Historical perspective

Spatial state distribution and phase transition of non-uniform water in soils: Implications for engineering and environmental sciences

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ABSTRACT

The physical behaviors of water in the interface are the fundamental to discovering the engineering properties and environmental effects of aqueous porous media (e.g., soils). The pore water pressure (PWP) is a key parameter to characterize the pore water state (PWS) and its phase transition in the micro interface. Traditionally, the water in the interface is frequently believed to be uniform, negative in pressure and tensile based on macroscopic tests and Gibbs interface model. However, the water in the interface is a non-uniform and compressible fluid (part of tensile and part of compressed), forming a spatial profile of density and PWP depending on its distance from the substrate interface. Herein, we introduced the static and dynamic theory methods of non-uniform water based on diffuse interface model to analyze non-uniform water state dynamics and water density and PWP. Based on the theory of non-uniform water, we gave a clear stress analysis on soil water and developed the concepts of PWS, PWP and matric potential in classical soil mechanics. In addition, the phase transition theory of non-uniform water is also examined. In nature, the generalized Clausius-Clapeyron equation (GCCE) is consistent with Clapeyron equation. Therefore, a unified interpretation is proposed to justify the use of GCCE to represent frozen soil water dynamics. Furthermore, the PWP description of non-uniform water can be well verified by some experiments focusing on property variations in the interface area, including the spatial water density profile and unfrozen water content variations with decreasing temperature and other factors. In turn, PWP spatial distribution of non-uniform water and its states can well explain some key phenomena on phase transition during ice or hydrate formation, including the discrepancies of phase transition under a wide range of conditions

1. Introduction

Aqueous interfaces are ubiquitous in nature and engineering technology. Processes at aqueous interfaces are paramount to the understanding of the most challenging questions in, e.g., atmospheric science, geochemistry, geoscience, frozen soil mechanics, electrochemistry, and corrosion [11]. For instance, permafrost plays an importance role in the hydrological processes and climate change of cold regions and the hydrothermal process is closely related to ice-water phase change in soil-water interface [5]; the electrochemical reactions depend on the

characteristics of the liquid/solid interface, in particular the properties of the electric double layer [11]; the phase transition behaviors in soil and concrete materials are controlled by the characteristics of the PWS [29]; the formation, decomposition and exploitation of hydrates are also constrained by the state of aqueous interfaces [8]. Therefore, increasing investigations focused on exploring the underlying physics of behaviors in various aqueous interfaces.

The state and behavior of interface water is remarkably different from the well-known behavior of bulk water due to the interface effects [18]. For instance, water crystallizes into hexagonal ice at normal

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pressure, while nanoconfined water may crystallize into a plethora of novel ices [24]. In addition, interface water can exhibit substantially different phase transition temperatures, thermodynamic properties and dynamical properties than bulk water [20,29]. In other cases, water's viscosity, and the associated shear forces, can increase by orders of magnitude relative to bulk water [32]. Therefore, understanding and modeling the state and behavior of water in the interface could provide insights into various scientific problems in surface and interface phenomena. Several models and theories have been proposed to investigate the state and behaviors of surface or interface water. For instance, in the Gibbs interface, the physical interface is modeled by a sharp manner, and water volume in the interface is zero (Fig.1a); in Guggenheim's method and pre-melting theory [11], the interface volume is not zero, but the water in the interface is considered as uniform without considering interface details (Fig.1b). In fact, the physical interface is diffuse, and the water state in interface is actually non-uniform (Fig.1c). Compared to the sharp Gibbs and uniform interface models, the diffuse interface model is more nature and should be played more attention. Several leading theories were developed based on this diffuse interface model. In the electric double layer theory, the liquid properties in interface depended on the diffuse electric charge density [17]. In van der Waals theory, a local free energy density was fist utilized a uniform term controlled by the local mass density and a non-uniform term controlled by the mass density gradient and then the surface tension can be obtained by minimizing the total Helmholtz free energy of the system [36]. Cahn and Hilliard [7] extended the van der Waals theory to binary mixtures for the purpose of discussing the interfacial characteristics and tension near the critical solution temperature. The density functional theory proposed by Hohenberg and Kohn (1964), was first dealt with the ground state of an interacting electron gas in an external potential and then was developed also to investigate the non-uniform properties in diffuse interface and its phase transition behaviors [10]. Although substantial progress has been recently made, investigation on nature of the interface is still a challenge, using both experimental and theoretical methods. Therefore, our knowledge of the fundamental physic-mechanical properties of aqueous interface is very limited.

Furthermore, although this principle has by no means escaped the attention of physicists, its importance does not appear to have been duly appreciated by researchers on the engineering and environment in cold regions. Therefore, there is still a widely application of the water state concept without considering a spatially varying nature at micro scale, which leads to some inabilities in describing some important interfacial phenomena and properties. For example, in the classical fluid mechanical approach, the free boundary description is usually used to model this interface between two immiscible fluids and has been a successful model in a wide range of situations. However, the physical model breaks down when the interfacial thickness is comparable to the length scale of the phenomena being examined [1]. For example, (a) in a near-critical fluid; (b) with a detailed consideration of the fluid motion in the

vicinity of the contact line; (c) for situation involving changes in the topology of the interface (e.g., the breakup of a liquid droplet); (d) with a detailed consideration of phase transition in the vicinity of substrate surface (e.g., soil freezing). Fortunately, a few investigations have recently realized the importance of the diffuse interface and focused on these issues. For example, Gilpin [19] developed a frost heave model based on a spatial variation of PWP. To describe the soil-water state in the micro interface, some research has investigated the PWP state in soil freezing through designing a novel PWP measurement method [29,46]. Zhang et al. [49] started to realize the spatial variation of the soil water density and pressure in their critical review. Lu and Zhang [27] gave a concept model on matric potential with considering the soil sorptive potential. The spatially varied pore water pressure concept has been well established in the soil sorptive potential theory [43,44], and can well explain supercooling [44]. Zhang and Lu [45] developed a new paradigm to predict the soil freezing curve based on soil sorptive potential and spatially varied pore water pressure. However, the spatial non-uniform in properties and phase transition behaviors of soil water is a new framework for frozen soil science to explore at a smaller scale, and thus very need further research work to describe and quantify it in theory or experiment.

To date, some key phenomena and scientific issues on phase transition during ice or hydrate formation have not been well explained, such as the freezing temperature discrepancy under different load and saturation conditions [29], the applicability and questioning of the GCCE [29], why synthetic methane hydrate grows under mild condition (3.5 MPa and 2 °C) in the porous media [8] and others. However, these issues are closely related to the spatial distribution (non-uniform) of PWS in the micro scale. Therefore, theoretical progress focusing on the details of non-uniform water in substrate-water interface will have a significant impact on engineering and environment in cold regions. Herein, we first expected to form an effective method of theory analysis to characterize the spatial property variations of interface (non-uniform) water based on the diffuse interface model, and then applied the method to describe the PWS and developed some key concepts in traditional soil science, finally settled these issues induced by phase transition of soil water in soil freezing and hydrate formation.

Combined with lab and field experiments, the goal of PWS and behavior analysis in soils were investigated based on the following sectional goals of theory of non-uniform water, PWS in soils, phase transition behaviors and application in engineering and environmental sciences. In the Section 2, the theory analysis method of non-uniform water was built based on diffuse interface model in a more micro scale, including static and dynamic analysis. In the Section 3, some macro concepts such as PWS function, PWP and matric potential were developed, and further the rules of phase transition were determined. In the Section 4, we applied the theory methods and results to clarify some key issues such as spatial non-uniform of soil water density, questions of GCCE, pressure melting, promoting effect of hydrate formation and others.

2. Methods

2.1. Overview on the theory of non-uniform water

The spatial variation of properties of pore water in the interface implies that the pore water is non-uniform. And the substrate-water system is the fundamental cell to characterize the non-uniform properties of pore water in the aqueous interface, with considering the range of interface effects (from substrate surface to water-air surface). Therefore, characterizing non-uniform water in the substrate-water system is the critical step for further investigating the PWS in soils, phase transition behaviors and its application in engineering and environmental sciences. Herein, a theory of the non-uniform water was provided with a novel and nature perspective based on theory analysis method. The theory analysis is closely related to model abstract, static analysis,
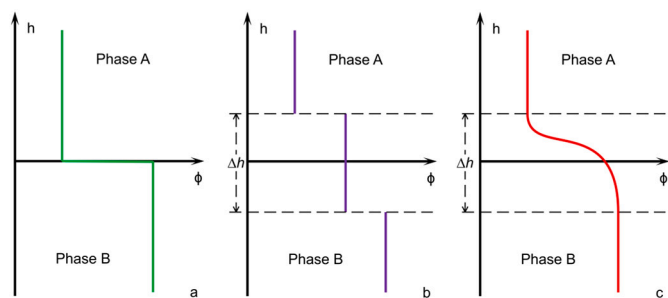

Fig. 1. The abstracted interface models between phase A and phase B. a: the sharp Gibbs interface model; b: the uniform interface model; c: the diffuse interface model. Δh is the interface thickness. Φ is the order parameter in the interface, which is a function of location h.

relaxation behavior and dynamic analysis. On model abstract, the diffuse interface model was applied to describe the substrate-water system rather than the traditional sharp interface model, because it is more nature and can describe the interface details at a more micro scale. In static theory analysis, the state profile of non-uniform water with fixed volume and mass was analyzed under scenarios of different potential sources, specially including the external potential and local intermolecular potential (the gradient effect). In dynamic theory analysis, the relaxation mode was first introduced and defined to describe the dynamic behaviors of non-uniform water, combined with the static theory. Consequently, the theory analysis provides the underlying mechanism of the following results. For instance, the PWS and its stress analysis in soils (Section 3.1) depends on the static theory, the unified matric potential associated with dynamic process (Section 3.2) on the relaxation mode and dynamic theory, the phase transition behavior in soils (Section 3.3) on the relaxation mode static and dynamic theories. Finally, the PWS and behavior analysis in soils were applied to solve some issues in engineering and environmental sciences.

2.2. Static theory of non-uniform water

The static analysis of non-uniform water with fixed (initial) water content will result in a static spatial distribution of PWS, in which the profiles of density, PWP and free energy density and its gradients remain constant with time. In the substrate-water interfacial system of interest, water in the interface keeps balance with substrates (soils, air or other substrates) under certain surrounding conditions. Based on the diffuse interface model, the interface water has fixed volume V [m^3] and mass M [Kg/m^3] and is non-uniform with spatial distributions of water density, stress and free energy density in equilibrium. The isothermal Helmholtz free energy F [J] of the non-uniform system (with fixed temperature T [K]) can be expressed as the definite integral of a local free energy density [7,16]:

$$F = \int_{\Gamma_1}^{\Gamma_2} d^3r \psi(r) \tag{1}$$

where Γ_1 and Γ_2 is the substrate-water boundary and water-air boundary of water volume V, respectively. $\psi(r)$ is the local free energy density [$J \cdot m^{-3}$] [16], which can be described as below

$$\psi(r) = U(r)\rho(r) + \psi(\rho(r)) + \frac{1}{2}A(\rho(r))\nabla\rho(r)^2 \tag{2}$$

where U(r) is an external potential energy function [J]; $\rho(r)$ is the molecular number density (i.e., the number of molecular per unit volume) [$1/m^3$], which varies in its spatial dependence on a scale set by the interaction range; $\psi(\rho)$ is the free energy density of an equilibrium uniform system with density ρ; $A(\rho(r))$ is related to the direct correlation function $C(r, \rho)$ of a uniform system with density ρ [16]:

$$A(\rho) = \frac{kT}{6}\int d^3r r^2 C(r, \rho) \tag{3}$$

Where k is the Boltzmann's constant [J/K]. In addition, the whole system is constrained with fixed volume V and fixed number of particles N. Therefore, the boundaries Γ_1 and Γ_2 remain constant due to fixed water volume, and the total number of particles N should be constrained with

$$\int_{\Gamma_1}^{\Gamma_2} d^3r \rho(x) = N \tag{4}$$

The free energy of non-uniform water in this system reaches minimum when it comes to equilibrium with constraints (Eq. 4), which is a constrained variation. Mathematically the variation problem can be settled using the Lagrange multiplier method. Then, the free energy I with constraints (Eq. 4) can be described as

$$I = \int_{\Gamma_1}^{\Gamma_2} d^3r(\psi(r) - \mu\rho(r)) \equiv -\int_{\Gamma_1}^{\Gamma_2} d^3r P_0(r) \tag{5}$$

where the Lagrange multiplier μ corresponding to Eq. (4) is the chemical potential [J/molecule]; where P_0 is the negative of local free energy density. The density profile which renders the integral (5) a minimum is a solution of the Euler-Lagrange equation

$$\frac{\partial P_0(r)}{\partial\rho(r)} - \frac{d}{dr}\frac{\partial P_0(r)}{\partial\rho'(r)} = 0 \tag{6}$$

Therefore, the density profile satisfies the equation below

$$\mu(\rho) - \mu + U = A\nabla^2\rho + \frac{1}{2}A'(\nabla\rho)^2 \tag{7}$$

The equation can then be written as

$$\nabla\cdot\sigma = -\rho\nabla U = f \tag{8}$$

where

$$\sigma = \{\mu\rho - \psi(\rho) - \rho U\}\bar{I} + A\left\{\nabla\rho\nabla\rho - \frac{1}{2}(\nabla\rho)^2\bar{I}\right\} = P_0(r)\bar{I} + A\nabla\rho\nabla\rho \tag{9}$$

is the stress tensor [Pa]. $\bar{I}$ is the identity tensor. This is the general statement of the condition for mechanical equilibrium. The internal force $\nabla\cdot\sigma$ balances precisely the external force f(r) [N/m^3]. While the surface tension at a particular point r_0 on the interface is obtained by integrating $A\nabla\rho\nabla\rho$ along the line which is everywhere parallel to the density gradient and passes through r_0. Consequently,

$$\sigma_{r_0} = \int dr_n A\nabla\rho\nabla\rho \tag{10}$$

where $\hat{n}(r) = \frac{\nabla\rho(r)}{|\nabla\rho(r)|}$ is the unit of density gradient and $r_n = r\cdot\hat{n}(r)$.

2.3. Dynamic theory of non-uniform water

2.3.1. Relaxation mode hypothesis of dynamic process

The amount and state of interface water may change over time as water content varies in the hydrodynamic process. Herein, we assume there are two responding modes for dynamic process: one is non-relaxation behavior mode and the other is relaxation behavior mode. When the substrate is fully saturated with water content W_0, the substrate-water system won't show any suction for other water molecules. All of the interface energy is fully consumed by water molecules through adjusting their own states (density, PWP and others). At that moment, the system is at the perfect state which should be the nonlocal extreme point of free energy. Based on the theory of non-uniform water, the free energy of this system is constant, can be described as below [27,41–44],

$$I^0 = -\int_{\Gamma_1}^{\Gamma_\infty} P_0(r, W_0)dr = C \tag{11}$$

where Γ_∞ denotes the critical boundary within which the substrate is saturated by water; I^0 denotes the free energy of system in the very saturation degree of 100% [J]. Based on the static theory the state function $P_0(r, W_0)$ with initial water content W_0 can be derived. However, with decreasing of (initial) water content, whether the PWS function changes depends on different relaxation modes of pore water. Therefore, the dynamic process can be described through different responding modes of PWS function with changing of initial water content. In the non-relaxation behavior mode, the PWS profile or function remains constant with changing of initial water content (i.e., water particles in pore water don't rearrange with changing of water content). In the relaxation behavior mode of non-uniform water, the PWS profile will vary with initial water content to remain the extremum of free

energy through relaxation behaviors (i.e., the water particles in pore water rearrange with changing of water content). The rigidity of interface water is not enough to resist deformation, and hence PWS will change with changing of initial water content through redistributing the density, pressure, pressure gradient and density gradient of pore water profile.

2.3.2. Two dynamic processes of non-uniform water

In the non-relaxation behavior mode, the PWS function $P_0(r, W_0)$ remains constant with changing of initial water content. Refer to the saturated state with initial water content W_0, part of free energy of system will disappear as water content decreases to W. Therefore, the free energy of system can be divided into two parts: the remaining part I_m^0 [J] and the disappeared part I_s^0 [J], as described below

$$I^0 = -\int_{\Gamma_1}^{\Gamma_\infty} P_0(r, W_0)dr = -\int_{\Gamma_1}^{\Gamma_r} P_0(r, W_0)dr - \int_{\Gamma_r}^{\Gamma_\infty} P_0(r, W_0)dr$$
$$= I_m^0 + I_s^0 = C \quad (12)$$

where Γ_r is the new water boundary of this system. In nature, refer to the saturation state, the remaining part of free energy I_m^0 denotes the pore water potential energy; while the disappeared part I_s^0 denotes the matric potential energy. Therefore, the Eq. (12) actually implies the energy conservation. Furthermore, taking the derivative on both sides of Eq. (12), we can obtain the matric potential as

$$-P_0(r_w, W_0) = \frac{\partial(I_m^0 - I^0)}{\partial r} = -\frac{\partial I_s^0}{\partial r} = -S_s^0 = \psi_m^0 \quad (13)$$

where $S_s^0 = \frac{\partial I_s^0}{\partial r}$ is the definition of matric suction [Pa], which is minus of the matric potential ψ_m^0; r_w is the surface location of soil water with water content W, corresponding to boundary condition of Γ_r. Based on Eq. (13), a definition of matric potential with non-uniform water was proposed, and also clarified the relationship between the matric potential and PWP.

In the relaxation behavior mode of non-uniform water, the PWS function varies from $P_0(r, W_0)$ into $P_j(r, W_j)$ with decreasing of water content from W_0 to W_j. Fig. 2 is the sketch map of PWPs with two different initial water contents in the diffuse interface. For example, under relaxation behavior, the PWS profile has a change with initial water content. In this way, the free energy of system can be described as,

$$I^j = I_m^j + I_s^j = -\int_{\Gamma_1}^{\Gamma_{r_j}} P_j(r, W_j)dr - \int_{\Gamma_{r_j}}^{\Gamma_\infty} P_j(r, W_j)dr = -\int_{\Gamma_1}^{\Gamma_{r_j}} P_j(r, W_j)dr$$
$$\neq C \quad (14)$$

Where $P_j(r, W_j)$ is the new state function when initial water content changed [Pa]; Γ_{r_j} is the new water boundary of the system after relaxation; r_j is the surface location of boundary condition of Γ_{r_j}. Under the condition, the substrate-water system is unsaturated and thus the free energy is not constant. Through comparing this state with the saturated state, the free energy can be divided into three parts: the remaining part I_m^j, the relaxation prat $I_m^0 - I_m^j$, and the disappeared part I_s^0, as described below

$$I^0 = I_m^j + (I_m^0 - I_m^j) + I_s^0$$
$$= -\int_{\Gamma_1}^{\Gamma_{r_j}} P_j(r, W_i)dr - \int_{\Gamma_1}^{\Gamma_{r_j}} (P_0(r, W_0) - P_j(r, W_j))dr - \int_{\Gamma_{r_j}}^{\Gamma_\infty} P_0(r, W_0)dr \quad (15)$$

It was noted that the matric potential and matric suction under relaxation mode should be described based on the functional concept, because the PWS function is not identical.
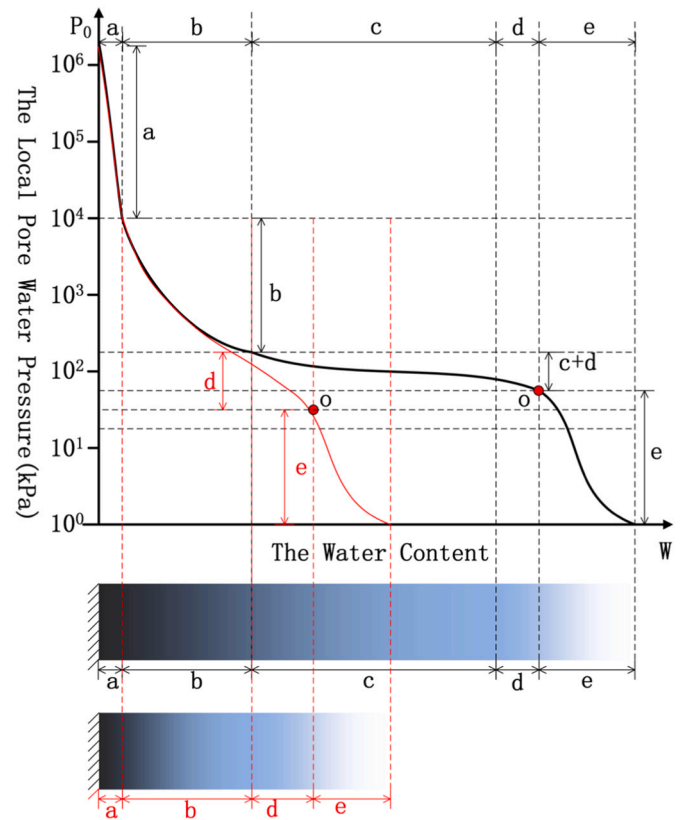

Fig. 2. The sketch map of pore water pressures with two different (initial) water contents in the diffuse interface. The black curve denotes the pressure with saturated initial water content; while the red curve denotes the pressure with unsaturated initial water content. Label a, b, c, d, e denotes the strongly absorption zone, film absorption zone, bulk water zone, capillary water zone and vapor zone, respectively. Point o denotes the liquid-vapor phase interface point which is according to the vapor pressure. The water in the capillary zone d and vapor zone e is generally presented as the surface water; while the water in the strongly absorption zone a and film absorption zone b is generally presented as the absorptive water, as shown in Fig. 3.

$$\psi_m^j = \frac{\partial(I_m^j - I^0)}{\partial r} = -\frac{\delta(I_m^0 - I_m^j)}{\delta r} - \frac{\partial I_s^0}{\partial r} = -\Delta\psi_m^{0j} - S_s^0 = -S_s^j \quad (16)$$

where $\Delta\psi_m^{0j} = \frac{\delta(I_m^0 - I_m^j)}{\delta r}$ is the relaxation potential at initial water content of W_j; S_s^j is the matric suction at initial water content of W_j. Therefore, it is found that the PWP with relaxation behavior actually is the sum of PWP without relaxation behavior and relaxation potential, as shown in Eq. (17a). Similarly, the relaxation PWP ΔP_{0j} is assumed to be equal to minus the relaxation potential $\Delta\psi_m^{0j}$. Therefore, there exist relationships of the matric potential and matric suction with considering relaxation, as shown in the Eqs. (17b) and (17c).

$$P_j(r_j, W_0) = P_0(r_j, W_0) + \Delta\psi_m^{0j} = P_0(r_j, W_0) - \Delta P_{0j} \quad (17a)$$
$$\psi_m^0 - \psi_m^j = \Delta\psi_m^{0j} \quad (17b)$$
$$S_s^0 - S_s^j = -\Delta\psi_m^{0j} \quad (17c)$$

However, in practical application, the matric potential and PWP are generally regarded as a function with water content. In this condition without relaxation, we found the pressures and potentials with different variables (water content and location) have relationship as below,

$$-P_0(W, W_0) = \psi_{mw}^0 = \frac{-\int_{\Gamma_0}^{\Gamma_w} P_0(W, W_0) dW}{\partial W} = \frac{-\int_{\Gamma_0}^{\Gamma_{rw}} P_0(r, W_0) dr}{W' \partial r} = \frac{\psi_m^0}{W'}$$

$$= \frac{-P_0(r_w, W_0)}{W'}$$

(18)

where W' is the derivation of water content with location r; ψ_{mw}^0 is the water-content-dependent matric potential with initial water content W_0; $P_0(W, W_0)$ is the water-content-dependent PWP with initial water content W_0; (PWPW); while $P_0(r_w, W_0)$ is the boundary location-dependent PWP with initial water content W_0 (PWPr). With considering relaxation behavior, there exists a similar relationship between the PWPs and matric potentials with different variables,

$$-P_j(W, W_j) = \psi_{mw}^j = \psi_m^j = \frac{-P_j(r_j, W_j)}{W'}$$

(19)

ψ_{mw}^j is the water-content-dependent matric potential with initial water content W_j; $P_j(W, W_j)$ is the water-content-dependent PWP with initial water content W_j (PWPW); while $P_j(r_j, W_j)$ is the boundary location-dependent PWP with initial water content W_j (PWPr). Therefore, the values of PWPr is equal to the PWPW multiplied by the derivation of water content W'.

3. Results

In this section, based on the theory of non-uniform water, some important concepts in soil mechanics such as PWS and matric potential were redefined and developed, and finally the phase transition mechanism of soil water was well clarified.

3.1. Pore water state in soils

PWP is a key parameter of charactering the PWS in soil mechanics. Based on the static theory in Section 2.2 above, the spatial distribution of PWP was described and its sources were clarified from the perspective of stress analysis. Therefore, the traditional PWP concept was developed and the PWS function for better charactering the soil water state was proposed.

3.1.1. Spatial distribution of pore water pressure

First, the PWP concept of soil water was described in detail based on the theory of non-uniform water, including the nonlocal PWP and local PWP. The nonlocal PWP, without considering the local intermolecular forces, is the stress tensor σ [Pa] induced by the external force f(r) [N/m³]. For instance, refer to Eq. (8), for the sake of analysis, the stress tensor σ of water in three-dimensional condition can be presented as P(x) [Pa] without considering the shear stress in two-dimensional condition as below,

$$P(x) = \mu\rho(x) - \psi(\rho) - \rho(x)U(x) + \frac{1}{2}A(\rho(x))\rho'(x)^2 = P_{\overline{R}} + \int_{x_0}^{x} dx f(x)$$

(20)

where $P_{\overline{R}} = \mu\rho - \psi(\rho)$ since $U(x)$, $f(x)$ and $\rho'(x)$ all tend to zero as $x \to \pm\infty$. Here, the pressure $P(x)$ is the nonlocal PWP, divergence of which generally balances the external force $f(r)$. However, when considering the local force such as the intermolecular force, the PWP should be called as local PWP which includes both of effects induced by the external force $f(r)$ and local force. The local PWP can be defined from the free energy density. For example, refer to Eq. (5), the local PWP P_0 [Pa] can be described as

$$P(x) = P_0(x) + A(\rho(x))\rho'(x)^2 = P_{\overline{R}} + \int_{x_0}^{x} dx f(x)$$

(21a)

$$P_0(x) = -A(\rho(x))\rho'(x)^2 - \int_{x_0}^{x} dx f(x) - P_{\overline{R}}$$

(21b)

Through Eq. (21a), the local PWP is equal to the sum of interface tension density (pressure induced by density gradient) and the nonlocal PWP. Through Eq. (21b), the local PWP is equal to the sum of the reference pressure $P_{\overline{R}}$, external force and the pressure induced by density gradient (interface tension density).

Second, the real PWP should be described by the local PWP. And the real PWP profile of soil water is a spatial function (non-uniform) depending on its distance to substrate interface, with spatial variations in pressure and density of water. For example, in classical soil mechanics, PWP is usually defined based on mechanical equilibrium, without considering the effects from local force and external force by substrate surface. However, research has found the physic-mechanical properties and phase transition behaviors of non-uniform water in the interface are closely related to the local force and external force by substrate surface. Therefore, the real PWP should be described by local PWP rather than nonlocal PWP in the porous media. In addition, refer to Eqs. (20) and (21a), the real PWP can described as

$$P_0(x) = \mu\rho(x) - \psi(\rho) - \rho(x)U(x) - \frac{1}{2}A(\rho(x))\rho'(x)^2$$

(22)

While the density of pore water can be obtained from Eq. (6),

$$\rho(r) = \rho_0 exp\left(-\frac{U(r)}{kT}\right) + C^{(1)}(\rho(r), r) - C_0^{(1)}(\rho_0)$$

(23)

where $C^{(1)}(\rho(r), r)$ and $C_0^{(1)}(\rho_0)$ are the direct correlation functions. Through Eqs. (21a) and (22), we found that the PWP (nonlocal and local) is a spatial function varying with location. The spatial distribution of PWP can be characterized by the non-uniform density profile of pore water, as shown in Eq. (23). The spatial variation of water density definitely implies that the water in the interface should be considered as a compressible fluid (part of tensile and part of compressed) [27,41–44].

3.1.2. Components of pore water pressure and its force sources

Based on stress analysis, it's found that the PWP can be divided into two parts: one part for balancing external force and the other part for balancing the local intermolecular force. Fig. 3 is the stress analysis on the non-uniform water in the diffuse interface of the substrate-water system. Assuming that the representative element of water in the system remains force equilibrium, the stress analysis is as below,

$$\nabla P_{ex} + \nabla P_{gra} = f_{ex} + f_{gra}$$

(24)

The right hand of Eq. (24) represents the element is subjected to external force f_{ex} [N/m³] induced by external potential (i.e., f(x) in the Eq. (21)) and the local intermolecular force f_{gra} [N/m³] induced by the particles non-uniform (or gradient) around this element. To remain force equilibrium, the water element will produce pressure gradient (or density gradient) in the left hand of Eq. (24) to balance the two forces in the right hand of Eq. (24). Therefore, the pressure gradient can be divided into two parts: the part ∇P_{ex} [Pa/m] for balancing f_{ex} and the part ∇P_{gra} [Pa/m] for balancing f_{gra}. The part ∇P_{ex} is the derivative of P(x) in the Eq. (20); while the part ∇P_{gra} is the derivative of $-A(\rho(x))\rho'(x)^2$ in the Eq. (21). Therefore, the Eq. (24) also can be derived through differentiating both sides of the Eq. (21a).

Pore water is generally divided into surface water (capillary water), free water (bulk water) or interface water (absorptive water), which correspond to different force sources, respectively. Generally, the PWP of interface water is larger than the PWP of surface water. As shown in Fig. 2, for surface water, the external potential (force) vanishes, the water is controlled by the local gradient effects (surface tension or capillary effect), and the force equilibrium Eq. (24) becomes

$$\nabla P_{gra} = f_{gra}$$

(25)

For interface water, the water is controlled by combination of the local effects (surface tension or capillary effect) and the external potential (force), which corresponds to the force equilibrium Eq. (15). For
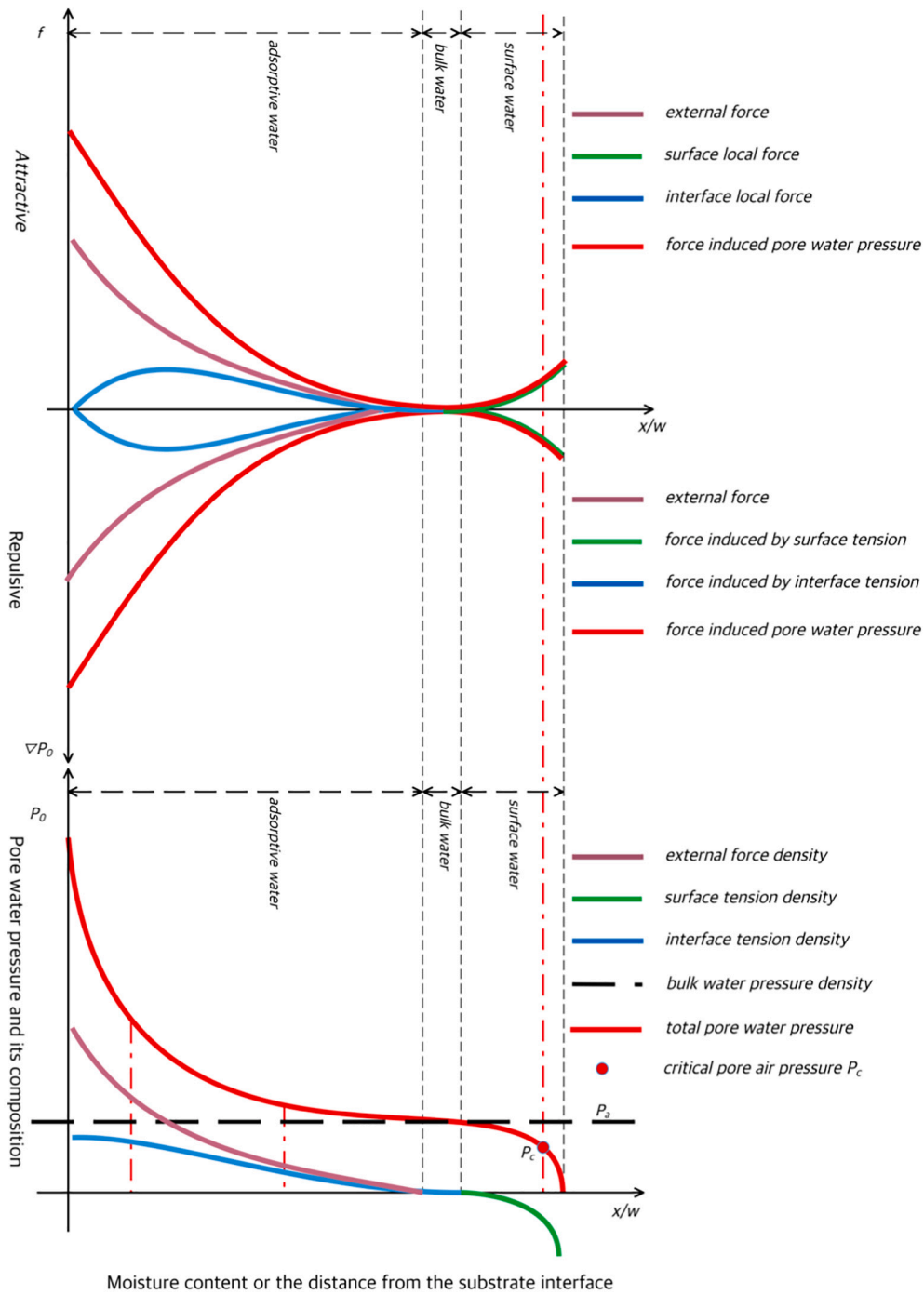
Fig. 3. The stress analysis on the non-uniform water in the diffuse interface of the substrate-water system. The top figure presents the force equilibrium of non-uniform water between attractive parts and repulsive parts; while the bottom figure presents the pore water pressure parts induced by each parts of force. Notably, Pa denotes the bulk water pressure density, i.e., standard atmospheric pressure; while Pc denotes the critical pore vapor pressure at the water-vapor interface.

free water, the external potential (force) and local gradient effects all vanish. For same liquid, comparing the force equilibrium in the interface (Eq. (24)) and surface (Eq. (25)), it is found that the interface pressure should be larger than the surface pressure.

3.1.3. Pore water state function

The non-uniform of PWS characterized by spatial water density or pressure in nature can be described completely by the pore state function in which when the derivatives (gradient) of water pressure or density is included. In fact, when the pore water is uniform, the state function of water is a one-variable function of pressure or density, which is one-dimensional.

$$S = S_{uniform}(p(x) \ or \ \rho(x)), p(x) = p \ or \ \rho(x) = \rho \qquad (26)$$

When the pore water is non-uniform, the state function of water is a multi-variable function with pressure or density and its derivatives (gradients), which is multi-dimensional.

$$S = S_{non-uniform}\big(p(x), \nabla p(x), \nabla^2 p(x), \cdots or \ \rho(x), \nabla \rho(x), \nabla^2 \rho(x), \cdots\big) \qquad (27)$$

To be simple, only its first derivative is included, without considering

its higher derivatives. So, the state function of water can be described as two-variable function as below

$$S = S_{non-uniform}(p(x), \nabla p(x) \text{ or } \rho(x), \nabla \rho(x))$$ (28)

Based on this analysis, it's found that the determination of PWS function depends not only on the variables of PWP or water density but also on the gradient variables of PWP or water density. In addition, the density is actually an order parameter for characterizing entropy but is more nature and convenient than entropy for describing non-uniform water.

3.2. A unified formula for matric potential in soils

Matric potential is a key parameter for soil water dynamical process. Through conceptual analysis from perspective of non-uniform water at a more micro scale, it's found that matric potential is a derivation of matric potential energy, and thus actually implies the ability what part of the interface energy is transferred into internal energy of pore water. Previous studies have pointed that the matric potential is the quantity how much of the interface energy can be transferred into internal energy of water, which depends on the availability of water molecules [27]. Based on the dynamic theory of non-uniform water in substrate-water system in Section 2.3, when the substrate surface is fully saturated by water, the relative humidity of this system is generally 1.0, the interface energy at the substrate surface is full transferred into the pore water potential energy. The interface energy first induces a variety of potential gradients in water such as van der Waals, electrical, cation and surface hydration, and osmosis. Then, these potential gradients were balanced by the non-uniform state of water such as spatial variations (increase or decrease) of PWP and water density. Therefore, the energy was finally stored in non-uniform water as a manner of pore water potential. When the substrate is partly saturated, the interface energy was partly balanced by the pore water potential; while the remaining part was regarded as matric potential energy. The matric potential is a derivation of the matric potential energy based on Eq. (13), and thus actually implies the ability that the interface energy is transferred into internal energy of pore water.

Matric potential is the key constitutive parameter for water migration and stress analysis in soil mechanics. However, in the practical applications, there exist unclear definitions and even incorrect applications for the parameter. Herein, a unified formula for matric potential of soils was proposed from the perspective of non-uniform water, which is more nature in concept. In classical soil mechanics, the water potential can be reduced to matric potential when excluding the effects of osmosis and elevation, and the matric potential is generally described as below,

$$\psi_m(W) = u_w - u_a$$ (29)

where $u_a - u_w$ is the matric suction [Pa]; u_a and u_w is the air pressure and water pressure in environment (e.g., reservoir bottle) [Pa], respectively. However, based on Eq. (13), regardless of the relaxation behavior, a formula associated with matric potential was proposed as below,

$$\psi_m(W) = -P_0(r_w, W_0) = -P_W$$ (30a)

$$\psi_m(W) = -(P_{0w} - P_R)$$ (30b)

Where P_w is the gauge local PWP of the soil water surface at location r_w [Pa] because the derivation of Eqs. (13) and (30a) refer to the saturated state with initial water content W_0 in which the matric potential is equal to zero. P_{0w} is the absolute local PWP of the soil water surface at location r_w [Pa]; P_R is the reference pressure. The Eq. (30a) implies the matric potential is minus of the gauge local PWP without relaxation behavior. In fact, the value of matric potential in Eqs. (30a) and (30b) is equal to that in Eq. (29). Therefore, we derived that

$$\psi_m = u_w - u_a = -P_W = -P_{0w} + P_R$$ (31a)

For instance, when the water flux vanishes, the porous material with initial water content W reaches equilibrium under certain air pressure u_a during measuring of matric potential. At that moment, the absolute local PWP P_{0w} is equal to the pore air pressure u_a for force equilibrium; while the reference pressure P_R is actually equal to the water pressure u_w, because pore water is directly connected to atmosphere and can flux out freely during matric potential measuring under open system. Therefore, we can derive a significant relationship as below

$$P_W = u_a - u_w \text{ or } P_{0w} = u_a$$ (31b)

Based on the analysis above, it was found that the matric potential definition (29) in classical soil mechanics is actually inaccurate in conception, which is mainly ascribed to the inaccurate point that the pore water is generally regarded as tensile due to capillary effect in classical soil mechanics but it is actually in a compression state due to adsorptive effect. However, the two definitions on matric potential are identical in value. Therefore, we can directly obtain the absolute local PWP P_{0W} and the gauge local PWP P_W using the Eq. (31b) based on the traditional measurement methods of matric potential.

3.3. Phase transition of non-uniform water in soils

Phase transition is the most critical constitutive relationship for frozen soil science. Based on the theory of non-uniform water in Section 2, it's found that the phase transition of non-uniform water at the pore scale is non-uniform but is consistent with that in bulk water in principle. For example, the phase transition in bulk water is uniform, which occurs at a single temperature; while the phase transition in porous media is non-uniform because of the spatial non-uniform of pore water. For example, pore water freezes in a temperature region rather than at a single temperature point, because the pore water with smaller PWP, in principle, freezes first as temperature decreases. For phase transition of non-uniform water, it still follows the phase transition conditions of uniform water that the free energy, pressure and temperature remains equal between two phases,

$$\begin{cases} F_\alpha = F_\beta \\ P_\alpha = P_\beta \\ T_\alpha = T_\beta \end{cases}$$ (32)

Where α, β denote the different phases, respectively. Furthermore, the free energy differential of water phase is equal to that of ice phase in the phase transition interface,

$$-s_w dT + \nu_w dP_w = -s_i dT + \nu_i dP_i$$ (33)

where s_w denotes the specific entropy of pore water [$J/(Kg \cdot mol)$]; s_i denotes the specific entropy of ice [$J/(Kg \cdot mol)$]; T denotes the phase transition temperature; P_w is the local PWP [Pa]; P_i denotes the ice pressure [Pa]; ν_w denotes the specific volume of pore water with phase transition [m^3/Kg]; ν_i denotes the specific volume of ice with phase transition [m^3/Kg].

Based on relaxation behavior, there exist two phase transition modes in porous media, one is the Clapeyron equation mode for closed system without relaxation; the other is the GCCE mode for open system with relaxation. Through analysis of pore water system with phase transition, we found it is consistent between the Clapeyron equation and GCCE in nature. Fig. 4 is the schematic diagram of two phase-transition modes. When phasing transition, pore water can be generally divided into two parts: one part of pore water associated directly with phase transition (pore water system with phase transition, PWSwPT) and the rest of pore water unassociated with phase transition (pore water system without phase transition, PWSaPT). Based on the responses of pore water in PWSwPT and PWSaPT, the phase transition process can be divided into two processes. In the closed condition, one process is that pore water in the PWSwPT with a state of (P_w, V_w) freezes into ice with (P_i, V_i) with an increase in pressure (ice pressure and PWP); the other process is that the
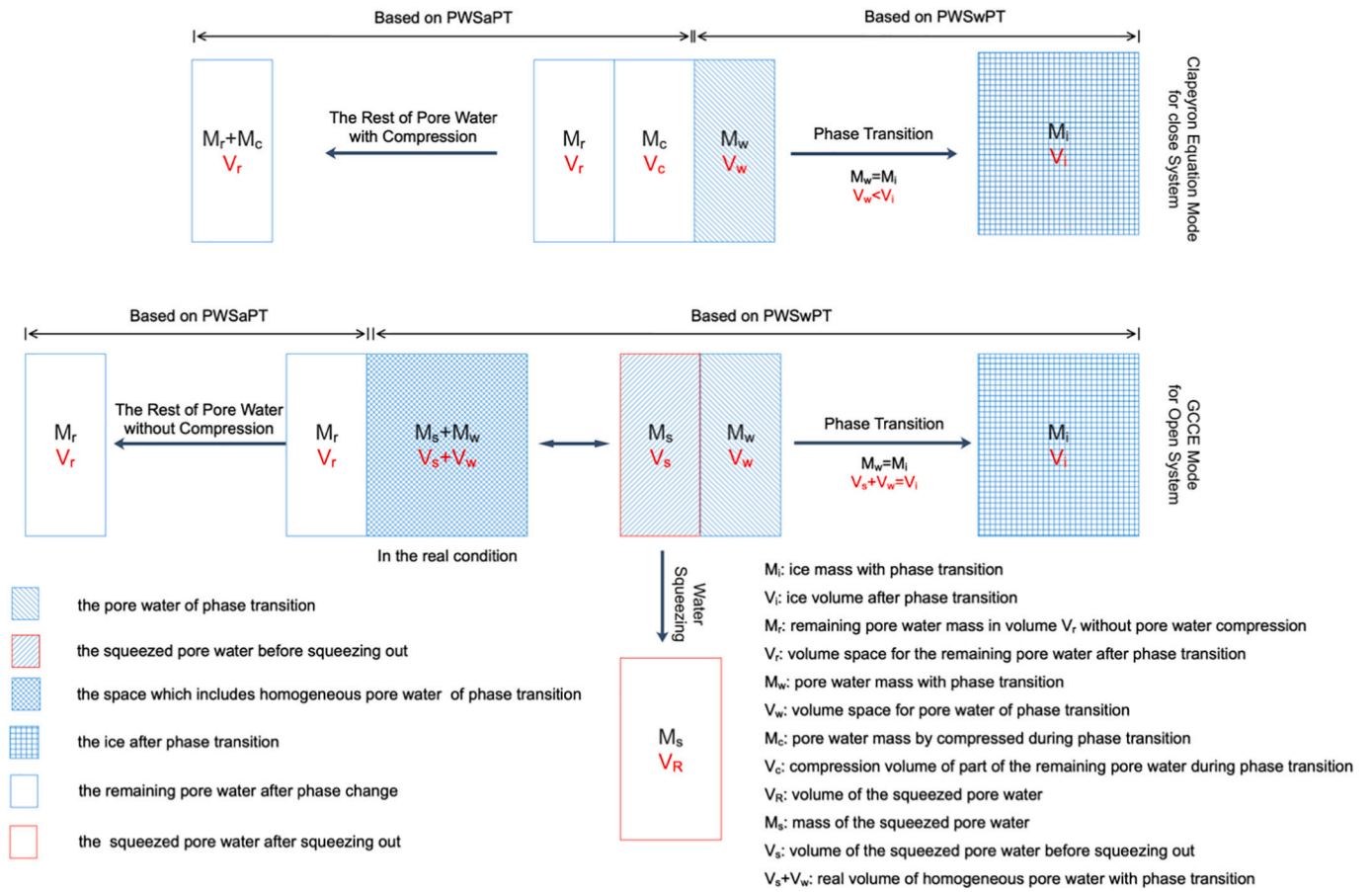
Fig. 4. The schematic diagram on two different phase transition modes. The blue cell and the blank cell present the phase transition volume space (PWSwPT) and the rest of pore water unassociated with but affected by phase transition (PWSaPT), respectively. The cell size denotes the pore water volume associated with relevant process. In the Clapeyron mode, the specific volume of water is less than that of ice due to constant mass ($M_i = M_w$) and changed volume ($V_w < V_i$) during phase transition, as shown in Eq. (35). In the GCCE mode, the effective volume of water is equal to that of ice due to constant mass ($M_i = M_w$) and constant volume ($V_s + V_w = V_i$) during phase transition, as shown in Eq. (38).

increased pressure has a compression to the pore water in PWSaPT with a decrease in volume from $V_c + V_r$ to V_r. With considering the phase transition in the PWSwPT, the pressure increase should include two parts: one part induced by phase transition, and the other part induced by the compression of pore water due to ice volume increase. The increase dP of pore water or ice can be described as Clapeyron equation based on Eq. (33) as below,

$$\frac{dP}{dT} = \frac{L}{T(\nu_w - \nu_i)} \tag{34}$$

where L denotes the latent heat [Kg/m^3]; the specific volume of water with phase transition is $\nu_w = \frac{V_w}{M_w}$; while the specific volume of ice with phase transition is $\nu_i = \frac{V_i}{M_i} = \frac{V_i}{M_w}$. The specific volume of water is less than that of ice due to the density differences,

$$\nu_w < \nu_i \tag{35}$$

However, in the open condition, the phase transition process also include two processes, as shown in Fig. 4. One process is that pore water with a state of (P_w, V_s) is pressed out with a reference state of (P_R, V_R). This process can be described as below,

$$P_w V_s = P_R V_R \tag{36}$$

The other process is that pore water with a state of (P_w, V_w) freezes into ice with a state of (P_i, V_i). The phase transition process also satisfies the Clapeyron equation, but the effective specific volume of water $\nu_w =$

$\frac{\widetilde{V_w}}{M_w}$ is equal to that of ice $\nu_i = \frac{V_i}{M_i} = \frac{V_i}{M_w}$ in this phase transition process. Where $\widetilde{V_w}$ is the effective volume of pore water V_w. In nature, in the phase transition volume space $V = V_w + V_s$, the pore water distributes homogeneously, and thus the real (effective) volume $\widetilde{V_w}$ of pore water V_w is as below,

$$\widetilde{V_w} = V = V_i \tag{37}$$

and the effective specific volume of water is equal to that of ice as below,

$$\nu_w = \frac{\widetilde{V_w}}{M_w} = \frac{V_i}{M_w} = \nu_i \tag{38}$$

Therefore, the phase transition can be described as the GCCE as below,

$$\frac{dP}{dT} = \frac{L}{T(\nu_w \text{ or } \nu_i)} \tag{39}$$

Furthermore, based on PWSaPT, we also can find that it is consistent between the Clapeyron equation and GCCE in nature using the theory of non-uniform water. Fig. 5 is the comparison between two phase transition modes of the Clapeyron equation and GCCE. For the Clapeyron equation process, it implies that the rest of pore water in PWSaPT has a compression due to volume increase induced by phase transition under some constraints. One constraint is that the total volume is not fixed before and after phase transition, from $V_{before} = V_r + (V - V_w) = \int_{\Gamma_1}^{\Gamma_2} d^3 r$ to $V_{after} = V_r + (V - V_w) = \int_{\Gamma_1}^{\Gamma_2 + \Delta\Gamma} d^3 r$. Another constraint is that the
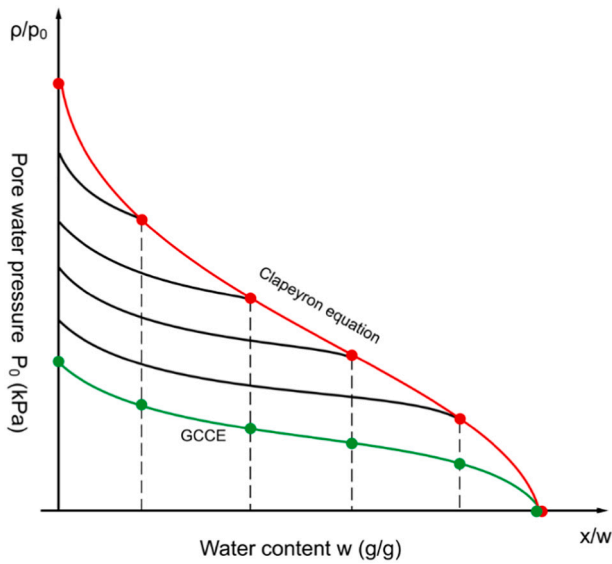
Fig. 5. Comparison between two phase transition modes of the Clapeyron equation mode and GCCE mode. The Clapeyron equation mode is presented by red solid line; while the GCCE equation mode by green solid line.

total number of particles *N* is fixed before and after phase transition, i.e.

$$N_{before} = \int_{\Gamma_1}^{\Gamma_2} d^3 r \rho(x) = N_{after} = \int_{\Gamma_1}^{\Gamma_2 + \Delta\Gamma} d^3 r \rho(x) \qquad (40)$$

The constraints imply that the density of pore water in PWSaPT has an increase after phase transition. The system depends on the ensemble with fixed particles number *N* and unfixed volume. Combined with Eq. (1), we get the real pore water pressure P_0 according to the constraints,

$$P_0(x) = P(x) - A(\rho_C(x)) \rho_C^{'}(x)^2 \qquad (41a)$$

$$P(x) = \mu - \psi(\rho_C) - \rho_C(x)U(x) + \frac{1}{2} A(\rho_C(x)) \rho_C^{'}(x)^2 \qquad (41b)$$

$$P_0(x) = \mu - \psi(\rho_C) - \rho_C(x)U(x) - \frac{1}{2} A(\rho_C(x)) \rho_C^{'}(x)^2 \qquad (41c)$$

While for the GCCE process, it implies that the rest of pore water in PWSaPT remains constant without compression after phase transition with some constraints. One constraint is that the total volume *V* is fixed before and after phase transition, $V_{before} = V_r = \int_{\Gamma_1}^{\Gamma_2} d^3 r$ to $V_{after} = V_r = \int_{\Gamma_1}^{\Gamma_2} d^3 r$. Another constraint is that the total number of particles *N* is fixed before and after phase transition, i.e.

$$N_{before} = \int_{\Gamma_1}^{\Gamma_2} d^3 r \rho(x) = N_{after} = \int_{\Gamma_1}^{\Gamma_2} d^3 r \rho(x) \qquad (42)$$

The constraints imply that the density of pore water in PWSaPT remain constant before and after phase transition. The system depends on canonical ensemble. Combined with Eq. (1), the real PWP P_0 can be expressed as Eq. (21b). Different constraints for deducing Clapeyron equation and the GCCE result in different profiles of density and pressure, and further result in different pressure slopes for both equations as temperature changes. For example, the pressure derivation with temperature is approximately 1.1 MPa/°C for the GCCE equation, 13.3 MPa/°C for Clapeyron equation.

4. Discussion

Based on theory of non-uniform water, the understanding on the PWS and its phase transition, some key phenomena and scientific issues on phase transition behaviors in porous media can be better explained.

4.1. Spatial non-uniform of soil water density

The spatial non-uniform of soil water density can be well illuminated using the theory of non-uniform water. Soil water density, as a basic physical variable, is an inescapable concept in defining the thermodynamic states of pore water and thus a cornerstone in describing and quantifying many geophysical processes. Despite its indispensable role in accurately describing many geophysical processes, the soil water density is still less understood and commonly treated as free water density of 0.997 g/cm³. However, the local soil water density is spatial non-uniform. It is remarkably different from the free water density and has an increase with gradually closing to the soil particle surface. Recently, some research has observed and realized the non-uniform [3,4,30,41,42]. The increase tendency of soil water density can be well explained based on the theory of non-uniform water. Eq. (23) is the soil water density equation of non-uniform water, which is related to the external potential and intermolecular interaction. When gradually closing to the soil particle surface, there is a spatial gradient of decreasing external potential or increasing external force (in absolute value), and the spatial gradient will result in a spatial gradient of soil water density increasing with considering interaction of water molecular (in absolute value). Generally, the soil water is compressed by the external potential associated with sorption effect, which results in increase in soil water density; while the soil water is stretched by surface tension associated with capillarity effect, which results in decrease in soil water density. Notably, the local water density smoothly increases at the pore scale but shows oscillations at an atomic or molecular scale with closing the wall of substrate.

4.2. Application of the generalized Clausius-Clapeyron equation

The recent questions of GCCE application in porous media can be well explained based on the phase transition of non-uniform water. In porous media, especially in soils, phase transition of pore water is generally described as the GCCE since the pressure difference between pore water and ice was observed based on experimental measurement [13]. The GCCE was considered valid under static conditions by some investigations [14,25,29,34,37]. However, numerous questions regarding the GCCE, recently, have been posted by researchers [29,33]. The inconsistent points for GCCE are mainly ascribed to two inappropriate understanding for interface water based on the sharp interface model at the macro scale: one is that the pressures of water and ice at the interface of phase transition are different; the other the PWP induced by phase transition is negative and in tension due to surface tension or capillary effect. However, based on the phase transition of non-uniform water in Section 3.3, the PWP should be equal to ice pressure at the interface of phase transition, and the PWP is spatial non-uniform from negative to positive. In other words, the spatial non-uniform of PWP based on the diffuse interface at a micro pore scale will result in the pressure differences of water and ice at the interface of phase transition based on the sharp interface at a macro scale. Therefore, the questions of GCCE is mainly ascribed to the lack of understanding on nature of the non-uniform water in a smaller scale and the inappropriate sharp-interface model simplification of the substrate-water system.

4.3. Drive force of water migration

Migration of pore water is of prime importance for geoscience. Based on the theory of non-uniform water, two leading drive forces of pore water, PWP and matric potential, have been always discussed. The PWP and matric potential are consistent when considering non-relaxation behavior, and the drive force of water migration can be expressed as derivative of PWP or matric potential; while when considering relaxation behavior, the drive force of water migration should be a functional concept of PWP or matric potential. In soil freezing, water migration generally described by Darcy's rule which highly depends on the

derivative of drive force. Considerable research has been focusing on the investigating on drive force. PWP and matric potential are two leading sources of drive force. For example, Wen et al. [38] investigated the matric potential in freezing soils and regarded it as the drive force of water migration; while Zhang et al. [46–49] investigated the PWP in freezing soils and regarded it as the drive force. Recent research has been focusing on which one should be the leading source. In non-uniform water, the water potential is also non-uniform with a spatial gradient. In the saturation state of interface, the drive force is zero because no water migration occurs even though there exists potential gradient with $P_o(r, W_0)$, and thus the potential gradient of $P_o(r, W_0)$ is regarded as the reference potential gradient. While the drive force should originate from the departure of the reference potential $\psi_m^j = \frac{\partial(I_m^j - I^0)}{\partial r}$, i.e., the matric potential. Therefore, for non-uniform water, the drive force of water migration should be described as a conception of functional derivative rather than derivative. However, in non-relaxation behavior mode, the functional derivative associated with matric potential can be reduced into the minus of PWP. For example, the matric potential is equal to the PWP based on the Eq. (30). Therefore, the drive force of Darcy's rule can be described as the derivation of matric potential or PWP which are actually same in nature. Furthermore, for non-uniform water, it's weird but nature that water flows from the location with lower PWP to that with higher PWP under drive force, which is similar that water flows downwards, from the location with lower gravity to that with higher gravity.

4.4. Frozen soil strength variation based on pressure melting

The challenge of ice melting induced by confining pressure can be well interpreted based on the non-uniform water. Researches have pointed that the frozen soil strength experiences three stages I, II and III as the confining pressure increases [28,39]. In stage I, the frozen soil strength increases with increasing confining pressure. This is because increasing confining pressure results mainly in an increasing in effective force but without ice pressure melting. In stage II, the frozen soil strength decreases with increasing confining pressure. This is because increasing confining pressure results mainly in a decreasing in effective force due to ice pressure melting. In stage III, the frozen soil strength remains constant with increasing confining pressure. The increasing confining pressure results almost in an increasing in PWP and no increasing in effective force because soil particle is almost around by pore water from ice pressure melting. Therefore, the key of interpretation is determining in which confining pressure the pressure melting occurs or not. However, it is a challenge for ice reaching that pressure required when pore water is regarded as uniform water. The confining pressure is too small to induce ice melting even through pressure melting is ascribed to stress concentration. Fortunately, based on theory of non-uniform water, the PWP in the phase transition interface is actually far larger than the confining pressure, and thus the pressure required by pressure melting can be easily reached. Furthermore, a key relationship between the phase transition behavior and the critical frozen soil strength was built here based on the theory of non-uniform water.

4.5. Origination of freezing point depression

The freezing point is a key parameter which can indirectly reflect the PWS in porous media. The increasing PWP is responsible for the decreasing of freezing point based on the theory of non-uniform water. Researches have pointed that the freezing point decreases when soils subjected to freezing as saturation degree decreases when water content is lower than saturation degree; while the freezing point has no obvious change when water content is equal to or larger than saturation degree [6]. In addition, the freezing point also decreases as external loading increases [21]. Based on the theory of non-uniform water, the PWP have an increase with decreasing water content and increasing external

loading, and its phase transition depends on GCCE rule in open system or Clapeyron equation in closed system. Therefore, the decreasing of freezing point is ascribed to the increasing PWP, and the freezing point depression related to external loading and saturation degree can be calculated using the GCCE or Clapeyron equation rules.

4.6. Cavitation pressure and improvement of measurement method to pore water pressure

Cavitation pressure increasing of non-uniform water is the key method to improve the measurement ranges of PWP using the tensiometer method. The measurement range of matric potential (approximately not lower than −80 kPa) is highly constrained by the cavitation occurrence in the chamber of prober when using the tensiometer method. The increase of density and PWP of liquid in the chamber of prober can vastly decreases the possibility of cavitation occurrence through increasing the cavitation pressure. Based on the theory of non-uniform water, the PWP can be improved by the substrate material and geometry of prober chamber. While the cavitation pressure is actually the PWP at the air-water boundary. Potentially suppression effect of cavitation occurrence has been observed using different materials. For example, the highest cavitation suction of 7 MPa has been reported for silica [12], 16 MPa for Pyrex glass beads [23], and 140 MPa for quartz [50]. In fact, the cavitation directly depends on how much tensile pressure is imposed on water molecules confined by surrounding substrate material and its geometry. Therefore, the measurement range of PWP directly depends on the interface effect of the substrate material and geometry in the prober chamber. Based on this mechanism, we have two methods to extend the measurement range of probe though: one is designing and decreasing the chamber size of prober because the interface effects result vastly in increase of PWP and density when the liquid locates in the chamber within the interface force; the other is choosing some materials with high interface energy.

4.7. Promoting effect of the hydrate formation

The promoting effect of porous material for hydrate formation can be well explained based on the theory of non-uniform water. Researches have pointed that the substrate surface of porous media has a promoting effect on the formation of hydrate. For instance, the confinement effects allow synthetic hydrates formation under less demanding conditions, faster growth kinetics and lower nucleation pressures [8]. The formation of gas hydrate blockages in oil and natural gas pipelines is closely related to the properties of the pipeline surfaces [26]. Cha et al. [9] observed thermodynamic as well as kinetic promotion of methane hydrates in the presence of this bentonite surface. Guggenheim and van Groos [22] found a thermodynamic promoting effect of clay surfaces on hydrate formation. Xue et al. [40] found that the nucleation and formation of tetrahydrofuran (THF) hydrates were greatly promoted compared to that without quartz glass beads. The promoting effects observed are also related to various other materials or porous mediums such as polyethylene oxide, metal, metal oxide, sand soil, etc. [15]. In addition, a smaller size of particle or pore radius has an improved promoting effect on the formation of hydrate. Therefore, there is a decreasing tendency in the temperature and pressure for hydrate formation in the following bulk water, sandy soil, silty soil and clay soil. The promoting effect is usually interpreted from providing nucleation sites or entropy which is related to water activity and the order properties of water [31,35]. Herein, we will account for the promoting effect from another perspective, i.e., from the PWP perspective. The water state in the bulk water is different from the following soil water in the sandy soil, silty soil and clay soil. PWP increase due to interface energy of porous media, and thus is larger than in the bulk water. Also, the increase magnitude in PWP depends on soil particle size, and increases as particle radius decreases from the coarse-grained soils to the fine-grained soils. Therefore, in the same external conditions of pressure and temperature during the

formation of hydrate, the PWP in the soil-water interface actually is larger than the external pressure. The spatial distribution and increasing PWP resulting in the differences of phase transition condition and the promoting effect. Therefore, based on the theory of non-uniform water, the issue that why the hydrate prefers forming in the solid-liquid interface can be well explained. Furthermore, according to the phase transition conditions (pressure and temperature) we can deduce the real PWS (PWP) in the soil-water interface.

4.8. Discrepancy of unfrozen water content with different initial water content

Unfrozen water content is crucial parameter which is also related to PWS during soil freezing. The discrepancy of unfrozen water content with different initial water content can be explained based the theory of non-uniform water and its relaxation behavior. In general, unfrozen water content decreases with decreasing temperature and is affected by initial water content [38]. The phenomenon observed for many years has not yet been well understood. Herein, we gave a novel explanation based on the theory of non-uniform water. Fig. 6 is the relationships between the PWP and unfrozen water content of soils with different initial water contents during freezing. As shown in Fig. 6a, three soil samples with different initial water contents of 16.30%, 22.85% and 29.40% was measured at different temperatures points of −0.5, −1.0, −2, −3.5, −5.5, −8, −11 and − 15 °C, and the unfrozen water content measured by NMR (Suzhou NIUMAG analytical instrument corporation, MiniMR60) gradually decreases as temperature decreases. It implies that the water in soils doesn't freeze in a single temperature point rather than in a temperature range, which is consistent with the non-uniform state of

interface water. In addition, there exist different unfrozen water curves for soil samples with different initial water contents, as shown in Fig. 6a. This is attributed to the relaxation process of soil water. For example, the soil samples have different profiles of density and PWP due to relaxation, as shown in Fig. 6b. In certain negative temperature, Soil samples CN1, CN2 and CN3 have same PWPs ($P_a = P_b = P_c$) but different PWP gradients, which are corresponding to different unfrozen water contents ($w_a \neq w_b \neq w_c$).

4.9. PWP calculation from experimental data

Based on theory of non-uniform water, the PWP can be directly obtained from some experimental measurement. The local PWP P_0 has a consistent tendency with that from Eq. (22). However, it is cumbersome to obtain PWP though Eq. (22) because the density parameter related to the direct correlation functions $C^{(1)}(\rho(r), r)$ and $C_0^{(1)}(\rho_0)$ is hard to calculate. Based on the definition, analysis and discussion of local PWP and phase transition of non-uniform water, we found the local PWP P_0 can be directly obtained from some laboratory experiments. In drying-wetting cycle of soil, the local PWP P_0 is equal to the vapor pressure in the water-air interface of phase change. The two pressures can be obtained through the measurement method of soil water potential using both the transient water release and imbibition method (TRIM) and a constant flow method (CFM) [2]. Fig. 3 is a typical soil water characteristic curve. During testing, the PWP with different water content can be deduced based on the air pressure and reference pressure and water content squeezed out of soil. In soil freezing or thawing, the local PWP is equal to the ice pressure in the ice-water interface of phase change. The two pressures can be calculated from the GCCE when we know the temperatures. Furthermore, the freezing characteristic curve can be obtained by combining the unfrozen water content curves measured by NMR with the local PWP.

5. Conclusions

Pore water in the porous medium is non-uniform with spatial variation in properties and behaviors, such as non-uniform density, PWP and phase transition behaviors. While the substrate-water system is the fundamental unit to characterize the pore water properties.

The diffuse interface model is a more appropriate model than the sharp interface model to describe the details of substrate-water system. At a more micro pore scale, the spatial state variations of interface water can be easy access to investigate, such as the spatial density and PWP.

A systematic method of theory analysis, the theory of non-uniform water, is built based on the diffuse interface model and relaxation behavior hypothesis, including the static theory and dynamic theory. The static theory characterizes the origin force sources of non-uniform water with fixed initial water content and its spatial non-uniform properties in the specific formula. The dynamic theory characterizes the spatial variation of non-uniform water with water content changing based on two different relaxation modes. In general, the relaxation mode is more universal than non-relaxation mode. When soil water subjected to a fast variation of water content (e.g., the early stage of unidirectional soil freezing) or in a confined space or constrained by external force (e. g., freezing in closed system), the non-relaxation mode maybe can consider be followed.

A PWS function including the gradient part is nature for describing the non-uniform state of pore water based on the theory of non-uniform water. While PWP function is effective to describe the non-uniform state of pore water. PWP is also spatial non-uniform, includes nonlocal PWP induced by external potential and interface tension induced by particle gradient. The non-uniform PWP can be used to well explain the non-uniform properties of water density, the freezing point, cavitation pressure and phase transition behaviors, which, in turn, further prove the PWP non-uniform.

The matric potential of non-uniform water is a functional concept. It
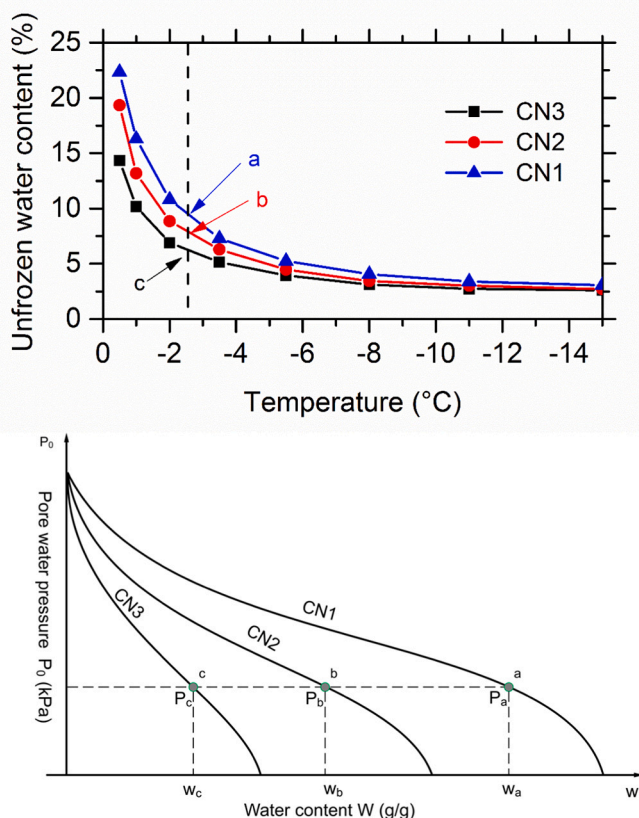

Fig. 6. The relationships between the pore water pressure and unfrozen water content when soils with different initial water contents subjected to freezing. a, variations of unfrozen water content of samples CN1, CN2 and CN3 with different initial water contents; b, variations of pore water pressure of samples CN1, CN2 and CN3 with different initial water contents.

reduces to PWP without considering relaxation behavior, and can be obtained using the measurement method of traditional matric potential (Eq. (30)). However, with considering relaxation behavior, it includes the PWP and pressure change induced by relaxation. The functional concept of matric potential can be more effective to describe the water migration of pore water. Based on the non-uniform water, a more nature formula of matric potential is proposed.

Phase transition of pore water is also non-uniform. There exist two phase transition modes based on the relaxation behavior hypothesis: the Clapeyron equation and the GCCE. The two modes of phase transition are, in nature, consistent because both are following the conditions that the free energy, pressure and temperature remain equal between two phases. Generally, the Clapeyron equation is for closed system and the GCCE is for open system. The questions of GCCE are ascribed to lack of understanding of non-uniform water in the substrate-water system. While the discrepancies of phase transition behavior in soil freezing and hydrate formation are ascribed to the PWP discrepancies induced by different porous material.

Data availability

The datasets generally during the study are available from the corresponding author on reasonable request.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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