundamental mechanisms that commonly deviate the water density in soil from the unity, causing the soil water density to not be a constant but rather a function of the soil water content. The effect of SSP on soil water density becomes particularly significant when soil's SSA is large. For example, Figure 11 shows the soil water density function determined for a clayey soil with SSA of 375 m^2 g^{-1}, along with the SWRC plotted at the same scale of water content (Dong et al., 2020). A water density of 1.19 g cm^{-3} was determined at the dry end for clay with water content of 0.03 g g^{-1}. This abnormally high density decreases as the water content increases and finally returns back to the free water density at water content of 0.16 g g^{-1}, which, inferred from the SWRC, is the maximum amount of water that can be retained by soil in the form of adsorption. This point of maximum adsorptive water content indicates the end of dominance of SSP, beyond which the soil water density becomes more or less a constant because the capillarity has limited effect on the water density.

5.4.2 | Soil water freezing behavior

Given that liquid water in soil can be cooled below the freezing point without solidification, the soil freezing curve

(SFC) or freezing characteristic curve was developed to depict the constitutive relationship between temperature and unfrozen water content. Until now, the capillary potential in van Genuchten's SWRC model has been commonly used along with the Clapeyron equation to interpret the freezing behavior of soil water (e.g., Liu & Yu, 2013). However, even though a metastable region (i.e., supercooled liquid water simultaneously under tension) has been experimentally achieved in water (Pallares et al., 2014), this supercooling phenomenon under ambient pressure is more likely to occur in highly purified water containing few impurities available as initial nucleation sites for ice crystals (Debenedetti, 1996). Because soil water generally contains both ions and impurities, freezing suppression observed in soil water must be attributed to other physicochemical mechanisms in soil, such as adsorption.

According to the water phase diagram, the fusion curve is completely determined by the temperature and pressure, specifically the intermolecular pressure (Wagner & Pruß, 2002). Although temperature can be easily measured and considered as a constant within soil water at equilibrium, a measurable intermolecular water pressure has long been absent and thus replaced by capillary pressure until the recent breakthrough in SSP theory. As illustrated in Figure 12, the SFC model developed based on the concept of local intermolecular water pressure can predict the experimental measurements for Georgia kaolinite over a wide range of temperature (Zhang & Lu, 2021). Due to the existence of adsorption-induced compressive pressure, the water freezing temperature can be suppressed down to at least −10 °C. It is also observed that the maximum adsorptive water content on the SWRC coincides with the inflection point (i.e., the start of significant freezing suppression) on the SFC, indicating the necessity of using a more general definition of matric potential than simply the capillary potential.

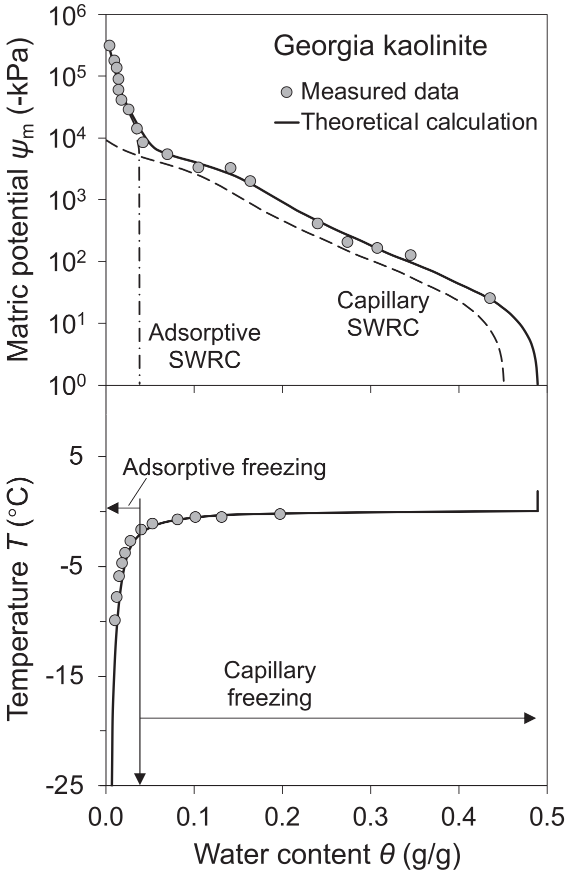

FIGURE 12 Soil water retention curve (SWRC) (top, data from Likos & Lu, 2003) and soil freezing curve (bottom, data from Smith & Tice, 1988) measured for Georgia kaolinite, showing the importance of adsorptive water in lowering of soil freezing temperature, hence the need for the unitary definition of matric potential

5.4.3 | Soil water cavitation

Cavitation is the process of forming vapor bubbles inside a liquid body under tension. When the liquid pressure drops below the saturated vapor pressure, the water molecules are stretched into a metastable state and prone to gasification. Because capillary water with negative pressure usually occupies the relatively large pore spaces in unsaturated soil, water cavitation has been considered as one of the important SWR mechanisms during the desaturation process (e.g., Frydman & Baker, 2009; Or & Tuller, 2002). Similar to water freezing, cavitation also requires the formation of an initial nucleus, or cavitation site, to promote the phase transition. Silty soils with pore size commonly ranging from 0.1 to 10 µm are particularly suitable for soil water cavitation because the air entrapped in the crevices of rough particle surfaces provides bubble nuclei that can grow and readily expand (Luo et al., 2021). Given the wide range of pore size distribution for natural soils, capillary water retained in soil pore spaces with a variety of sizes can thus cavitate gradually, but not suddenly, over the range of matric potential during drying, leading to a smooth and continuous SWRC and SWI. Theoretically, water cavitation can also take place via homogeneous nucleation of vapor bubbles inside the water body or heterogeneous nucleation at the solid–liquid interface. However, it has been quantitatively illustrated that neither homogeneous nor heterogeneous nucleation is likely to occur in soil water as the SSP will prevent the nucleation of vapor bubbles by converting the negative water pressure to the positive one (Luo et al., 2021). Likewise, soil water cavitation will not happen in nanosized pores (mostly clay) where adsorption is dominant over capillarity.

5.5 | Fundamental properties of the soil–water system

5.5.1 | Hydraulic conductivity

Limits of current technology render the local intermolecular water pressure not directly measurable by either piezometer or tensiometer, which are the two instruments commonly used for measurement of water pressure in soil. It is an issue of scale, as these devices measure water pressure averaged over bulk water retained in pores having micro- to millimeter sizes. Nonetheless, pore water pressure determined from the piezometer or tensiometer gauges has long been used for analyses of nearly all problems in practice such as fluid flow. In Darcy's law, the gauge pressure is used to calculate the gradient and the fluid viscosity is assumed constant within the water body. Although this approach may be sufficient to describe water movement in relatively large pores (e.g., >1 mm) where capillarity prevails, considerable errors will be produced in fine-grained soils with small pores where SSP plays a dominant role. For instance, the water pressure near the soil particle surface can be as high as 600 MPa and it decays quickly to the negative capillary pressure within approximate 100 layers of adsorbed water molecules. Correspondingly, the viscosity of water at 25 °C will increase nearly three orders of magnitude within the region of adsorption (Bair, 2016), making the adsorptive film flow in small pores very different than the capillary water flow in large pores.

5.5.2 | Thermal conductivity

Heat transfer in the natural condition can take place via conduction, convection, and thermal radiation. Among them, conduction through the contact between soil grains is generally considered as the dominant mechanism for heat transport in many shallow soil environments. Because the soil water content near the ground surface is subject to seasonal variation, the thermal conductivity function (TCF) from dry to saturated state is the key physical parameter in practice for assessing a soil's thermal behavior, such as energy foundation, radioactive waste disposal, and geothermal applications.

Figure 13 shows two TCFs measured separately for a coarse-grained sandy soil (i.e., Accusand #40/50 and hereinafter referred to as Accusand) and a fine-grained clayey soil (i.e., Denver claystone). The distinct thermal behaviors between the two soils are determined by their different SWR mechanisms. When soils are near the oven-dried condition, their thermal conductivities are almost the same with a value of ∼0.35 W mK^{-1}. However, the TCFs of the two soils diverge in both magnitude and pattern when the water content increases. The thermal conductivity of Accusand increases significantly as the water content increases, ending with a thermal conductivity of 2.98 W mK^{-1} measured at a maximum water content of 0.2 g g^{-1}. On the other hand, the TCF of Denver claystone has an S-shaped pattern where the thermal conductivity also increases with increasing water content but at a much smaller rate than the sand. For Denver claystone, the thermal conductivity measured at the same water content of 0.2 g g^{-1} is 0.87 W mK^{-1}, only one third of that of the Accusand. Such a discrepancy in TCF between sand and clay is the result of difference in their fundamental SWR mechanisms.

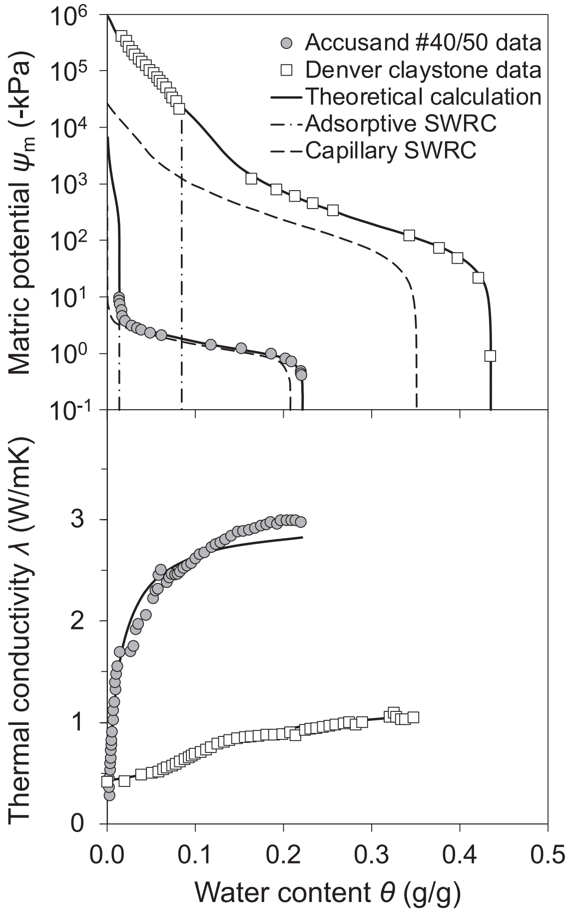

FIGURE 13 Soil water retention curves (SWRCs) (top) and thermal conductivity functions (bottom) measured for two different soils with distinct soil water retention mechanisms, illustrating the importance of adsorptive water in altering soil's thermal property, hence the need for the unitary definition of matric potential (data from Lu & Dong, 2015)

According to the SWRC (Figure 13), the Accusand has very little adsorption capacity of 0.01 g g^{-1}, and thus most soil water is capillary water retained in pores around the contacts between sand particles. As such, heat conduction is sensitive to the increase in water content and becomes more effective owing to the markedly increasing cross-sectional solid–liquid–solid contact area. In contrast, the Denver claystone has an adsorption capacity of 0.08 g g^{-1}, which is eight times higher than that of the Accusand. Therefore, more water is retained in the form of adsorption occurring on the particle surfaces instead of the particle contacts. In this case, the cross-sectional contact area does not change significantly until the soil water content reaches its adsorption capacity, beyond which capillary water starts to condense near the particle contacts. The high correlation between the onset of significant increase in thermal conductivity and the onset of capillary condensation evident in the SWRC indicates that the magnitude of thermal conductivity is positively associated with the amount of capillary water in soil, which warrants further investigation in better understanding the relationship between SWRC and TCF.

5.5.3 | Suction stress characteristic curve

Terzaghi's effective stress defined as the difference between the total stress σ_{mn} and the pore water pressure P_w in a fully saturated soil has historically been the most important physical quantity for stress, strength, and deformation problems in soil mechanics. Modern design and construction of earthen structures have been largely reliant on the effective stress principle to quantify the strength and deformation of the materials. Prior to the conceptualization of suction stress in the early 2000s (Lu & Likos, 2006), Bishop's effective stress and the independent stress variable concept for unsaturated soils have been widely used to extend Terzaghi's effective stress principle to unsaturated soil, a condition more generally encountered in shallow geotechnical applications. Bishop's effective stress uses the product of a scaling parameter χ and the capillary pressure ($P_w - P_{air}$) as a stress variable in lieu of the water pressure in Terzaghi's effective stress equation (e.g., Khalili & Khabbaz, 1998). The independent stress state variables concept erroneously replaces the effective stress with net total stress ($\sigma_{mn} - P_{air}$) and capillary pressure ($P_w - P_{air}$) (e.g., Coleman, 1962; Fredlund & Morgenstern, 1977) because the latter is a nonstress quantity (Lu, 2008).

Completely overlooking the contributions of adsorption to the matric potential of soil water and the effective stress in soil is the fundamental problem inherent to the above two adaptions of Terzaghi's effective stress, given that only capillary pressure is present in the expressions of both approaches. To resolve this issue, suction stress has been coined as a general interparticle stress that takes both SWR mechanisms of capillarity and adsorption into account (Lu & Likos, 2004, 2006), leading to a unified effective stress equation for both saturated and unsaturated conditions (e.g., Lu et al., 2010; Zhang & Lu, 2020b):

$$\sigma'_{mn} = \sigma_{mn} - P_{air}\delta_{mn} - \sigma^s(\theta)\,\delta_{mn} \tag{62}$$

where m and n are tensor indices varying from 1 to 3; σ'_{mn} and σ^s are effective stress and suction stress, respectively; and δ_{mn} is Kronecker delta. It is natural to perceive the dependence of suction stress on the soil water content by means of the SWRC shown in Figure 9. According to Equation 62, the effective stress in soil consists of two parts: Terzaghi's skeleton stress actively propagating through the soil grains and interparticle stress passively self-balanced by Born's repulsion (Lu & Likos, 2006). The latter (i.e., suction stress) is equivalent to the effective stress when soil is free from external forces. An imaging-based method called drying cake test was invented to measure the suction stress characteristic curve (SSCC), a constitutive relationship between suction stress and soil water content [i.e., $\sigma^s(\theta)$], using disk-shaped soil cakes under zero total stress condition (i.e., negligible effect of gravity and no friction) (Dong & Lu, 2017; Lu & Kaya, 2013).

Likewise, a theoretical model of SSCC was also proposed based on the unitary definition of matric potential (Zhang & Lu, 2020b):

$$\sigma^s(\theta) = \sigma^s_{cap}(\theta) + \sigma^s_{ads}(\theta) \tag{63}$$

where σ^s_{cap} is capillary suction stress and σ^s_{ads} is adsorptive suction stress, whose closed-form equations are available in Zhang and Lu (2020b). The above model has been validated by the SSCCs measured for a variety of soil types from sand to clay. Figure 14 exhibits the SWRC and SSCC of two different soils measured and modeled at the full range of soil water content from fully saturated to completely dry conditions, where the contributions of capillarity and adsorption to the suction stress are explicitly identified. The adsorptive water content of Esperance sand is less than 0.01 (Figure 14a), and thus the SSCC is completely determined by its capillary component, making the suction stress vanish at both dry and wet ends (Zhang & Lu, 2020b). Missouri clay possesses a much higher adsorptive water content of 0.07 (Figure 14b), so the adsorptive suction stress of Missouri clay will dominate the SSCC behavior of clay at the low water content range where capillary water disappears due to cavitation. It is also found that the suction stress becomes more negative (i.e., increasing effective stress) monotonically with decreasing soil water content. These observations indicate that the suction stress concept developed based on the unitary definition of matric potential is indispensable for correct appreciation of effective stress in soil and hence better prediction of the soil deformation at all saturation levels.

5.5.4 | Elastic modulus

Surficial soils are usually subject to seasonal wetting and drying that is generally accompanied by changes in

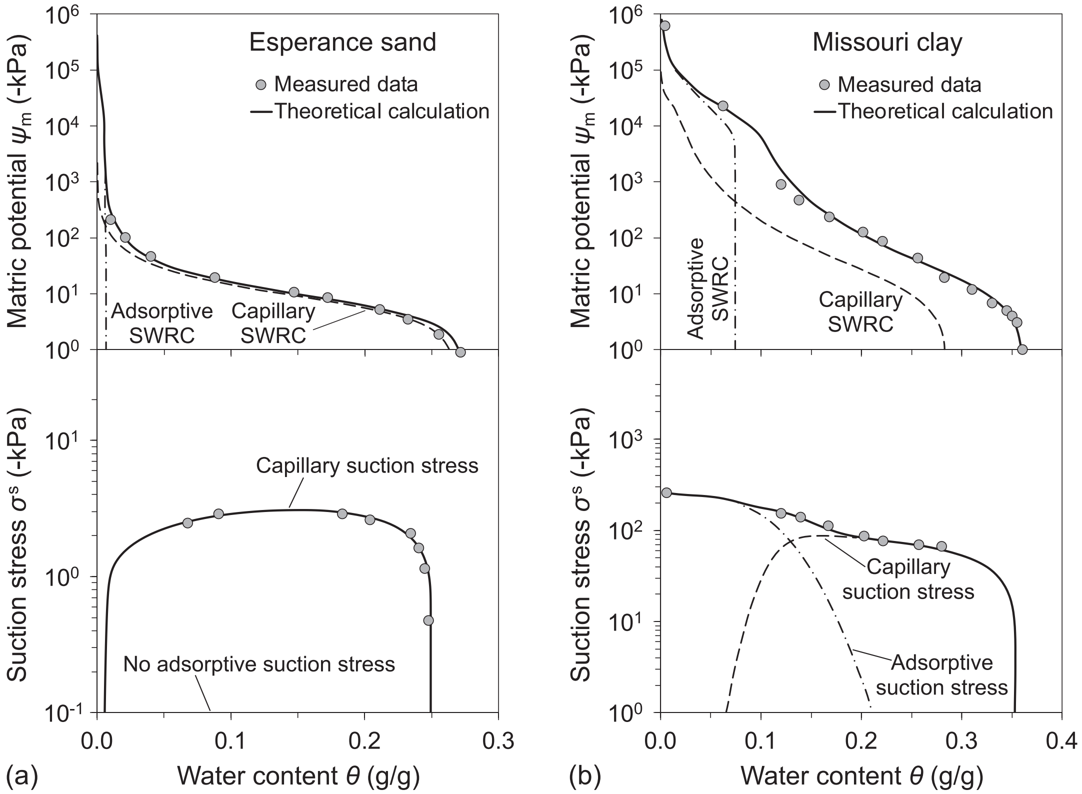

FIGURE 14 Soil water retention curves (SWRCs) (top) and suction stress characteristic curves (bottom) measured for two different soils with distinct soil water retention mechanisms: (a) Esperance sand and (b) Missouri clay, revealing the influence of adsorptive water on suction stress of soil and the need for a unitary definition of matric potential (data from Zhang & Lu, 2020b)

elastic modulus. By definition, elastic modulus is the ratio of stress to elastic strain and quantifies the resistance of a material to recoverable deformation. Depending on the soil type, the elastic modulus of a soil undergoing drying can experience various degrees of hardening. For example, experimental studies using a drying cake method indicate that uncemented sand has negligible change in elastic modulus as the soil water content decreases from its saturated state. For clayey soils, on the other hand, a substantial increase up to 50 times can be observed in the elastic modulus function (EMF), which is the relationship between elastic modulus and water content (Lu & Kaya, 2014). Understanding how the elastic modulus of soil varies with water content is important for routine analysis, design, and construction of infrastructure.

As illustrated in Figure 15 by the EMF and the SWRC of a bentonite soil (Lu, 2018), the EMF is controlled by the physical mechanisms of SWR (i.e., capillarity and adsorption), as well as the transition process between them. Drying from a water content of 0.7 g g^{-1}, the elastic modulus first steadily increases until water content of 0.35 g g^{-1}, where an abrupt increase is observed in the EMF due to the transition from a capillary regime to an adsorptive regime. When the Denver bentonite further dries, the adsorption mechanism dominates the SWRC and takes over most of the subsequent hardening evident in elastic modulus. This multistage hardening behavior can be correlated to the evolution of interparticle stress (i.e., suction stress) in soils, because the higher local pressure in the adsorptive regime than that in the capillary regime can lead to the decrease in suction stress (more negative in magnitude) and hence an increase in effective stress.

For Denver bentonite (Figure 15), the adsorption capacity (i.e., the maximum adsorptive water content) of SWRC is lower than that of the onset water content of adsorptive hardening. Although this mismatch can be attributed to the difference in sample preparation, the dependence of EMF on SWR mechanisms is clearly distinguishable. For soils with low adsorption capacity, the capillary hardening effect can be more propounding than the adsorptive hardening effect at the entire range of water content (Lu, 2018). Therefore, a general definition of matric potential that can capture the local water pressure by explicitly accounting for capillarity and adsorption is favorable for better predictions of shallow soil deformation due to the changing environmental conditions.

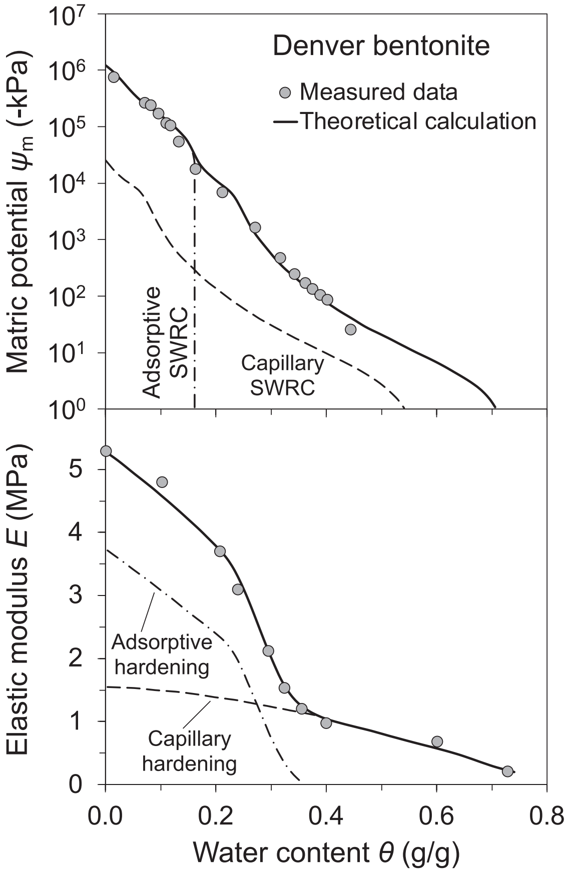

FIGURE 15 Soil water retention curve (SWRC) (top, data from Lu, 2016) and hardening of elastic modulus due to capillarity and adsorption (bottom, data from Lu, 2018) measured for Denver bentonite, illustrating the need for the unitary definition of matric potential

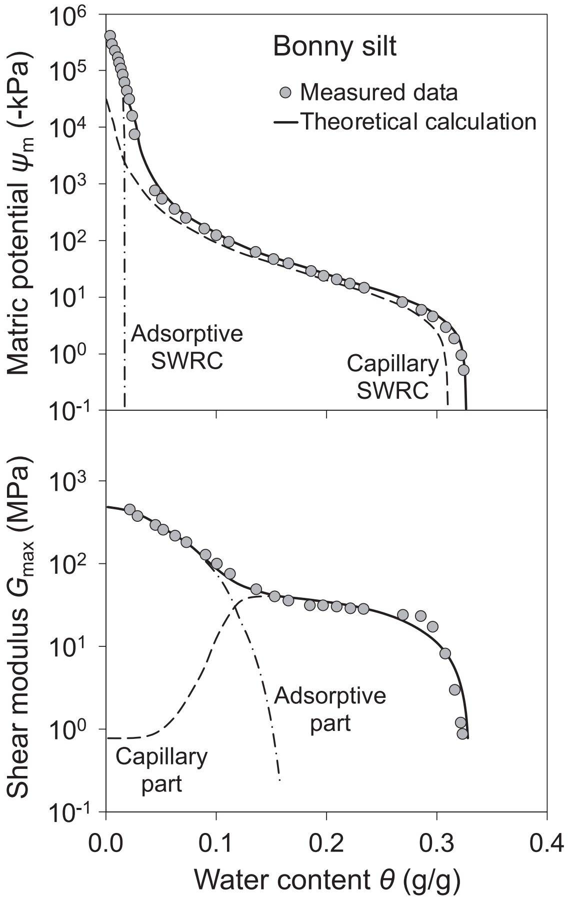

FIGURE 16 Soil water retention curve (SWRC) (top) and small-strain shear modulus function (bottom) measured for Bonny silt, proving the importance of adsorptive water in the hardening of small-strain shear modulus, hence the need for the unitary definition of matric potential (data from Dong & Lu, 2016)

5.5.5 | Small-strain shear modulus

Small-strain shear modulus represents the stiffness of the soil skeleton at low shear strain (e.g., <0.001%) and is a key parameter for studying the dynamic, linear–elastic response of soils to the shear wave propagation such as liquefaction, seismic ground motion, and dynamic soil–structure interactions (e.g., Dong & Lu, 2016). Similar to the elastic modulus, the small-strain shear modulus is also a function of the soil water content because it is controlled by the interparticle contact forces within the load-bearing framework of the unsaturated soils (i.e., the effective stress) (Cho & Santamarina, 2001; Dong et al., 2016). The change in effective stress in partially saturated soil is commonly attained through changes in suction stress, such that the small-strain shear modulus of a soil also depends on its SWR characteristics. Figure 16, for example, shows experimental results obtained from a silty soil illustrating the respective contributions of capillarity and adsorption to the small-strain shear modulus (Dong & Lu, 2016). When the capillary water plays a major role, the small-strain shear modulus slowly increases as the water content decreases. Initiation of adsorptive components at water content of 0.15 g g^{-1} corresponds to a sharp increase in small-strain shear modulus, indicating the increasing importance of adsorption in governing both SWR and suction stress. Therefore, the unitary definition of matric potential should be used for better description of the small-strain shear modulus in soil, especially at the low water content range.

6 | CONCLUSIONS AND OUTLOOK

This paper aims at clarifying long-standing misconceptions of soil water potential and efforts towards a better definition, especially for matric potential. An extensive review of previous definitions and derivations of the soil water potential identifies their weaknesses and fallacies. A unitary definition of soil matric potential defined as the sum of capillary potential, SSP, and adsorption-induced pressure potential (Equation 57a) is proposed based on comprehensive understanding of fundamental soil–water interaction mechanisms. This new definition is experimentally validated in terms of soil water properties and implications to unsaturated soil behavior. Major conclusions are summarized below:

1. Matric potential $\psi_m(\theta, C)$ is the energy of soil matrix available to transfer to mechanical energy in the form of interwater molecular force in pore water via multiple mechanisms of soil–water interaction, including external interaction of capillary potential $P_{cap}(\theta) - P_{air}$ and internal interaction of adsorptive potential $\psi_{sorp}(x, C) + P_{sorp}(x, \theta, C)$. Matric potential in expansive soils involves further internal interaction with interlayer energy barrier. Thus, matric potential is a function of soil water content θ and bulk solute concentration C, and it can be unitarily defined by Equation 60 {i.e.,$\psi_m(\theta, C) = [P_{cap}(\theta) - P_{air}] + [\psi_{sorp}(x, C) + P_{sorp}(x, \theta, C)]$}.
2. Soil water potential $\psi_t(h, \theta, C)$ is the total mechanical energy state of pore water contributed by gravitational potential $\psi_g(h)$, osmotic potential $\psi_o(\theta, C)$, and matric potential $\psi_m(\theta, C)$, as it can be unitarily defined by Equation 61 [i.e., $\psi_t(h, \theta, C) = \psi_g(h) + \psi_o(\theta, C) + \psi_m(\theta, C)$].
3. The REV at which matric potential is defined should include all three phases of the soil–water–air system. Conventional treatment of matric potential as the equivalent of capillary potential (i.e., the difference between water pressure and air pressure) is erroneous because it only considers the water phase. This ignores all the physicochemical mechanisms associated with water adsorption occurring both on the soil surface and in the interlayer space and thus does not explicitly account for the energy contribution by adsorption.
4. All the adsorptive mechanisms in soil, which include surface hydration, interlayer hydration, and multilayer adsorption, are electromagnetic in nature and can be unified by the theory of SSP. The SSP is an intrinsic soil–water property with a magnitude depending only on the statistical distance to the soil particle surface and the solute concentration of pore fluid. Based on the principle of thermodynamic equilibrium, matric potential is a constant throughout the entire air–water–soil REV. As such, both capillary potential, SSP, and adsorption-induced local pressure can be cast into a unitary definition of matric potential. The local water pressure will mirror the SSP and become most prominent, instead of vanishing, in fully saturated soil where matric potential diminishes to zero.
5. In defining total soil water potential, most previous definitions considered pore water pressure independent from the SSP. This is double counting, as the former is the result of the latter, and they should be considered coupled. The relationship between the two, along with capillary pressure, should and can be established through local thermodynamic energy equilibrium imposed over the entire matric potential REV.
6. Total soil water potential is commonly defined as the superposition of three independent potential functions (i.e., gravitational, osmotic, and matric potentials) of three state variables (i.e., elevation, ion concentration, and water content). This definition is questionable because the effects of water content and ion concentration on water potential are inseparable. Instead, osmotic and matric potentials exhibit non-negligible coupling effects, and both should be expressed as functions of water content and ion concentration.
7. The proposed unitary definition of matric potential provides a theoretical basis for separating capillary and adsorptive components of the SWRC. The capillary SWRC occurs most commonly in the range of matric potential from 0 to -10^4 kPa, whereas the adsorptive SWRC exists over the entire range but dominates matric potential lower than -10^5 kPa. Transitional behavior from capillarity to adsorption is determined by soil water cavitation, which limits the capillary potential to no less than -10^5 kPa.
8. Due to the existence of SSP, the local water pressure is highly spatially dependent within the REV. Water pressure near the soil particle surface can be as high as 1.6×10^6 kPa and then exponentially decay to the negative capillary pressure with increasing distance from the soil particle surface, typically within 100 layers of adsorbed water molecules.
9. Soil water density is recognized as a function of soil water content. Water density as high as 1.7 g m^{-3} has been experimentally quantified in clayey soil at very low water content. Measurements of SFC also show that the liquid water in soil can resist freezing down to −20 °C. These two phenomena can be explained with the aid of abnormally high, adsorption-induced compressive pressure, which differentiates the physical properties of soil water from that of free water.
10. Experimentally measured macroscopic soil properties and engineering behaviors (e.g., effective stress, thermal conductivity, elastic modulus, and small-strain shear modulus) all display strong correlation to different stages of SWR and reflect transitions between capillarity and adsorption. The SWRC proposed in accordance with the unitary definition of matric potential shows good agreement with the experimental data, supporting the necessity for using a better definition of matric potential in the current research and practice of unsaturated soil mechanics.

These conclusions not only show great promise for answering some enduring questions in scientific and engineering practice but also highlight some experimental and theoretical challenges that need to be tackled in future studies:

1. Fundamentally, both contact angle and SSP represent the energy state of soil surface and can potentially be unified for capillary and adsorptive mechanisms in future research.
2. There is a great demand for accurate measurements and better theories of the soil water density and soil water freezing temperature as functions of water content and wetting–drying state.
3. Because water evaporation and condensation in soils are controlled by the matric potential, a framework incorporating the SSP is needed to better understand these two natural processes ubiquitously occurring near the soil–atmospheric surface.
4. A reliable and time-efficient technique for continuously measuring high resolution data in the range of matric potential from -100 to -10^4 kPa is required.
5. A theoretical framework can be constructed based on both the SSP and the unitary definition of matric potential for better interpretation of soil consolidation phenomenon.

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AUTHOR CONTRIBUTIONS

Shengmin Luo: Data curation; Formal analysis; Resources; Software; Visualization; Writing – original draft. Ning Lu: Conceptualization; Funding acquisition; Project administration; Supervision; Writing – review & editing. Chao Zhang: Conceptualization; Formal analysis; Methodology; Writing – review & editing. William J. Likos: Funding acquisition; Writing – review & editing.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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