Soil Sorptive Potential: Concept, Theory, and Verification

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Abstract: Despite the widely accepted notion that water potential is the fundamental variable for describing soil–water interactions in soil under unsaturated conditions, it is unable to describe several basic soil properties and behaviors such as pore-water pressure, soil water density, and phase changes of soil water. A variable with greater explanatory power, sorptive potential, is conceptualized as the origin of matric potential and pore-water pressure. The sorptive potential is the sum of the locally varying electromagnetic potentials comprising van der Waals attraction, electrical double-layer repulsion, and surface and cation hydration. Local thermodynamic energy equilibrium dictates that the sorptive potential is always transformed or equal to matric potential minus the pressure potential within a representative elementary volume of matric potential. Limited verification was demonstrated by reducing the sorptive potential to the two well-established concepts of disjoining pressure and osmotic swelling pressure. A parametric study was conducted to illustrate how soil and pore-fluid properties affect sorptive and pressure potentials, indicating that the pore-water pressure under unsaturated conditions can be as high as 0.6 GPa. Such locally high pore-water pressure is induced by the sorptive potential and provides an explanation for phenomena such as abnormally high soil water density, supercooling, and decreased cavitation observed in fine-grained soils. **DOI: [10.1061/(ASCE)GT.1943-5606.0002025](https://doi.org/10.1061/(ASCE)GT.1943-5606.0002025).** © *2019 American Society of Civil Engineers.*

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Introduction

Soil water potential is the free energy change in a unit volume of water transferred from the free water state to the soil water state. Free energy refers to transferable energies through physical or chemical interactions such as mechanical and osmotic pressures and hydration among soil, water, and other dissolved matters. In general, soil–water interaction tends to decrease the free energy level. This free energy change is the physical source of soil water retention (e.g., Iwata et al. 1995), suction stress evolution (Lu and Likos 2006; Lu et al. 2010), hydraulic conductivity (e.g., van Genuchten 1980; Lu et al. 2014), thermal conductivity (Lu and Dong 2015), and freezing temperature reduction (Iwata et al. 1995; Zhang and Liu 2018). Consequently, all current frameworks for unsaturated soil mechanics invariably employ the water potential as the fundamental physical variable characterizing soil behavior. As such, under the thermodynamic equilibrium conditions, the soil water potential is uniquely defined for a given representative elementary volume (REV) of the soil-water-air system and is equal to the ambient water potential.

Nonetheless, soil water potential cannot be directly used as the governing variable for some important soil properties such as pore-water pressure; soil water density; and soil water phase transition boundaries among solid, liquid, and gas states. Instead, these properties are governed by local or intermolecular scale pressure and temperature within the REV defined for soil water potential, which generally vary spatially under a constant soil water potential. For instance, in a clay–water system under an equilibrium ambient water potential, the pore-water pressure was reported as nonuniform across the REV (Bolt and Miller 1958; Mitchell 1960). Consequently, the water properties vary significantly, especially near the particle surface (e.g., Boţan et al. 2011).

An outstanding dilemma is that nearly all existing frameworks based on the soil water potential predict that soil water pressure is always negative or lower than the ambient pressure under unsaturated conditions. At the scale defining pore-water pressure (molecular scale), the negative pore-water pressure suggests a relatively large distance among water molecules in soil compared with that of free water. The increased intermolecular distances imply a soil water density less than that of free water at the pore scale, contradicting frequent observations of higher soil water density relative to that of free water (e.g., De Wit and Arens 1950; Mackenzie 1958; Martin 1960; Zhang and Lu 2018a, b). This contradiction suggests that the description of pore-water pressure is incomplete under existing frameworks, and thereby precludes the accurate quantification of supercooling and cavitation of adsorptive water. Until recently, there was no single unified theory to reconcile this contradiction.

Herein, the authors contend that the soil water potential is not the most fundamental variable for the state of soil water. A new concept of the sorptive potential is constructed as the origin of both the soil water potential and pore-water pressure. First, two different types of chemical potentials, external and internal, are identified to classify the water potential. Based on the underlying intermolecular forces, capillarity is recognized as an internal interaction among water molecules generated on the air–water interface, whereas adsorption is characterized as an external interaction between soil

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Table 1. Terminologies used for defining potentials

Terminology	Definition
Gibbs free energy, G (kJ)	Maximum energy stored in soil-water-air systems available for reversible physicochemical interaction process under isothermal and isobaric conditions
Total chemical potential, μ_t (kJ/mol)	Total partial molar Gibbs free energy change
Internal chemical potential, μ_{int} (kJ/mol)	Partial molar Gibbs free energy change induced by internal interaction in the matter of interest
External chemical potential, μ_{ext} (kJ/mol)	Partial molar Gibbs free energy change induced by the interaction between the matter of interest and external matter
Total water potential, ψ_t (kJ/m^3 or kPa)	Total Gibbs free energy change per unit volume of water induced by physicochemical interactions in soil-water-air systems, gravitational field, and osmosis
Internal water potential, ψ_{int} (kJ/m^3 or kPa)	Gibbs free energy change per unit volume of water induced by the intermolecular forces among water molecules or pore-water pressure
External water potential, ψ_{ext} (kJ/m^3 or kPa)	Gibbs free energy change per unit volume of water induced by the interaction between water molecules and external matters like gravitational field, electromagnetic fields generated by soil matrix and dissolved matters
Osmotic potential, ψ_o (kJ/m^3 or kPa)	Gibbs free energy change per unit volume of water induced by the interaction between water molecules and electromagnetic fields generated by dissolved matters (only depends on the ion concentration at the far field)
Matric potential, ψ_m (kJ/m^3 or kPa)	Gibbs free energy change per unit volume of water induced by physicochemical interactions in soil-water-air systems
Pressure potential or internal matric potential, ψ_{pre} or $\psi_{m,int}$ (kJ/m^3 or kPa)	Gibbs free energy change per unit volume of water induced by the intermolecular forces among water molecules or pore-water pressure during physicochemical interactions in soil-water-air systems
Sorptive potential or external matric potential, ψ_{sorp} or $\psi_{m,ext}$ (kJ/m^3 or kPa)	Gibbs free energy change per unit volume of water induced by the interaction between water molecules and electromagnetic fields generated by soil matrix
Van der Waals component of sorptive potential, ψ_{vdW} (kJ/m^3 or kPa)	Gibbs free energy change per unit volume of water induced by van der Waals forces between water molecules and solid crystals
Electrical component of sorptive potential, ψ_{ele} (kJ/m^3 or kPa)	Gibbs free energy change per unit volume of water induced by interaction between water molecules and electric field generated by soil matrix
Osmotic component of sorptive potential, ψ_{osm} (kJ/m^3 or kPa)	Gibbs free energy change per unit volume of water induced by the ion concentration gradient produced by the soil matrix
Hydration component of sorptive potential, ψ_{hyd} (kJ/m^3 or kPa)	Gibbs free energy change per unit volume of water induced by hydration forces between water molecules and surface hydroxyls or retained exchangeable cations

particles and water molecules. Then, a new theoretical framework is proposed to describe the local or pore-scale water potential, with the sorptive potential decomposed into matric potential and pressure potential. Mathematical formulations are derived for each component of the sorptive potential and pressure potential. Verification of the sorptive potential is demonstrated by reducing it to the well-established swelling pressure and disjoining pressure in the soil–water system. The significance of the sorptive potential is illustrated through parametric analysis of the parallel-plate pores, elucidating the controls of basic soil water properties of pore size, Hamaker constant, surface potential, ion concentration, and decay length on the strengths of the sorptive and pressure potentials.

Concepts Pertinent to Sorptive Potential

Several new concepts relating to water potentials are coined here and defined in Table 1.

Capillarity and Adsorption

Current understanding of the universally negative pore-water pressure under unsaturated conditions mostly relies on the capillarity. Due to the hydrophilicity of soil particles, the surface tension of the air–water interface imposes negative water pressure on the pore water (e.g., Lu and Likos 2004; Zhang et al. 2016). This negative water pressure is frequently referred to as capillary pressure, and matric potential has been universally defined as the capillary pressure

$$\psi_m = p_w - p_a \tag{1}$$

where ψ_m = matric potential (kPa); p_w = pore-water pressure (kPa); and p_a = ambient air pressure (kPa). For convenience, the negative

matric potential is historically called matric suction. Negative pore-water pressure is the presumption for many frequently used theories in geotechnical engineering, e.g., the axis-translation technique (Hilf 1956), Bishop's effective stress (Bishop 1960), and the independent stress state variables (Fredlund and Morgenstern 1977).

However, matric potential arises from not only capillarity but also adsorption (McQueen and Miller 1974; Lu and Likos 2004; Lu 2016), suggesting that Eq. (1) is incomplete (Lu 2016). Fig. 1 schematically illustrates a conceptual soil water retention curve (SWRC) proposed by Lu (2016). The SWRC can be explicitly divided into three regimes, i.e., I (tightly adsorptive), II (adsorptive film), and III (capillary), in order from low to high matric potential. In Regime I, only a small amount of water remains in soil, and most
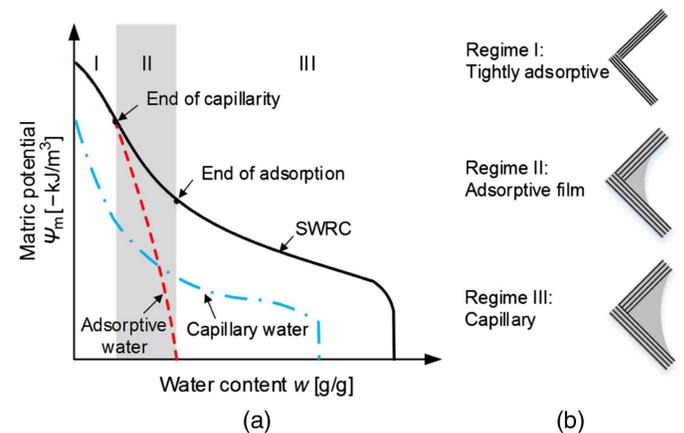

Fig. 1. (a) Generalized soil water retention curve; and (b) soil water retention regimes. (Reprinted from Lu 2016, © ASCE.)

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of the water molecules are adsorbed in the interlamellar space of clay minerals or intensively adsorbed on the particle surface, leading to possibly high interwater-molecular forces or compressive pore-water pressure. In this regime, matric potential is low and dominated by the adsorptive forces between soil particles and water molecules. In Regime II, some continuous water films on the soil particle surface become interconnected and form liquid menisci, enabling the excess free energy of the air–water interface, i.e., the presence of curved air–water interfaces or capillarity. Thus, this regime is marked as the interplay between capillarity and adsorption. In Regime III, as more and more water molecules condense on the soil matrix, the soil particle surface becomes fully coated by thick water films, reducing the adsorptive forces, and thereafter water molecules can only condense on the water film relatively far from the soil particle surface. Consequently, only capillarity persists in lowering the free energy of water, leading to tensile or negative pore-water pressure near the air–water interface.

As such, the conventional viewpoint of negative pore-water pressure can only reflect capillarity-induced negative pore-water pressure far from the particle surface and cannot reflect pore-water pressure in Regimes I and II in which adsorption dominates or participates in reducing the free energy of soil water. Therefore, the conventional water potential theories are incomplete due to the lack of comprehensive physical mechanisms for pore-water pressure.

Internal and External Water Potentials

From the thermodynamic viewpoint, the water potential quantifies the free energy change from the free water to the soil water. Excluding the effects of osmosis and elevation, the total water potential can be reduced to matric potential. The water potential can be expressed as a function of chemical potential, which is the partial molar free energy change (Noy-Meir and Ginzburg 1967; Slatyer and Taylor 1960)

$$\psi_t = \frac{\partial G}{\partial V} = \frac{\partial N_w}{\partial V}\frac{\partial G}{\partial N_w} = \frac{1}{v_w}\mu_t \qquad (2)$$

where ψ_t = total water potential (kJ/m³ or kPa); G = Gibbs free energy (kJ), and herein refers to the maximum energy stored in soil-water-air systems available for reversible physicochemical interaction processes under isothermal and isobaric conditions; V = volume of water (m³); N_w = number of moles of water (mol); v_w = molar volume of water (m³/mol); and μ_t = total chemical potential (kJ/mol).

Based on the sources of interaction, the total chemical potential can be decomposed into external and internal chemical potentials (Kittel and Kroemer 1980)

$$\mu_t = \mu_{\text{int}} + \mu_{\text{ext}} \qquad (3)$$

where μ_{int} = internal chemical potential; and μ_{ext} = external chemical potential. The internal chemical potential describes the thermodynamic energy state associated with the internal interaction in the matter of interest as illustrated in Fig. 2(a). For water molecules, the internal chemical potential is exclusively determined by the relative position and momentum of the water molecules, regardless of any interaction with external matter. The relative position represents the entropy and potential energy of water, whereas the momentum of water molecules denotes the kinetic energy of water molecules. The internal chemical potential can be expressed in terms of the Gibbs free energy (e.g., Çengel and Boles 2011)
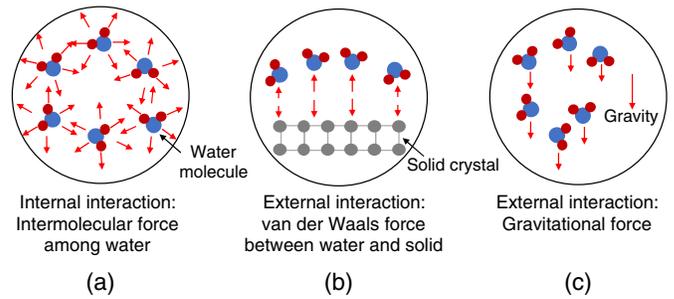

Fig. 2. Internal and external interactions: (a) intermolecular forces among water molecules; (b) van der Waals force between water molecules and solid crystals; and (c) gravitational force.

$$\mu_{\text{int}} = \frac{\partial G}{\partial N_w} \qquad (4)$$

The Gibbs free energy change can be further expressed as (e.g., Çengel and Boles 2011)

$$dG = Vdp - SdT \qquad (5)$$

where p = pressure (kPa); S = entropy of water (kJ/K); and T = absolute temperature (K). Under isothermal conditions, the Gibbs free energy change can be reduced to

$$dG = Vdp \qquad (6)$$

Substituting Eq. (6) into Eq. (4), the internal chemical potential is written

$$\mu_{\text{int}} = \frac{\partial G}{\partial N_w} = \int_{p_a}^{p_w} \frac{V}{N_w}dp = \int_{p_a}^{p_w} v_w dp \qquad (7)$$

In contrast, the external chemical potential is induced by the interaction between the matter of interest (water) and the external matter (soil matrix and dissolved matter) [Figs. 2(b and c)]. For instance, the presence of an external electric field or gravitational field will change the chemical potential of water in the fields. This change in chemical potential is attributable to the external chemical potential rather than to the internal chemical potential.

According to Eq. (2), the water potential is proportional to the chemical potential. Therefore, the total water potential can be explicitly divided into two components

$$\psi_t = \frac{1}{v_w}\mu_t = \frac{1}{v_w}\mu_{\text{int}} + \frac{1}{v_w}\mu_{\text{ext}} = \psi_{\text{int}} + \psi_{\text{ext}} \qquad (8)$$

where ψ_{int} = internal water potential resulting from the interaction among water molecules in the form of intermolecular force or pore-water pressure [Eq. (7)]; and ψ_{ext} = external water potential associated with the interaction of water molecules with external matter such as surface hydroxyls, exchangeable cations, and soil particles.

Matric Potential and Intermolecular Forces

A fundamental question regarding matric potential is which type of water potential is pertinent to conventional matric potential, internal or external. This section synthesizes the intermolecular forces underlying matric potential to answer this question. The physical source for matric potential is the lowering of free energy by the so-called soil–water interaction (Iwata et al. 1995). Two types of soil–water interaction contribute to this free energy change,
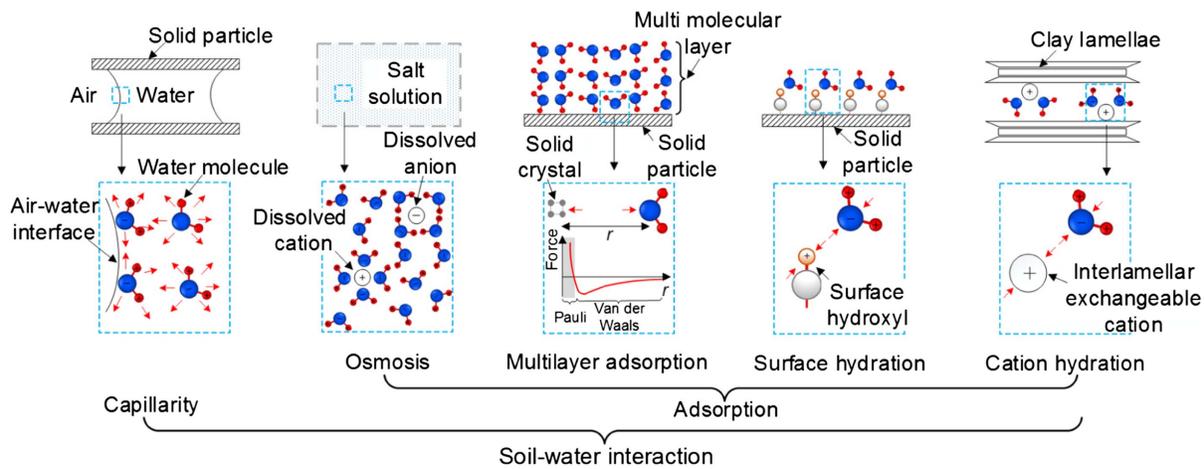
Fig. 3. Intermolecular forces underlying soil–water interaction mechanisms contributing to water potential.

i.e., capillarity and adsorption (Fig. 1). Therefore, matric potential can be explicitly decomposed into capillary and disjoining pressures (e.g., Lu and Khorshidi 2015)

$$\psi_m(\theta) = C(\kappa) + \Pi(h) \tag{9}$$

where θ = volumetric water content; $C(\kappa)$ = capillary pressure produced by capillarity (kPa), where κ = curvature of the air-water interface; and $\Pi(h)$ = disjoining pressure generated by adsorption (kPa), where h = adsorptive water film thickness (nm).

The intermolecular force underlying capillarity is the intermolecular tension among water molecules along the air–water interface (Fig. 3). This intermolecular tension integrates over the air–water interface, forming the interfacial tension. To sustain the force equilibrium along the air–water interface, a pressure difference generates across the air–water interface. Because most soil minerals are hydrophilic, the shape of the curved interface is concave, rendering a negative water pressure relative to the ambient air pressure. This negative water pressure is homogeneous in all capillary water. The intermolecular tension is generated among water molecules and therefore is an internal interaction. Thus, it can be concluded that capillarity belongs to the internal water potential, although the boundary of capillarity is constrained by the soil–water interaction. This conclusion can be further verified by the following formulation:

$$C(\kappa) = \frac{\partial G}{\partial V} = \frac{1}{v_w} \mu_{\text{int}} = \frac{1}{v_w} \int_{p_a}^{p_w} v_w \mathrm{d}p = p_w - p_a \tag{10}$$

In this formulation, capillarity is derived by assuming that it belongs to the internal water potential. The deduction here based on this assumption leads to a formula identical to the conventional definition of capillary potential [Eq. (1)]. This agreement verifies the validity of the assumption that capillarity produces the internal water potential.

In contrast, adsorption represents the interaction between water molecules and the soil matrix. This interaction depends on the surface properties of soil and is thus sensitive to the mineralogy of soil and the relative position to the particle surface. Fig. 3 shows four types of soil–water interaction contributing to adsorption, i.e., osmosis by electrical double layer, multilayer adsorption by van der Waals force, surface hydration by hydrogen bonds, and interlamellar cation hydration. Osmosis is produced by the solvation forces of cations and anions interacting with water molecules. For multilayer adsorption, the water molecules are attached to the soil

particle surface by the attractive forces between soil particles and water molecules. Pauli repulsion also exists, limiting the distance between water molecules and solid atoms. Surface hydroxyls are frequently observed on the soil mineral surface, counterbalancing the charges caused by the breakdown of solid crystals. The positively charged end of these surface hydroxyls attracts the negatively charged end of water dipoles, forming strong hydrogen bonds. In addition, expansive clay minerals typically possess exchangeable cations in the interlamellar space, which can strongly hydrate water molecules by attracting the negatively charged end of water dipoles. The magnitude of these intermolecular forces decays nonlinearly with the increasing distance from the particle surface, surface hydroxyls, or exchangeable cations (e.g., Israelachvili 2011). In summary, these intermolecular forces underlying adsorption are characterized as attractive forces between the soil matrix and water molecules and depend highly on the relative position in soil. Therefore, it can be inferred that the water potential generated by adsorption is external and nonhomogenous in the REV of soil water potential.

Theory of Sorptive Potential

Matric potential consists of both internal and external water potentials, as summarized in the previous section. Therefore, matric potential can be logically divided into two components

$$\psi_m(\theta) = \psi_{m,\text{int}} + \psi_{m,\text{ext}} \tag{11}$$

where $\psi_{m,\text{int}}$ = internal matric potential; and $\psi_{m,\text{ext}}$ = external matric potential. The rest of this section elucidates the physical meanings of the internal and external matric potentials and how these potentials relate to conventional soil water retention.

Sorptive Potential

As reasoned in the previous section, the external matric potential is exclusively induced by adsorption. Herein, a new concept of sorptive potential (ψ_{sorp}) is proposed to represent the external matric potential. The sorptive potential is defined as the free energy change per unit volume of soil water caused by its interaction with external matter. The sorptive potential is a spatial function because the local adsorptive forces vary with the distance to particle surfaces, surface hydroxyls, and cations. Therefore, the sorptive potential concept differs from the conventional concept of disjoining
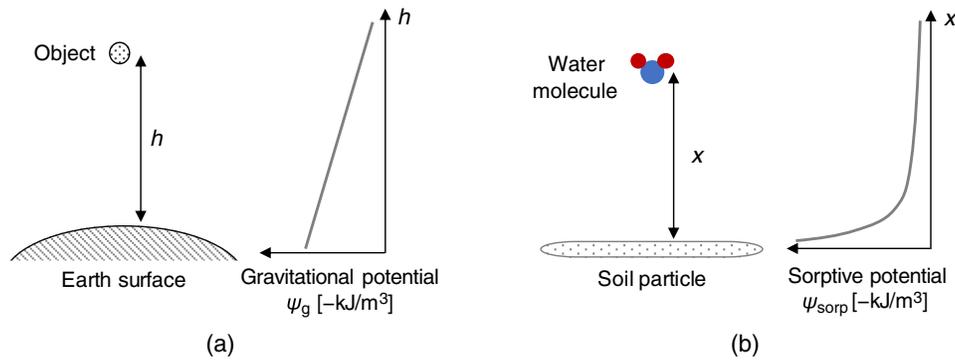
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Fig. 4. Comparison of spatial variation between (a) gravitational potential; and (b) sorptive potential.

pressure $\Pi(h)$. The difference between sorptive potential and disjoining pressure is highlighted via analogy to the Earth gravitational potential.

The gravitational potential stems from the attractive force between Earth and an object of interest. As the object approaches the Earth's surface, this attractive force turns the gravitational potential energy into other types of energy, and thereby the gravitational potential decreases. The gravitational potential is almost proportional to the distance of the object to the Earth's surface if the object is near the Earth's surface [Fig. 4(a)]. Thus, the magnitude of gravitational potential depends on the absolute distance of the object to the Earth's center. That is, the gravitational potential varies spatially and is not homogeneous. Similarly, the sorptive potential originates from the attractive forces between the soil matrix and water molecules. When water molecules approach the soil matrix, these attractive forces turn sorptive potential energy into other types of energy, for example, internal energy of water. Accordingly, the sorptive potential decreases with the decreasing distance between water molecules and soil matrix [Fig. 4(b)]. Therefore, the sorptive potential is not constant but is instead a nonlinear function of distance. This spatially varying nature of adsorptive potential is not reflected in the disjoining pressure, which only considers the total potential of the stabilized film water or the pressure along the midplane of parallel particles.

Therefore, the sorptive potential can be formulated as a function of both soil properties and spatial coordinates. The attractive forces between the soil matrix and water molecules can be produced by several physical mechanisms, i.e., van der Waals attraction, electrical double layer, and hydration on cation or surface hydroxyls. As such, the sorptive potential can be formulated in terms of four components

$$\psi_{sorp}(x) = \psi_{m,ext}(x) = \psi_{vdW}(x) + \psi_{ele}(x) + \psi_{osm}(x) + \psi_{hyd}(x)$$
(12)

where x = statistical distance to the adjacent particle surface and represents the spatial coordinate; $\psi_{vdW}(x)$ = van der Waals component; $\psi_{ele}(x)$ = electrical component; $\psi_{osm}(x)$ = osmotic component; and $\psi_{hyd}(x)$ = hydration component. The physical meanings of these four components are conceptually illustrated in Fig. 5. Obviously, the magnitudes of these four components nonlinearly decay with the distance to the particle surface. The detailed formulation for each component is provided in the Appendix.

Pressure Potential

The internal matric potential is conceptualized as the pressure potential (ψ_{pre}). The underlying physical meaning and formulation are elaborated herein. Considering a saturated or unsaturated soil in equilibrium with the ambient environment, the total soil water potential can be expressed as a function of relative humidity via Kelvin's equation (e.g., Lu and Likos 2004)

$$\psi_t(\theta, c_0) = \psi_m(\theta) + \psi_o(c_0) = \frac{RT}{v_w}\ln RH$$
(13)

where ψ_o = osmotic potential, and only depends on the ion concentration (c_0) at a far-field boundary; R = gas constant ($Jmol^{-1}K^{-1}$); and RH = relative humidity. Because the osmotic potential only depends on the ion concentration in pore water, Eq. (13) states that matric potential only depends on the boundary conditions defined at the water–air interface, i.e., relative humidity and ion concentration in pore water. That is, under given relative humidity and pore-water properties, matric potential is constant over the entire soil–water system. Furthermore, if excluding hysteresis, matric potential is unique for a given water content.

Because matric potential is a constant and the sorptive potential varies spatially, Eq. (11) suggests that the internal matric potential is inevitably a function of spatial coordinates and water content. Substituting Eq. (12) into Eq. (11) leads to

$$\psi_{m,int}(x, \theta) = \psi_m(\theta) - \psi_{sorp}(x)$$
(14)

Eq. (14) states that the internal matric potential varies spatially depending on the local sorptive potential. Neglecting the entropy changes corresponding to intensive structural changes and molar volume changes, the internal matric potential can be formulated by rewriting Eq. (7)

$$\psi_{m,int}(x, \theta) = \frac{1}{v_w}\mu_{m,int}(x, \theta) = \frac{1}{v_w}\int_{p_a}^{p_w(x,\theta)} v_w dp = p_w(x, \theta) - p_a$$
(15)

where $p_w(x, \theta)$ = local pore-water pressure.

Eq. (15) indicates that, physically, the pressure potential or internal matric potential is the pore-scale or local pressure difference between soil water and ambient air. That is, the pressure potential can be defined as the free energy change per unit volume of soil water caused by its pressure difference with respect to ambient air. Substituting Eq. (15) into Eq. (14), the pressure potential or local pressure difference can be calculated from the local sorptive potential

$$\psi_{pre}(x, \theta) = \psi_{m,int}(x, \theta) = p_w(x, \theta) - p_a = \psi_m(\theta) - \psi_{sorp}(x)$$
(16)

Eq. (16) indicates that when the sorptive potential vanishes, the pressure difference is identical to matric potential, reducing to the conventional definition of matric potential as the pressure
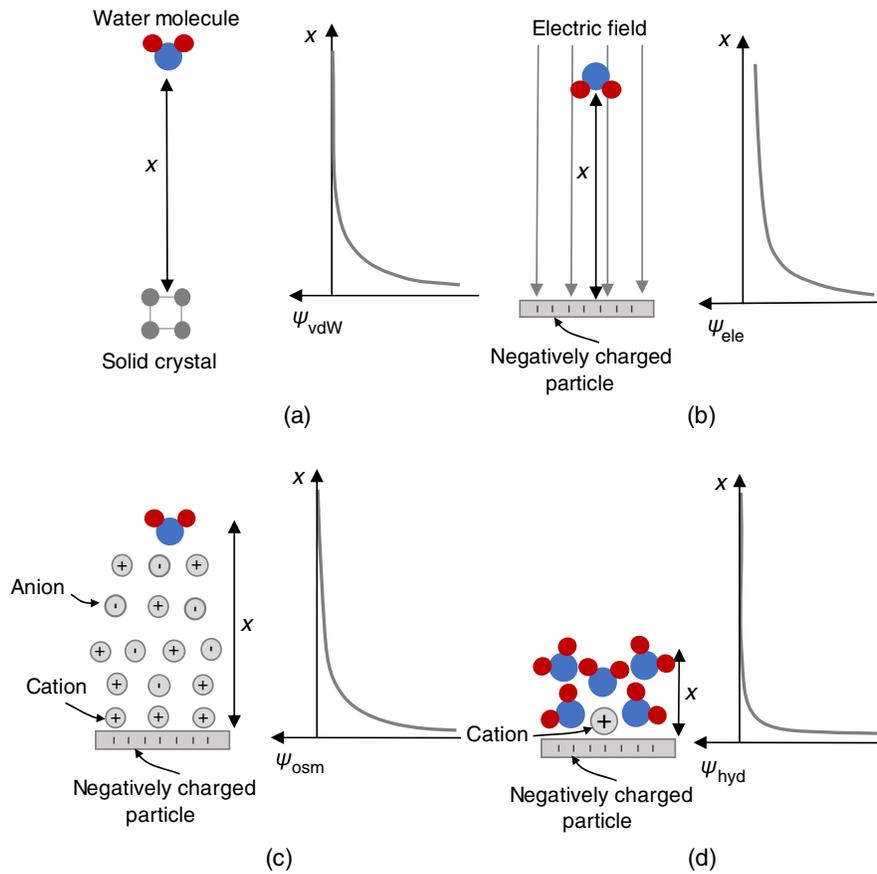
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Fig. 5. Sorptive potential components: (a) van der Waals; (b) electrical; (c) osmotic; and (d) hydration.

difference. However, if the sorptive potential is nonzero, the conventional definition of matric potential as the pressure difference does not hold, and the local pore-water pressure is not a constant, but instead varies spatially. That is, the local pore-water pressure depends on not only matric potential but also the local sorptive potential. Because the pressure is a basic thermodynamic state variable, the physical properties of soil water, e.g., density, supercooling, and cavitation, also vary spatially and highly depend on the local sorptive potential.

Relevance to Soil Water Retention Curves

With the aid of the conceptualized sorptive and pressure potentials, the local thermodynamic energy equilibrium statement can be written

$$\psi_{\text{sorp}}(x) + \psi_{\text{pre}}(x, \theta) + \psi_o(c_o) = \psi_t(\theta, c_o) = \psi_m(\theta) + \psi_o(c_o) \tag{17}$$

Eq. (17) can be rearranged to express the sorptive potential as

$$\psi_{\text{sorp}}(x) = \psi_m(\theta) - \psi_{\text{pre}}(x, \theta) \tag{18}$$

Eq. (18) suggests that, in a soil–water system equilibrated with the ambient environment, the local sorptive and pressure potentials vary spatially, although matric potential is unique over the REV of soil. Alternatively, Eq. (18) can be interpreted from an energy perspective. The sorptive potential quantifies how much energy is stored in the soil matrix in different forms of electromagnetic fields. How much of the electromagnetic field energy can be transferred

into internal energy of water depends on the availability of water molecules. If the relative humidity is 1.0, the supply of water molecules is so sufficient that the electromagnetic field energy is fully consumed by water molecules, and matric potential is zero. In contrast, if the relative humidity is less than 1.0, the electromagnetic field energy is only partly consumed by water molecules in the form of pore-water pressure, and the rest remains as matric potential $\psi_m(\theta)$ retained by the water molecules, striving for a thermodynamic equilibrium with the ambient vapor pressure.

Verification of Sorptive Potential

Deduction of Sorptive Potential to Disjoining Pressure

To verify the generality of the sorptive potential, the proposed formulation was used to predict two well-established concepts: disjoining pressure and swelling pressure. For disjoining pressure, the contribution of van der Waals interaction is referred to as the molecular component. The molecular component of water film with a thickness of h can be expressed as (e.g., Derjaguin et al. 1987)

$$\Pi(h) = -\frac{A_{\text{H}}}{6\pi h^3} \tag{19}$$

where A_{H} = Hamaker constant (J).

The disjoining pressure can be understood as the matric potential of the water film. The curvature at the water–air interface is zero for a water film, suggesting that the pressure potential is zero. Thus, according to Eq. (18), the disjoining pressure is equal to the
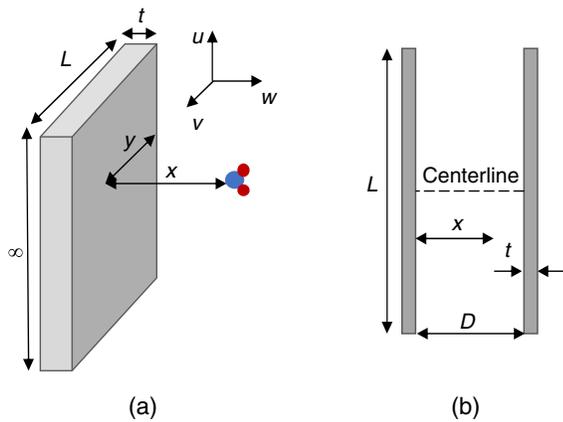
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Fig. 6. Geometric model: (a) semi-infinite platy soil particle with thickness t and width L; and (b) pore formed by two parallel plates with separation distance D.

sorptive potential at the water–air interface. Because Eq. (19) describes a water film adsorbed on a semi-infinite solid, the disjoining pressure can be formulated as

$$\Pi(h) = \lim_{\substack{L \to \infty \\ t \to \infty}} \psi_{\text{vdW}}(x = h, y) = -\frac{A_{\text{H}}}{6\pi h^3} \qquad (20)$$

where $\psi_{\text{vdW}}(x, y)$ = van der Waals component of sorptive potential for a semi-infinite plate in Fig. 6(a), and is derived in the Appendix [Eq. (26)]. Eq. (20) leads to an identical formulation with Eq. (19), confirming the inclusiveness of sorptive potential.

Deduction of Sorptive Potential to Swelling Pressure

The proposed sorptive potential also can be used to predict the swelling pressure. Conventionally, the swelling pressure (p_s) of a symmetric double layer can be expressed as (e.g., Mitchell and Soga 2005)

$$p_s = 2c_0 k_{\text{B}} T(\cosh u_d - 1) \qquad (21)$$

where u_d = midplane potential; and k_{B} = Boltzmann constant, i.e., 1.38×10^{-23} $(\text{m}^2\text{kgs}^{-2}\text{K}^{-1})$. The swelling pressure is predicted as the water pressure along the midplane between two symmetric clay particles. In the proposed formulation, this water pressure can be estimated via the electrical and osmotic components of the sorptive potential. Specifically, the swelling pressure can be derived from the proposed formulation [Eqs. (28) and (32) in the Appendix]

$$p_s = -\psi_{\text{ele}}(d) - \psi_{\text{osm}}(d)$$

$$= -\frac{1}{2}\varepsilon_0(1 - \varepsilon_{\text{r}})\mathbf{E}(d)^2$$

$$+ c_0 k_{\text{B}} T\left\{\exp\left[\frac{eV_{\text{edl}}(d)}{k_{\text{B}}T}\right] + \exp\left[-\frac{eV_{\text{edl}}(d)}{k_{\text{B}}T}\right] - 2\right\} \qquad (22)$$

where d = distance from midplane to the particle surface (m); ε_0 = permittivity of a vacuum, i.e., 8.85×10^{-12} (F/m); ε_r = dielectric constant, e.g., 78.54 for water at 25°C; $\mathbf{E}$ = electric field intensity (V/m); e = charge of an electron, i.e., 1.60×10^{-19} (C); and V_{edl} = electric potential (V).

Due to the symmetric electric potential of the double layer, the gradient of electric potential is zero at the midplane, i.e., $\mathbf{E}(d) = 0$. Then Eq. (22) can be rewritten

$$p_s = c_0 k_{\text{B}} T\left\{\exp\left[\frac{eV_{\text{edl}}(d)}{k_{\text{B}}T}\right] + \exp\left[-\frac{eV_{\text{edl}}(d)}{k_{\text{B}}T}\right] - 2\right\}$$

$$= 2c_0 k_{\text{B}} T\left\{\cosh\left[\frac{eV_{\text{edl}}(d)}{k_{\text{B}}T}\right] - 1\right\} = 2c_0 k_{\text{B}} T(\cosh u_{\text{d}} - 1) \qquad (23)$$

As shown previously, Eq. (23) leads to the same formula as conventional formula Eq. (21), further verifying the generality of the sorptive potential.

Magnitude of Sorptive Potential

Basic Properties of Soil–Water System

If the ambient air pressure is taken as a reference, i.e., $p_a = 0$ kPa, Eq. (16) can be reduced to

$$p_w(x, \theta) = \psi_{\text{pre}}(x, \theta) = \psi_m(\theta) - \psi_{\text{sorp}}(x) \qquad (24)$$

Using Eq. (24), a series of quantitative analyses was conducted to assess how soil and pore-fluid properties influence the magnitudes of sorptive potential and water pressure. For simplicity, only fully saturated soil with $\psi_m(\theta) = 0.0$ was considered, the pressure results of which can be easily transferred to unsaturated soils by adding matric potential. A parallel-plate pore was considered as a prototype clay pore [Fig. 6(b)]. The Appendix gives the detailed formulation.

Table 2 summarizes the pertinent parameters and their values used to define the sorptive potential. Configuration 1 was selected as the reference configuration. The pore size (separation distance) was 10, 20, or 50 nm, representing different pore sizes. The Hamaker constant A_{H} was 2.2×10^{-20}, 2.5×10^{-20}, or 3.1×10^{-20} J, representing different clay minerals, as suggested by Lu et al. (2008). The surface potential was 50, 100, or 200 mV. The ion concentration c_0 was 0.01, 0.1, or 1.0 mol/m³, reflecting

Table 2. Pertinent parameters selected for parametric study

Configuration number	Pore size (nm)	Hamaker constant (J)	Surface potential (mV)	Ion concentration (mol/m^{-3})
1	20	2.5×10^{-20}	100	0.1
2	10	2.5×10^{-20}	100	0.1
3	50	2.5×10^{-20}	100	0.1
4	20	2.2×10^{-20}	100	0.1
5	20	3.1×10^{-20}	100	0.1
6	20	2.5×10^{-20}	50	0.1
7	20	2.5×10^{-20}	200	0.1
8	20	2.5×10^{-20}	100	0.01
9	20	2.5×10^{-20}	100	1.0

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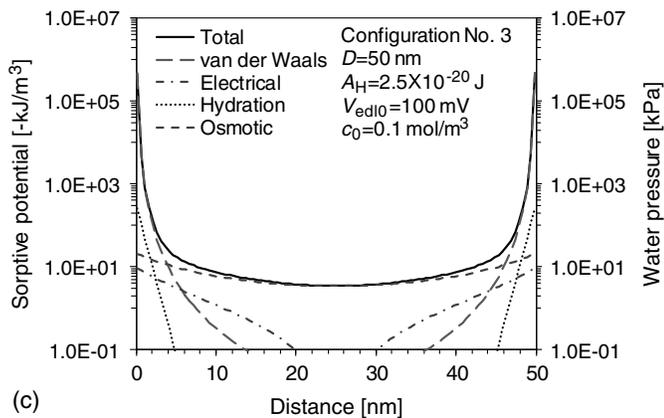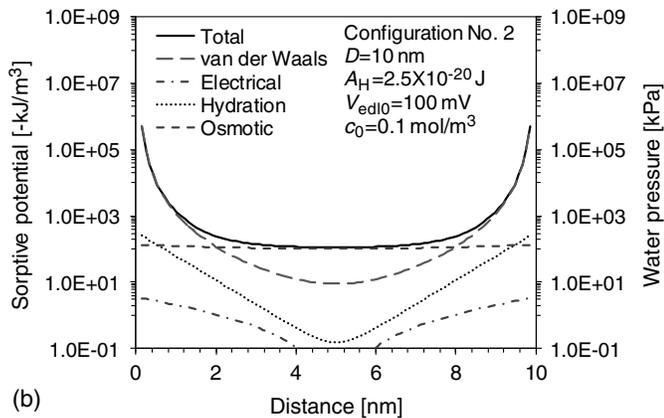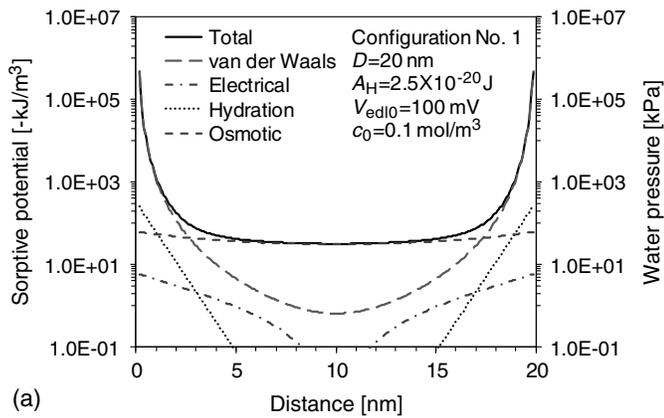J. Geotech. Geoenviron. Eng., 2019, 145(4): 04019006

Fig. 7. Sorptive potential and water pressure along the centerline of parallel-plate pore with pore size: (a) $D = 20$ nm (Configuration 1); (b) $D = 10$ nm (Configuration 2); and (c) $D = 50$ nm (Configuration 3). All curves represent both potential (left vertical axis) and pressure (right vertical axis).

pore-fluid chemistry. The other parameters were fixed at $T = 298$ K, $L = 50$ nm, $t = 1$ nm, $\lambda_h = 0.6$ nm, and $\psi_{hyd0} = -3.2 \times 10^5$ J/m^3. The sorptive potential and water pressure curves started from the half thickness of the water molecular film, i.e., $x = 0.14$ nm (e.g., Mitchell and Soga 2005).

In Configuration 1, pertinent parameters were calibrated as $D = 20$ nm, $A_H = 2.5 \times 10^{-20}$ J, $V_{edl0} = 100$ mV, and $c_0 = 0.1$ mol/m^3. Fig. 7(a) illustrates the sorptive potential and water pressure profiles for Configuration 1. The sorptive potential generally decayed with increasing distance to the particle surface.

The water pressure was positive and was high as 483 MPa, which can potentially explain why the soil water density can be much higher than the free water density. The van der Waals component dominated the sorptive potential at a distance of $x < 3$ nm, whereas the osmotic component took over at $x > 3$ nm. Compared with the van der Waals and osmotic components, the contribution of the electrical and hydration components was negligible.

Effect of Pore Size

Fig. 7 illustrates the influence of pore size on the sorptive potential and water pressure, i.e., Configurations 1–3. In general, the sorptive potential and water pressure profiles were very sensitive to the pore size, which can be explained by the fast decay rate of the sorptive potential. The osmotic component remained almost constant along the pore with $D = 10$ nm [Fig. 7(b)]. In addition, the influence scope of the sorptive potential covered the entire pore space, and the water pressure was as high as 112 kPa even at the center. For the pore with $D = 50$ nm in Fig. 7(c), the sorptive potential was dominated by the van der Waals component at a short distance x but by the osmotic component at a large distance x. The water pressure was around 3.5 kPa at the center of the pore with $D = 50$ nm, which was much smaller than that with $D = 10$ nm.

Effect of Hamaker Constant

The sensitivity analysis for different values of the Hamaker constant indicated that it has a very limited influence on the variability of sorptive potential; only the water pressure within 3 nm from the particle surface was sensitive to the Hamaker constant, but its variability was within 30% in magnitude. Specifically, the highest water pressure was 425 MPa with $A_H = 2.2 \times 10^{-20}$ J, 483 MPa with $A_H = 2.5 \times 10^{-20}$ J, and 599 MPa with $A_H = 3.1 \times 10^{-20}$ J. It is concluded that the Hamaker constant is important for the sorptive potential but only has a marginal influence on the variability of the water pressure in the zone close to the particle surface.

Effect of Surface Potential

Figs. 7 and 8(a) illustrate how surface potential impacts the sorptive potential and water pressure. Generally, an increase in surface potential can remarkably influence the osmotic component of sorptive potential. Specifically, the component dominating the sorptive potential changed from van der Waals to osmotic at $x = 6$ nm with $V_{edl0} = 50$ mV [Fig. 8(a)]. This transition point decreased to 3 nm with $V_{edl0} = 100$ mV due to the significant increase in the osmotic component [Fig. 7(a)]. For $V_{edl0} = 200$ mV, the osmotic component almost dominated the sorptive potential in the entire pore. In addition, the electrical component increased with the increasing surface potential. However, the electrical component was negligible compared with the osmotic component and thus was not well reflected in the sorptive potential. Therefore, an increase in the surface potential significantly increases both the electrical and osmotic components and accordingly, increases the sorptive potential.

Effect of Ion Concentration

The sorptive potential and water pressure profiles with different ion concentrations are illustrated in Figs. 7(a) and 9. The electrical double-layer thickness ($1/\kappa$) is a function of the ion concentration [Eq. (29) in the Appendix]. Hence, the double-layer thickness was calculated as 96.2, 30.4, and 9.6 nm for ion concentrations 0.01, 0.1, and 1.0 mol/m^3, respectively. In general, a higher ion concentration indicates a higher magnitude of the electrical and osmotic
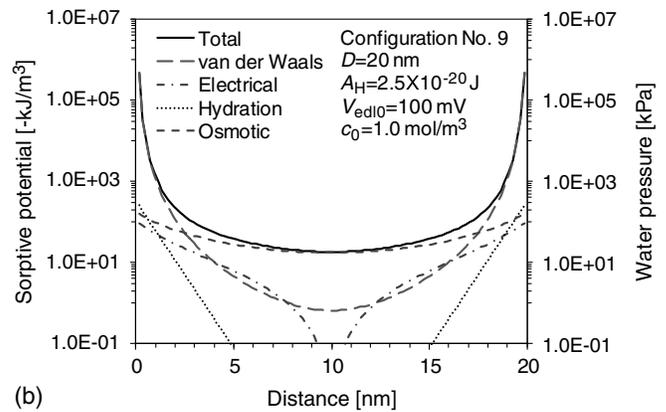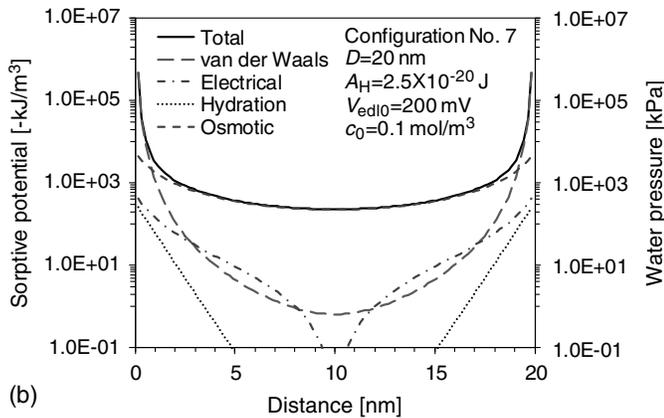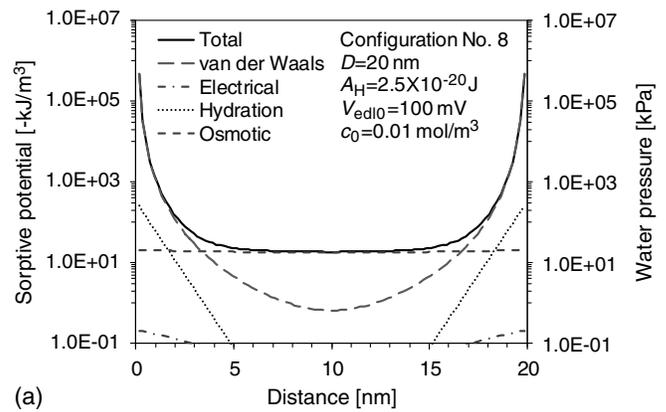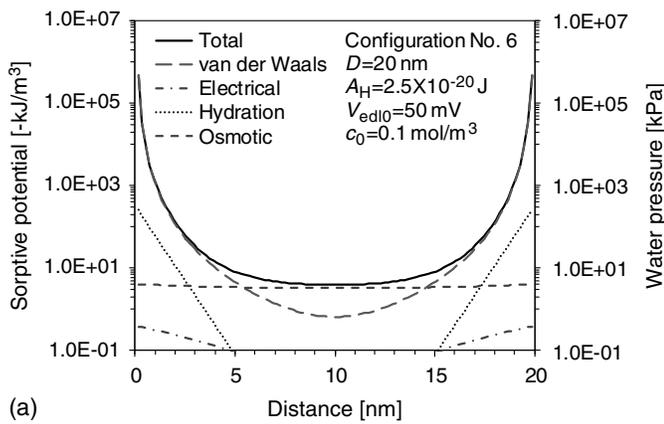
Fig. 8. Sorptive potential and water pressure along the centerline of parallel-plate pore with surface potential: (a) 50 mV (Configuration 6); and (b) 200 mV (Configuration 7). All curves represent both potential (left vertical axis) and pressure (right vertical axis).

Fig. 9. Sorptive potential and water pressure along the centerline of parallel-plate pore with ion concentration: (a) 0.01 mol/m^3 (Configuration 8); and (b) 1.0 mol/m^3 (Configuration 9). All curves represent both potential (left vertical axis) and pressure (right vertical axis).

components but a smaller electrical double-layer thickness, suggesting a higher decay rate of electrical and osmotic components. Consequently, an increase in the ion concentration increases the water pressure close to the particle surface but decreases the water pressure farther from the particle surface.

Implications of Sorptive Potential to Soil Fundamental Behavior

Soil Water Supercooling

Pore-water pressure, together with temperature, is the thermodynamic variable governing the phase transition behavior of soil water. The sorptive potential partly converts to locally varying water pressure, shifting the local pore-water pressure well above the ambient air and substantially altering the phase boundaries. In the preceding section, the magnitude of the local pore-water pressure increased to as high as 0.6 GPa, suggesting that the surface adsorbed water film is under high pressure. According to the phase diagram of water, water under such high pressure maintains a glassy state and cannot be transformed into regular ice. Therefore, the high pore-water pressure can greatly decrease the freezing point, which explains why the film water remains in the liquid phase under extremely low temperatures, as reported by many researchers (e.g., Anderson and Hoekstra 1965; Mitchell and Soga 2005; Zhang and Liu 2018).

Soil Water Decreased Cavitation

The high pore-water pressure induced by the sorptive potential can potentially prevent the adsorptive water from cavitating. Under negative pressure, the water reaches a metastable state and spontaneously vaporizes once it reaches the cavitation pressure, which is considered to be an important mechanism in the drainage and drying process in porous materials (e.g., Or and Tuller 2002; Toker et al. 2003; Duan et al. 2012). The cavitation probability directly depends on how much tensile pressure is imposed on water molecules. Therefore, the locally positive pressure induced by the sorptive potential significantly alters the tensile pressure and thus reduces the cavitation probability.

In clayey soils, a considerable amount of retained water is affected by the sorptive potential. For example, Fig. 7(a) shows that the local water pressure can be potentially shifted to 42 kPa even at a distance of 5 nm (~18 water molecular layers) from the particle surface, indicating that a considerable amount of water is present due to the large surface area of clayey soils. As such, the sorptive potential shifts a great portion of soil water to a considerably higher pressure, leading to phase transition behavior distinct from free water or capillary water. Therefore, it is necessary to include the sorptive potential when developing the phase diagram of soil water.

Summary and Conclusions

Water potential has been considered to be the most fundamental variable for describing soil–water interactions for soil under

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unsaturated conditions. However, scientifically its origin remains ambiguous, and practically it cannot be directly used to describe several fundamental soil properties and behaviors, e.g., local pore-water pressure, abnormally high soil water density, soil water supercooling, and decreased cavitation phenomena in fine-grained soils. Together with temperature, local pore-water pressure, rather than matric potential, is the thermodynamic variable defining the phase transition behavior of soil water among solid, liquid, and gas.

The conventional water potential concept was revisited with the aid of basic thermodynamics and intermolecular forces. The conventional understanding of a single-valued negative pore-water pressure at the REV of matric potential concept was recognized as incomplete due to the absence of adsorption. Components of water potential were reclassified into internal and external water potentials. Capillarity stems from the intermolecular tension among water molecules and thus was identified as internal water potential, whereas adsorption originates from water molecules interacting with external matters, e.g., particle surface, surface hydroxyls, and exchangeable cations, and was classified as external water potential.

The sorptive potential was conceptualized as the common source of both pore-water pressure (pressure potential) and matric potential. The sorptive potential was defined as the free energy change per unit volume of water due to its interaction with external matter, whereas the pressure potential was defined as the free energy change per unit volume of water due to its pressure change. The sorptive potential depends on the relative position between water molecules and external matter and thus varies within the REV of matric potential. Physically, the sorptive potential consists of four components, all electromagnetic in nature, i.e., van der Waals, electrical, osmotic, and hydration. Theoretical equations were derived for each component of the sorptive potential.

The pressure potential was derived as equal to the pressure difference between pore water and ambient air. The pore-water pressure was found to spatially vary due to the spatial variation of sorptive potential. The sorptive potential was found to induce positive water pressure, showing consistency with the persistently observed phenomenon of higher soil water density than the free water. A mathematical equation was derived to calculate the sorptive potential and pore-water pressure profiles in the parallel-plate pore. The generality of the proposed sorptive potential theory was verified by reducing it to the two well-established theories of disjoining pressure and swelling pressure.

A parametric study was conducted to illustrate how soil and pore-fluid properties affect the magnitude of sorptive potential and pore-water pressure. In general, the sorptive potential is dominated by the van der Waals component at close distances to the particle surface but the osmotic component dominates farther away. The induced pore-water pressure is always positive and can be as high as 0.6 GPa, demonstrating high dependence on the surface potential and ion concentration. The induced pore-water pressure can significantly shift the freezing point and decrease the cavitation pressure, demonstrating that the sorptive potential can physically and quantitatively describe the supercooling and reduced cavitation phenomena in fine-grained soils.

Appendix. Formulation of Sorptive Potential Components

Van der Waals Component

The van der Waals component is produced by the van der Waals force between solid crystals and water molecule [Fig. 5(a)]. The

van der Waals force is the sum of the Keesom force, the Debye force, and the London force, and is the driving force for the multilayer adsorption. The van der Waals potential energy between molecules A and B can be formulated as (e.g., Butt and Kappl 2009; Israelachvili 2011)

$$U_{AB}(x) = -\frac{C_{AB}}{x^6}$$

where U_{AB} = potential energy of van der Waals interaction between molecules A and B (J); x = distance between molecules A and B (m); C_{AB} = material-specific constant (J · m^6) which is related to the Hamaker constant as

$$C_{AB} = \frac{A_H}{\pi^2 \rho_A \rho_B}$$

where A_H = Hamaker constant (J); and ρ_A and ρ_B = molecular densities of molecules A and B, respectively (m^{-3}). The van der Waals component of sorptive potential can be calculated as

$$\psi_{vdW}(x) = \int_\Omega U_{AB}(x) d\Omega \tag{25}$$

where Ω = domain of interest, e.g., a soil particle and a unit volume of soil water.

A semi-infinite plate is considered to represent typical clay particles in Fig. 6(a). The thickness and width of the particle are t and L, respectively, whereas the length of particle is infinite. The water molecule of interest is placed at a distance x from the particle surface and y from the particle edge. The van der Waals component can be calculated by integrating Eq. (25) over the semi-infinite plate

$$
\begin{aligned}
\psi_{vdW}(x,y) &= \rho_A \rho_B \int_{-x-t}^{-x} \int_{-y}^{L-y} \int_{-\infty}^{+\infty} U_{AB} du dv dw \\
&= -\rho_A \rho_B C_{AB} \int_{-x-t}^{-x} \int_{-y}^{L-y} \int_{-\infty}^{+\infty} \frac{1}{(u^2+v^2+w^2)^3} du dv dw \\
&= \frac{A_H[2y^4 + y^2(x+t)^2 + 2(x+t)^4]}{24\pi y^3 (x+t)^3 \sqrt{y^2 + (x+t)^2}} \\
&\quad - \frac{A_H[2(y-L)^4 + (y-L)^2(x+t)^2 + 2(x+t)^4]}{24\pi(y-L)^3(x+t)^3 \sqrt{(y-L)^2 + (x+t)^2}} \\
&\quad - \frac{A_H[2x^4 + x^2 y^2 + 2y^4]}{24\pi x^3 y^3 \sqrt{x^2 + y^2}} \\
&\quad + \frac{A_H[2(y-L)^4 + (y-L)^2 x^2 + 2x^4]}{24\pi(y-L)^3 x^3 \sqrt{(y-L)^2 + x^2}}
\end{aligned}
\tag{26}
$$

In Fig. 6(b), a parallel-plate pore is considered to mimic pores in clayey soils. The width and thickness of the clay particle are respectively L and t. To simplify formulation, the sorptive potential is calculated via assembling semi-infinite plates. The total van der Waals component is a sum of the van der Waals components of clay particles

$$\psi_{vdW}(x,y) = \sum_{i=1}^{N} \psi_{vdW,i}(x,y) \tag{27}$$

where $\psi_{vdW,i}$ = van der Waals component of ith clay particle; and N = number of clay particles.

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Electrical Component

The clay particles are not neutrally charged due to the isothermal substitution and breakage of crystals. The negative surface charge on clay particles will adsorb cations, produce a local electric field, and subsequently alter the ion distribution around the particles. Conventionally, this electrostatic interaction in soil is modeled by electrical double-layer theories, which only quantify the water pressure at the boundary, e.g., the midplane between two particles. Herein, both the electrical and osmotic components were considered to quantify the spatially varying water pressure in soil.

The external electric field produced by the particles reorients polarized water molecules and thereafter alters the energy of water molecules [Fig. 5(b)]. Consequently, some electrostatic energy is stored in the water molecules in the electric field. The amount of electrostatic energy stored in water can be estimated as (e.g., Cheng 1989)

$$U_{\text{elew}}(x) = \frac{1}{2}\varepsilon_0\varepsilon_r\mathbf{E}(x)^2$$

where $U_{\text{elew}}(x)$ = electrostatic energy stored in water (J/m^3); ε_0 = permittivity of a vacuum, i.e., 8.85×10^{-12} F/m; ε_r = dielectric constant, e.g., 78.54 for water at 25°C; and $\mathbf{E}(x)$ = electric field intensity (V/m). The electrical component of sorptive potential is defined as the difference between the electrostatic energy stored in a vacuum and water (Bolt and Miller 1958; Iwata 1972). Therefore, the electrical component can be formulated as

$$\psi_{\text{ele}}(x) = U_{\text{ele0}}(x) - U_{\text{elew}}(x) = \frac{1}{2}\varepsilon_0(1-\varepsilon_r)\mathbf{E}(x)^2 \quad (28)$$

where $U_{\text{ele0}}(x)$ = electrostatic energy stored in a vacuum (kJ/m^3). The decay rate of the electrical component is lower than the van der Waals component (Fig. 5).

For a negatively charged infinite plane, the electric potential (V_{edl}) can be expressed as (e.g., Mitchell and Soga 2005; Butt and Kappl 2009)

$$V_{\text{edl}}(x) = \frac{2k_{\text{B}}T}{e}\ln\left(\frac{1 + \alpha e^{-\kappa x}}{1 - \alpha e^{-\kappa x}}\right)$$

where e = charge of an electron, i.e., 1.60×10^{-19} C; k_{B} = Boltzmann constant, i.e., 1.38×10^{-23} m^{2}kgs^{-2}K^{-1}; T = absolute temperature (K); and $1/\kappa$ = electrical double-layer thickness (nm)

$$\kappa = \sqrt{\frac{2c_0 N_A e^2}{\varepsilon_r\varepsilon_0 k_{\text{B}}T}} \quad (29)$$

where N_A = Avogadro's number, i.e., 6.02×10^{23} mol^{-1}; and α is expressed as a function of surface potential V_{edl0}

$$\alpha = \tanh\left(\frac{eV_{\text{edl0}}}{4k_{\text{B}}T}\right)$$

The electric field intensity ($\mathbf{E}$) can be calculated as the gradient of electric potential

$$\mathbf{E}(x) = -\frac{dV_{\text{edl}}(x)}{dx} = \frac{4k_{\text{B}}T\alpha\kappa}{e}\frac{e^{\kappa x}}{e^{2\kappa x} - \alpha^2} \quad (30)$$

For the parallel-plate pore, the electrical component is estimated from the vector sum of electric field intensities of clay particles

$$\psi_{\text{ele}}(x) = \frac{1}{2}\varepsilon_0(1-\varepsilon_r)\mathbf{E}(x)^2 = \frac{1}{2}\varepsilon_0(1-\varepsilon_r)\left[\sum_{i=1}^{N}\mathbf{E}_i(x)\right]^2 \quad (31)$$

where $\mathbf{E}_i$ = electric field intensity of ith clay particle in Eq. (30).

Osmotic Component

In addition to generating the electric field, the exchangeable cation adsorbed on the clay particle surface will try to diffuse into pore water, forming a unique ion distribution normal to the particle surface [Fig. 5(c)]. This ion concentration gradient produces the osmotic component of sorptive potential, which can be formulated as (e.g., Butt and Kappl 2009; Israelachvili 2011)

$$\psi_{\text{osm}}(x) = -c_0 N_A k_{\text{B}}T\left\{\exp\left[\frac{eV_{\text{edl}}(x)}{k_{\text{B}}T}\right] + \exp\left[-\frac{eV_{\text{edl}}(x)}{k_{\text{B}}T}\right] - 2\right\} \quad (32)$$

where c_0 = bulk concentration of salt (mol/m^3).

For the parallel-plate pore, the osmotic component is calculated from the sum of electric potential of clay particles

$$\psi_{\text{osm}}(x) = -c_0 k_{\text{B}}T\left\{\exp\left[\frac{e}{k_{\text{B}}T}\sum_{i=1}^{N}V_{\text{edl},i}(x)\right]\right.$$
$$\left. + \exp\left[-\frac{e}{k_{\text{B}}T}\sum_{i=1}^{N}V_{\text{edl},i}(x)\right] - 2\right\} \quad (33)$$

where $V_{\text{edl},i}(x)$ = electric potential of ith clay particle.

Hydration Component

On the surface of soil minerals, some surface hydroxyls or exchangeable cations may be present and intensively hydrate water molecules. The corresponding hydration free energy can be extremely low or negative (Zhang et al. 2017). As a result, some structural changes in water molecules may occur to accommodate such intensive soil–water interaction [Fig. 5(d)]. These structural changes produce another component of sorptive potential, the hydration or structural component.

Although hydrations on both surface hydroxyls and cations are electrostatic in nature, the underlying intermolecular forces are different: dipole–dipole interaction for surface (hydroxyl) hydration, and cation–dipole interaction for cation hydration. The hydration component $\psi_{\text{hyd}}(x)$ can be further decomposed into surface hydration $\psi_{\text{hyd}}^s(x)$ and cation hydration $\psi_{\text{hyd}}^c(x)$. The surface hydration component can be empirically formulated as (e.g., Butt and Kappl 2009)

$$\psi_{\text{hyd}}^s(x) = \psi_{\text{hyd0}}^s \exp(-x/\lambda_s) \quad (34)$$

where ψ_{hyd0}^s = surface hydration component adjacent to particle surface (J/m^3); and λ_s = decay length of surface hydration component, i.e., 0.2–1.0 nm.

The cation hydration component originates from the interacting cation and water dipole. The energy of cation–dipole interaction can be written (Israelachvili 2011)

$$U(r, \gamma) = -\frac{zeu\cos\gamma}{4\pi\varepsilon_0\varepsilon_r r^2} \quad (35)$$

where z = valence of cation; u = dipole moment of water molecule, i.e., 1.85 D; γ = average angle between the dipole moment and the line joining the two molecules, referred to as the orientation angle; and r = distance between cation and water molecule, and can be

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upscaled to gravimetric water content (w) with the cation exchange capacity (CEC) as

$$w = \text{CEC} \times \frac{N_A}{z} \times \frac{4}{3}\pi(r^3 - r_h^3)\rho_w^{\text{ave}}(w) \tag{36}$$

where r_h = minimum distance between cation and water molecule, i.e., a sum of the radiuses of cation and water molecule; and $\rho_w^{\text{ave}}(w)$ = average soil water density. Substituting Eq. (34) into Eq. (33), the cation hydration component of soil sorptive potential is expressed as

$$\psi_{\text{hyd}}^c(w) = -\frac{zeuN_A\cos\gamma}{4\pi\varepsilon_0 v_w\varepsilon_r}\left[\frac{3}{4\pi}\frac{z}{\text{CEC}\times N_A\rho_w^{\text{ave}}(w)}w + r_h^3\right]^{-2/3} \tag{37}$$

where v_w = molar volume of water (m^3/mol). To be consistent in the spatial variable of local distance, the gravimetric water content can be downscaled to local distance with specific surface area (SSA), and the cation hydration component of soil sorptive potential can be rewritten

$$\psi_{\text{hyd}}^c(x) = -\frac{zeuN_A}{4\pi\varepsilon_0 v_w}\left[\frac{3}{4\pi}\frac{\text{SSA}\times z(x-x_0)}{\text{CEC}\times N_A} + r_h^3\right]^{-2/3}S_{\text{hyd}}(x) \tag{38}$$

where x_0 = 0.14 nm = dimension of half of one water molecule (e.g., Mitchell and Soga 2005), which is the minimum physically possible distance to the particle surface; and S_{hyd} is a structural parameter reflecting structural changes

$$S_{\text{hyd}}(x) = S_{\text{hyd0}}\exp(-x/\lambda_c) = \frac{\cos\gamma_0}{\varepsilon_{r0}}\exp(-x/\lambda_c) \tag{39}$$

where γ_0 and ε_{r0} = orientation angle and dielectric constant in the first hydration shell, respectively; λ_c = decay length of structural parameter, and should be on the order of monomolecular thickness, i.e., 0.1–1.0 nm; and S_0 = structural parameter of first hydration shell, representing the most ordered structural orientation of water molecules. The value of S_{hyd0} is constrained in the range 0–1.

For the parallel-plate pore, the hydration component is a sum of hydration potential of clay particles

$$\psi_{\text{hyd}}(x) = \sum_{i=1}^{N}\psi_{\text{hyd},i}(x) \tag{40}$$

where $\psi_{\text{hyd},i}$ = hydration component of ith clay particle.

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