



RESEARCH ARTICLE

Work input for unsaturated soils considering interfacial effects

Yan Liu¹ | Chang-Fu Wei² | Cheng-Gang Zhao¹ | Qian Fang¹ | Jian Li¹

¹School of Civil Engineering, Beijing Jiaotong University, Beijing, China

²State Key Laboratory of Geomechanics and Geotechnical Engineering, Institute of Rock and Soil Mechanics, Chinese Academy of Science, Wuhan, China

Correspondence

Liu Yan, School of Civil Engineering, Beijing Jiaotong University, Beijing, China.

Email: yanl@bjtu.edu.cn

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Summary

In this research, the interfacial energy is taken into account in the deformation work for unsaturated soils. Based on porous media theory, the thermodynamic balance equations for each phase and the interface are used to derive the work input for unsaturated soils. The work input equation serves as the basis and starting point for the choice of stress state variables, based on which the conjugate stresses and strain increments are derived. The influences of the interfaces on the effective stress and the constitutive law for the liquid phase are then discussed based on the work input equation. The effective stress can be expressed as Bishop's type, and the effective stress parameter is shown to be a function of both the degree of saturation and the interfacial area. The constitutive law for the liquid phase under dynamic condition is also presented. The relationship among interfacial area, saturation, and capillary pressure is proposed to calculate the value of the effective stress. Experimental data obtained from literature are used to validate the proposed model equations. Results show that our findings are in accordance with the existing research. Unlike the phenomenal study, our research has a rigorous theoretical basis, which lays a foundation for further research of unsaturated soils considering the interfacial effects.

KEYWORDS

effective stress, interfacial effects, unsaturated soils, work input

1 | INTRODUCTION

Work is a way of energy transfer between system and its surroundings. It is usually defined as the product of a force applied and the distance through which that force acts. In thermodynamics, work is done by all the macroscopic forces exerted on the system. These forces are associated with the macroscopic state variables of the system and always occur in conjugate pairs, for example pressure and volume, surface tension and surface area. Therefore, the work input equation derived from the energy balance equation provides a theoretical basis to deal with the relationship between a force and its conjugated deformation. It has greatly attracted researchers' attention because it is beneficial to understand the mechanical properties of unsaturated soils. Houlsby^{1,2} derived the specific work input equation for both saturated and unsaturated granular material. He provided a valuable tool for the selection of the appropriate stress variables and showed that the selection was not unique. Extensive studies have then been conducted on the subject, and the effective stress of porous media for more complex problem has also been discussed (Borja,³ Coussy et al,⁴ Zhao et al,^{5,6} Broja and Koliji,⁷ Tamagnini,⁸ Li et al,^{9,10} Fuentes et al¹¹).

The work input into unsaturated soils is equal to the product of the generalized stresses and their conjugate strain increments, which includes the information about the mechanical and hydraulic behavior in unsaturated soils. It is therefore reasonable to use the work input equation to describe the interaction and mutual transformation caused by the general stresses and conjugated strain increments. The soil skeleton stress, which is work conjugated with the soil skeleton strain, can be defined as the effective stress. Thus, the work input equation is usually used to study the effective stress, which serves as the basis and starting point for constitutive modeling and strength analysis. Some of these studies have been proposed by Jommi,¹² Vaunat et al.,¹³ Wheeler et al.,¹⁴ Sheng et al.,¹⁵ Li,^{16,17} Nuth and Laloui,¹⁸ Buscarnera and Nova,¹⁹ Borja and White,²⁰ Lu et al.,²¹ Buscarnera and Einav,²² Lloret-Cabot et al.,²³ Hu et al.,²⁴ Choo et al.²⁵

However, the work input equation given in the above research did not take into account the interfacial energy, or neglected it for simplicity. The unsaturated soil is typically considered as a 3-phase system (ie, solid, gas, and liquid), and there are interfaces between each of the 2 phases. These interfaces may influence the macroscopic soil behavior. Unbalanced force exerted on 2 sides of the interface will bring about interface force. The interface force originates from the physical and chemical effects, such as the surface tension forces, van der Waals forces, electric double layer forces, and polar molecule reaction forces. The interface force could lead to excess energy at the surface compared to the bulk, called interface energy.²⁶ Similar to the external forces, these interface forces may also affect the deformation and strength of soil. Therefore, a complete local energy balance was imposed taking into account phase interfaces. It is necessary to consider interface energy in the work input equation. To address this shortcoming, Coussy^{4,27} who formulated the strain work expression included the contribution from interfacial energy. The change of surface energy was because of displacement of the air-water interface during the invasion process. Gray et al.²⁸ investigated the work input for unsaturated elastic porous media and considered the interfacial effect because of all the mobile interfaces in porous media. But they did not give the details about how to determine the interface deformation.

Interfaces play a key role in the modeling of multiphase flows and contaminant transport in porous media. The interfacial energy has been adopted to explain the capillary effect^{4,29} and other physicochemical effects.³⁰ Hassanizadeh and Gray³¹ discussed the capillary pressure in detail based on thermodynamic theory and pointed out that the capillary pressure must be recognized as a function of degree of saturation and interfacial area. In recent years, relationships among capillary pressure, saturation, and interfacial areas have been proposed by several investigators.³¹⁻³⁸ Traditional capillary pressure-saturation relationship was in fact regarded as the projection of such complex capillary pressure function onto a single plane. These achievements are very helpful to the interpretation of the mechanical and hydraulic behavior of unsaturated soils.

The existence of interfaces could also change the soil stress state, which is very crucial to analyze the deformation, strength, and flow behavior of unsaturated soils. Fredlund and Morgenstern³⁹ were probably the first researchers who introduced interfaces into stress analysis of unsaturated soils. They treated the contractile skin or air-water interface as an independent phase and considered the unsaturated soil as a 4-phase system when performing a stress analysis on an element. Lu and Likos⁴⁰ proposed the concept of suction stress, which is conceptualized as the resultant of interparticle physicochemical stresses attributable to cementation, van der Waals attraction, double-layer repulsion, capillary stress arising from surface tension, and negative pore-water pressure. In this case, apart from the capillary stress, other interfacial effects are also lumped into the suction stress. Nikoee et al.⁴¹ took into account the role of interfacial energy and the contribution of air-water specific interfacial area to the effective stress tensor based on thermodynamic approach. Kim et al.⁴² investigated the equivalent pore pressure which considered the interfacial energy and showed that it could lead to unconditionally stable and accurate solutions. Likos⁴³ suggested a general form of suction stress and gave an effective stress formulation for unsaturated soils accounting for surface tension and interfacial area. Osipov⁴⁴ pointed out that the actual total effective stress should be taken to study the averaged effective stress value caused by external and internal forces, and the interfacial effect was included in the internal forces in his formulation. All these research efforts provide a basis for further studies on the interfacial effect on unsaturated soil mechanics.

In this research, the interfacial energy is taken into account in the deformation work for unsaturated soils. The deformation work input to unsaturated soils considering interfacial effect can be derived directly from the energy equations. The derivation method adopted in this paper is different from the approaches in the literature and is easier to apply. Moreover, previous studies have not used work input equation to explain the interfacial effects on stress state and flow behavior. The benefit of our research is that it provides a systematic method to analyze the above problems simultaneously with a rigorous theoretical basis. The structure of the paper is as follows. First, the thermodynamic balance equations for each phase and the interface are used to derive the work input into unsaturated soils. The

influences of the interfaces on the effective stress and the constitutive law for liquid phase are then discussed based on the work input equation. Experimental data obtained from literature are used to validate the proposed model equations in the end.

2 | DERIVATION OF WORK INPUT EQUATION

2.1 | Conservation equations

Unsaturated soils are 3-phase porous media, consisting of a solid skeleton, pore water, and pore gas. The mechanical and thermodynamical balance equations and constitutive models of single-phase media developed from the continuum mechanics serve as the basis for the development of multiphase porous medium theory. However, continuum mechanics deals with ideal homogeneous materials and cannot be used to describe porous media directly. In this case, a thermodynamics constrained average method is adopted to replace the microheterogeneous media with a macrohomogeneous media. Average theorems facilitate the transformation of variables and equations between different scales, and the detailed explanation of this theory can be found in the literature.⁴⁵

In this study, the soil skeleton, pore water, and pore gas in the unsaturated soils are denoted by s , w , and g , respectively, as shown in Figure 1. These phases are separated by 3 different interfaces denoted by sw , sg , and wg . Additionally, a common line denoted by swg may exist. To specify a phase, Greek letter α or β is used. In the past few decades, a lot of effects have been done to develop a thermodynamically constrained macroscale description of porous media in which the presence of interfaces can be explicitly taken into account.⁴⁵⁻⁴⁹ Making use of the average theorems, the macroscale conservations for phases and interfaces of unsaturated soils can be obtained as shown below.

2.1.1 | Conservation of mass

For the α phase

$$\frac{d^\alpha}{dt}(n^\alpha \rho^\alpha) + n^\alpha \rho^\alpha (\nabla \cdot \mathbf{v}^\alpha) = \sum_{\beta \neq \alpha} \widehat{e}_{\alpha\beta}^\alpha \quad (1)$$

For the $\alpha\beta$ interface

$$\frac{d^{\alpha\beta}}{dt}(a^{\alpha\beta} \Gamma^{\alpha\beta}) + a^{\alpha\beta} \Gamma^{\alpha\beta} (\nabla \cdot \mathbf{v}^{\alpha\beta}) = -\widehat{e}_{\alpha\beta}^\alpha - \widehat{e}_{\alpha\beta}^\beta + \widehat{e}_{swg}^{\alpha\beta} \quad (2)$$

where n^α denotes volumetric fraction of α phase, ρ^α denotes the density of α phase, \mathbf{v}^α denotes the average velocity of α phase, $\widehat{e}_{\alpha\beta}^\alpha$ denotes the rate of mass exchange between the $\alpha\beta$ interface, $a^{\alpha\beta}$ denotes the specific interfacial area of $\alpha\beta$ interface, which is equal to the amount of interface area per unit volume, $\Gamma^{\alpha\beta}$ denotes the areal mass density of the $\alpha\beta$ interface, and $\widehat{e}_{swg}^{\alpha\beta}$ denotes the rate of mass exchange between a contact line and the $\alpha\beta$ interface. The contact lines do not possess excess mass; thus, the following relation holds.

$$\sum_{\alpha\beta} \widehat{e}_{swg}^{\alpha\beta} = 0 \quad (3)$$

Summing up Equation 1 over all the phases and Equation 2 over all the interfaces, the overall conservation mass equation of unsaturated soils can be derived.

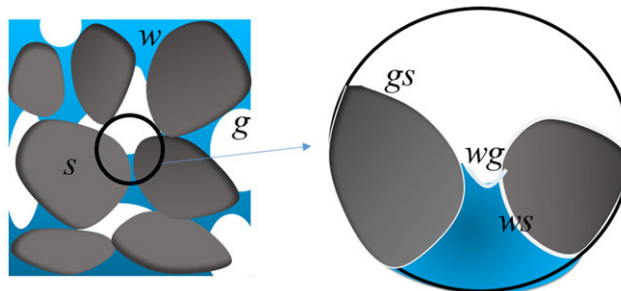


FIGURE 1 Diagram of unsaturated soils [Colour figure can be viewed at wileyonlinelibrary.com]

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 \quad (4)$$

where ρ is the overall density of unsaturated soil given as follows:

$$\rho = \sum_{\alpha} n^{\alpha} \rho^{\alpha} + \sum_{\alpha\beta} a^{\alpha\beta} \Gamma^{\alpha\beta} \quad (5)$$

and \mathbf{v} is the average velocity of the whole unsaturated soil.

$$\mathbf{v} = \frac{1}{\rho} \left(\sum_{\alpha} n^{\alpha} \rho^{\alpha} \mathbf{v}^{\alpha} + \sum_{\alpha\beta} a^{\alpha\beta} \Gamma^{\alpha\beta} \mathbf{v}^{\alpha\beta} \right) \quad (6)$$

2.1.2 | Conservation of momentum

For the α phase

$$n^{\alpha} \rho^{\alpha} \frac{d^{\alpha} \mathbf{v}^{\alpha}}{dt} - \nabla \cdot (n^{\alpha} \boldsymbol{\sigma}^{\alpha}) - n^{\alpha} \rho^{\alpha} \mathbf{b}^{\alpha} = \sum_{\beta \neq \alpha} \widehat{\mathbf{T}}_{\alpha\beta}^{\alpha} \quad (7)$$

For the $\alpha\beta$ interface

$$\begin{aligned} & a^{\alpha\beta} \Gamma^{\alpha\beta} \frac{d^{\alpha\beta} \mathbf{v}^{\alpha\beta}}{dt} - \nabla \cdot (a^{\alpha\beta} \mathbf{s}^{\alpha\beta}) - a^{\alpha\beta} \Gamma^{\alpha\beta} \mathbf{b}^{\alpha\beta} \\ &= - \left(\widehat{\mathbf{T}}_{\alpha\beta}^{\alpha} + \widehat{\mathbf{e}}_{\alpha\beta}^{\alpha} \mathbf{v}^{\alpha,s} \right) - \left(\widehat{\mathbf{T}}_{\alpha\beta}^{\beta} + \widehat{\mathbf{e}}_{\alpha\beta}^{\beta} \mathbf{v}^{\beta,s} \right) + \left(\widehat{\mathbf{e}}_{\alpha\beta}^{\alpha} + \widehat{\mathbf{e}}_{\alpha\beta}^{\beta} \right) \mathbf{v}^{\alpha\beta,s} + \widehat{\mathbf{s}}_{\text{swg}}^{\alpha\beta} \end{aligned} \quad (8)$$

where $\boldsymbol{\sigma}^{\alpha}$ is the macroscale stress tensor of the α phase and $\mathbf{s}^{\alpha\beta}$ is the macroscale stress tensor of the $\alpha\beta$ interface; \mathbf{b}^{α} and $\mathbf{b}^{\alpha\beta}$ are the external supply of momentum such as the gravity; $\widehat{\mathbf{T}}_{\alpha\beta}^{\alpha}$ denotes the momentum exchange between the $\alpha\beta$ interface and the α phase; $\widehat{\mathbf{s}}_{\text{swg}}^{\alpha\beta}$ denotes the momentum exchange between the common line and the $\alpha\beta$ interface and satisfies the following restriction:

$$\sum_{\alpha\beta} \left(\widehat{\mathbf{s}}_{\text{swg}}^{\alpha\beta} + \widehat{\mathbf{e}}_{\text{swg}}^{\alpha\beta} \mathbf{v}^{\alpha\beta} \right) = 0 \quad (9)$$

The relative velocities in Equations 7 and 8 are defined as follows:

$$\begin{aligned} \mathbf{v}^{\alpha,s} &= \mathbf{v}^{\alpha} - \mathbf{v}^s \\ \mathbf{v}^{\alpha\beta,s} &= \mathbf{v}^{\alpha\beta} - \mathbf{v}^s \\ \mathbf{v}^{\alpha\beta,\alpha} &= \mathbf{v}^{\alpha\beta} - \mathbf{v}^{\alpha} \end{aligned} \quad (10)$$

Summing up Equation 7 over all the phases and Equation 8 over all the interfaces, the overall conservation momentum equation of unsaturated soils can be derived.

$$\frac{\partial (\rho \mathbf{v})}{\partial t} + \nabla \cdot \left(\sum_{\alpha} n^{\alpha} \rho^{\alpha} \mathbf{v}^{\alpha} \mathbf{v}^{\alpha} + \sum_{\alpha\beta} a^{\alpha\beta} \Gamma^{\alpha\beta} \mathbf{v}^{\alpha\beta} \mathbf{v}^{\alpha\beta} \right) = \nabla \cdot \boldsymbol{\sigma} + \rho \mathbf{b} \quad (11)$$

where $\boldsymbol{\sigma}$ is the total stress of the unsaturated soil mixtures and \mathbf{b} is the total body force, which are defined by

$$\boldsymbol{\sigma} = \sum_{\alpha} n^{\alpha} \boldsymbol{\sigma}^{\alpha} + \sum_{\alpha\beta} a^{\alpha\beta} \mathbf{s}^{\alpha\beta} \quad (12)$$

$$\mathbf{b} = \frac{1}{\rho} \left[\sum_{\alpha} n^{\alpha} \rho^{\alpha} \mathbf{b}^{\alpha} + \sum_{\alpha\beta} a^{\alpha\beta} \Gamma^{\alpha\beta} \mathbf{b}^{\alpha\beta} \right] \quad (13)$$

2.1.3 | Conservation of energy

For the α phase

$$n^\alpha \rho^\alpha \frac{d^\alpha u^\alpha}{dt} - n^\alpha \boldsymbol{\sigma}^\alpha : \mathbf{d}^\alpha - \nabla \cdot (n^\alpha \mathbf{q}^\alpha) - n^\alpha \rho^\alpha h^\alpha = \sum_{\beta \neq \alpha} \widehat{Q}_{\alpha\beta}^\alpha \quad (14)$$

For the $\alpha\beta$ interface

$$\begin{aligned} & a^{\alpha\beta} \Gamma^{\alpha\beta} \frac{d^{\alpha\beta} u^{\alpha\beta}}{dt} - a^{\alpha\beta} \mathbf{s}^{\alpha\beta} : \mathbf{d}^{\alpha\beta} - \nabla \cdot (a^{\alpha\beta} \mathbf{q}^{\alpha\beta}) - a^{\alpha\beta} \Gamma^{\alpha\beta} h^{\alpha\beta} \\ &= - \left[\widehat{Q}_{\alpha\beta}^\alpha + \widehat{\mathbf{T}}_{\alpha\beta}^\alpha \cdot \mathbf{v}^{\alpha,\alpha\beta} + \widehat{\mathbf{e}}_{\alpha\beta}^\alpha \left(u^{\alpha,\alpha\beta} + \frac{1}{2} \mathbf{v}^{\alpha,\alpha\beta} \cdot \mathbf{v}^{\alpha,\alpha\beta} \right) \right] \\ & - \left[\widehat{Q}_{\alpha\beta}^\beta + \widehat{\mathbf{T}}_{\alpha\beta}^\beta \cdot \mathbf{v}^{\alpha,\alpha\beta} + \widehat{\mathbf{e}}_{\alpha\beta}^\beta \left(u^{\beta,\alpha\beta} + \frac{1}{2} \mathbf{v}^{\beta,\alpha\beta} \cdot \mathbf{v}^{\beta,\alpha\beta} \right) \right] + \widehat{Q}_{\text{swg}}^{\alpha\beta} \end{aligned} \quad (15)$$

where u^α and $u^{\alpha\beta}$ denote internal energy density of the α phase and the $\alpha\beta$ interface, respectively. \mathbf{q}^α and $\mathbf{q}^{\alpha\beta}$ denote the heat vector of the α phase and the $\alpha\beta$ interface, respectively. h^α and $h^{\alpha\beta}$ denote the external energy supply of the α phase and the $\alpha\beta$ interface, respectively. \mathbf{d}^α and $\mathbf{d}^{\alpha\beta}$ are the strain rate tensor, which are equal to the symmetric parts of the velocity gradients. $\widehat{Q}_{\alpha\beta}^\alpha$ is the energy exchange between the $\alpha\beta$ interface and the α phase; $\widehat{Q}_{\text{swg}}^{\alpha\beta}$ denotes the momentum exchange between the common line and the $\alpha\beta$ interface and satisfies the following restriction:

$$\sum_{\alpha\beta} \left[\widehat{Q}_{\text{swg}}^{\alpha\beta} + \widehat{\mathbf{e}}_{\text{swg}}^{\alpha\beta} \left(u^{\alpha\beta} + \frac{1}{2} \mathbf{v}^{\alpha\beta} \cdot \mathbf{v}^{\alpha\beta} \right) + \widehat{\mathbf{s}}_{\text{swg}}^{\alpha\beta} \cdot \mathbf{v}^{\alpha\beta} \right] = 0 \quad (16)$$

The relative velocity and relative internal energy in Equation 15 are defined as follows:

$$\begin{aligned} \mathbf{v}^{\alpha,\alpha\beta} &= \mathbf{v}^\alpha - \mathbf{v}^{\alpha\beta} = -\mathbf{v}^{\alpha\beta,\alpha} \\ u^{\alpha,\alpha\beta} &= u^\alpha - u^{\alpha\beta} \end{aligned} \quad (17)$$

Summing up Equation 14 over all the phases and Equation 15 over all the interfaces, the overall conservation energy equation of unsaturated soils can be derived.

$$\begin{aligned} & \frac{\partial}{\partial t} \left[\sum_{\alpha} n^\alpha \rho^\alpha \left(u^\alpha + \frac{1}{2} \mathbf{v}^\alpha \cdot \mathbf{v}^\alpha \right) + \sum_{\alpha\beta} a^{\alpha\beta} \Gamma^{\alpha\beta} \left(u^{\alpha\beta} + \frac{1}{2} \mathbf{v}^{\alpha\beta} \cdot \mathbf{v}^{\alpha\beta} \right) \right] \\ & + \nabla \cdot \left[\sum_{\alpha} n^\alpha \rho^\alpha \mathbf{v}^\alpha \left(u^\alpha + \frac{1}{2} \mathbf{v}^\alpha \cdot \mathbf{v}^\alpha \right) + \sum_{\alpha\beta} a^{\alpha\beta} \Gamma^{\alpha\beta} \mathbf{v}^{\alpha\beta} \left(u^{\alpha\beta} + \frac{1}{2} \mathbf{v}^{\alpha\beta} \cdot \mathbf{v}^{\alpha\beta} \right) \right] \\ & = W + \nabla \cdot \mathbf{q} + \rho h \end{aligned} \quad (18)$$

The left hand side of Equation 18 denotes the variation of the total internal energy because of the 3 items in the right hand side. W accounts for the total strain work, \mathbf{q} is the total heat flux vector, and h is total energy supply, respectively

$$W = \sum_{\alpha} n^\alpha \boldsymbol{\sigma}^\alpha : \mathbf{d}^\alpha + \sum_{\alpha\beta} a^{\alpha\beta} \mathbf{s}^{\alpha\beta} : \mathbf{d}^{\alpha\beta} \quad (19)$$

$$\mathbf{q} = \sum_{\alpha} (n^\alpha \mathbf{q}^\alpha) + \sum_{\alpha\beta} (a^{\alpha\beta} \mathbf{q}^{\alpha\beta}) \quad (20)$$

$$h = \frac{1}{\rho} \left(\sum_{\alpha} n^\alpha \rho^\alpha h^\alpha + \sum_{\alpha\beta} a^{\alpha\beta} \Gamma^{\alpha\beta} h^{\alpha\beta} \right) \quad (21)$$

2.2 | Work input equation for unsaturated soils

Based on the conservation equations, Zhao et al^{5,6} derived a specific work expression for unsaturated soils, without considering the interfacial effect. Here, we consider the impact of interface and give a more complete expression for work input into unsaturated soils. Some basic assumptions are required:

1. The 3 phases, solid, water and gas, have the same temperature.
2. The solid, water and interfaces are all incompressible.
3. The fluid viscosity is ignored.
4. The exchanges in mass are negligible.

The total work is expressed as Equation 19 and can be rewritten as follows:

$$W = \sum_{\alpha} \text{tr}(n^{\alpha} \boldsymbol{\sigma}^{\alpha} \cdot \nabla \mathbf{v}^{\alpha}) + \sum_{\alpha\beta} \text{tr}(a^{\alpha\beta} \mathbf{s}^{\alpha\beta} \cdot \nabla \mathbf{v}^{\alpha\beta}) \quad (22)$$

where the symbol tr represents trace of the matrix.

The solid stress tensor is derived from Equation 12.

$$n^s \boldsymbol{\sigma}^s = \boldsymbol{\sigma} - \sum_{f=w,g} n^f \boldsymbol{\sigma}^f - \sum_{\alpha\beta} a^{\alpha\beta} \mathbf{s}^{\alpha\beta} \quad (23)$$

Because we do not consider the fluid viscosity, the stress tensor for the fluid and interface is^{46,49}

$$\boldsymbol{\sigma}^w = p^w \boldsymbol{\delta}, \quad \boldsymbol{\sigma}^g = p^g \boldsymbol{\delta}, \quad \mathbf{s}^{\alpha\beta} = -\gamma^{\alpha\beta} \boldsymbol{\delta} \quad (24)$$

where p^w is the pore water pressure, p^g is the pore gas pressure, and $\gamma^{\alpha\beta}$ is the surface tension. $\boldsymbol{\delta}$ is the unit tensor. Equation 24 has opposite signs compared to continuum mechanics, because we adopt the convention in soil mechanics that compression is positive and tension is negative.

As $\text{tr}(\boldsymbol{\delta} \cdot \nabla \mathbf{v}^{fs}) = \nabla \cdot \mathbf{v}^{fs}$, substituting Equations 23 and 24 into Equation 22 yields

$$W = \text{tr}(\boldsymbol{\sigma} \cdot \nabla \mathbf{v}^s) + n^w p^w \nabla \cdot \mathbf{v}^{w,s} + n^g p^g \nabla \cdot \mathbf{v}^{g,s} - \sum_{\alpha\beta} a^{\alpha\beta} \gamma^{\alpha\beta} \nabla \cdot \mathbf{v}^{\alpha\beta,s} \quad (25)$$

As shown in Appendix, substitution of the mass balance equation into Equation 25, and neglecting compressibility of solid, water, and interface, the following expression for the total work of unsaturated soils is derived:

$$\begin{aligned} W = & \left\{ \left[\boldsymbol{\sigma} - \left(S_r p^w + (1-S_r) p^g - \sum_{\alpha\beta} a^{\alpha\beta} \gamma^{\alpha\beta} \right) \boldsymbol{\delta} \right] : \mathbf{d}^s \right\} \\ & + \left\{ n(p^g - p^w) \frac{d^s S_r}{dt} + \sum_{\alpha\beta} \gamma^{\alpha\beta} \frac{d^s a^{\alpha\beta}}{dt} \right\} - \left\{ p^g n^g \beta^g \frac{d^s p^g}{dt} \right\} \\ & - \left(p^w \nabla n^w \cdot \mathbf{v}^{w,s} + p^g \nabla n^g \cdot \mathbf{v}^{g,s} - \sum_{\alpha\beta} \gamma^{\alpha\beta} \nabla a^{\alpha\beta} \cdot \mathbf{v}^{\alpha\beta,s} \right) \end{aligned} \quad (26)$$

The total work in Equation 26 consists of 4 terms. The first term is caused by deformation of solid skeleton. The second term is caused by the variation of fluid saturation. The third term is caused by the gas compression. The last term is caused by the flow of water, air, and interface. It provides a helpful reference for the development of constitutive models for unsaturated soils. Some constitutive relationships can be established with a linear assumption.

The impact of the third term with respect to the gas phase in unsaturated soils can be found in reference,⁵⁰ and is not discussed here. The interfacial energy has significant influence on the solid phase, liquid phase, and flow equations. We will focus on the first 2 terms as follows:

$$W_1 = \left[\boldsymbol{\sigma} - \left(S_r p^w + (1-S_r) p^g - \sum_{\alpha\beta} a^{\alpha\beta} \gamma^{\alpha\beta} \right) \boldsymbol{\delta} \right] : \mathbf{d}^s \quad (27)$$

$$W_2 = n(p^g - p^w) \frac{d^s S_r}{dt} + \sum_{\alpha\beta} \gamma^{\alpha\beta} \frac{d^s a^{\alpha\beta}}{dt} \quad (28)$$

Compared to the expression given by Zhao et al,⁵ additional terms accounting for the interfacial effect is used in Equations 27 and 28. All these extra terms must have effect on the soil behavior and will be discussed in the following parts.

3 | EFFECTIVE STRESS CONSIDERING INTERFACIAL AREA

The effective stress, which is work conjugate to the strain in Equation 27, is defined as

$$\tilde{\sigma} = \sigma - \left(S_r p^w + (1 - S_r) p^g - \sum_{\alpha\beta} a^{\alpha\beta} \gamma^{\alpha\beta} \right) \delta \quad (29)$$

Or rewritten as

$$\tilde{\sigma} = (\sigma - p^g \delta) + S_r (p^g - p^w) \delta + \sum_{\alpha\beta} a^{\alpha\beta} \gamma^{\alpha\beta} \delta \quad (30)$$

It is indicated that the effective stress is caused by both external stress and internal stress. The first part in Equation 30 is external stress, usually called net stress, which is produced by gravity and external loadings. The rest of Equation 30 is internal stress, which is generated by physicochemical forces including van der Waals attraction, electrical double-layer repulsion, chemical cementation, surface tension at air-water interfaces, and negative pore-water pressure. As pointed by Lu and Likos,⁴⁰ the abovementioned physicochemical forces may be considered “active” in nature, meaning that it does not develop in response to external forces responsible for the total stress or pore pressure, but rather arises independently from other physical and/or chemical mechanisms. Osipov⁴⁴ approved that stresses arising in soils may be of 2 genetic types: external and internal stresses. Stresses calculated with consideration of both external and internal forces correspond to the actual effective stresses existing in a structured porous body. This viewpoint can also be verified by the effective stress in Equation 30 derived from work input equation.

The internal stress in Equation 30 is defined as suction stress by Lu and Likos,⁴⁰ and can be expressed as

$$\sigma^s = S_r (p^g - p^w) \delta + \sum_{\alpha\beta} a^{\alpha\beta} \gamma^{\alpha\beta} \delta \quad (31)$$

Similar to the expression given by Lu et al,²¹ Nikoee,⁴¹ and Likos,⁴³ the suction stress σ^s in Equation 31 has 2 terms: The first one is concerned with matric suction, and the other is affected by interface related to surface tension and interfacial area. Most of the unsaturated soil constitutive models only consider the first term and neglect the interfacial effect. Likos⁴³ selected 11 coarse-grained materials to compare the suction stress considering interfacial forces with those neglecting interfacial forces. Results showed that there is little difference in saturated state, but the difference varied in unsaturated state. The largest percent increase caused by interfacial effect was reported to be about 200%, which indicates that the second term in suction stress Equation 31 is of the same order of magnitudes as the first term. The interfaces have significant influence on the effective stress of unsaturated soils and cannot be ignored.

According to Hassanizadeh and Gray,³¹ the surface tension arisen from the solid-liquid interface and solid-gas interface can be ignored compared with the liquid-gas interface. In this case, only the surface tension γ^{wg} needs to be considered in Equation 31. The macroscale surface tension γ^{wg} is assumed to be a function of matric suction as⁵¹

$$\gamma^{wg} = \frac{1}{J} (p^g - p^w) \quad (32)$$

The parameter J is the mean curvature of the interfaces, depending on saturation, porosity, and specified surface area.^{48,49} Equation 32 has the same form as the Young-Laplace equation, but they are essentially not the same. The Young-Laplace equation expresses the equilibrium relationship between surface tension and matric suction at microscopic scale, and could only be applied at equilibrium. Equation 32 indicates the relationship at macroscopic scale, which is obtained by means of the thermodynamically constrained averaging approach.³¹ With the help of the thermodynamic theory, the macroscopic relation between surface tension and capillary pressure can be derived, which is similar to Equation 37 in the next section. According to the discussion in the next section, the macroscale matric suction is equal to the capillary pressure only at equilibrium. In this case, Equation 37 is equivalent to Equation 32.

Using Equation 32, Equation 30 can be rewritten as Bishop's type equation

$$\tilde{\sigma} = (\sigma - p^g \delta) + \chi(p^g - p^w) \delta \quad (33)$$

where χ is the effective stress parameter and can be expressed as

$$\chi = S_r + \frac{1}{J} a^{wg} \quad (34)$$

χ has a value of 1 for saturated soils and a value of 0 for dry soils.

Bishop's type effective stress is now widely used in unsaturated soils, but it is still controversial because of the difficulties in determining the Bishop parameter χ . A common method is to use saturation to replace the Bishop parameter. The effective stress is thus equal to the total stress minus an equivalent pore pressure which is weighted by the volumetric fraction of pore water and pore gas, respectively. The advantage of such substitution is that the effective stress can be degraded to Terzaghi's effective stress when saturated. The expression can also be derived from work input equation if the interfacial effect is ignored.^{2,6,28} Nevertheless, Loret and Khalili⁵² pointed out that it was more appropriate to weigh the water and air pressures according to their respective areal contributions around grains. Alonso et al⁵³ indicated that the effective stress parameter should be based on an areal definition, because stresses act on areas. However, as the areal degree of saturation is not easily measurable, it is generally assumed to be equal to the volumetric degree of saturation. Gray et al⁵⁴ argued that the fluid pressures exerted on the solid should depend on the fraction of the surface in contact with each fluid, not on the fraction of the pore space that each fluid occupies. If the factor χ is assumed to be equal to the degree of saturation of the liquid phase, it often leads to gross prediction errors.^{18,55} Consequently, some other formulae of Bishop parameter are proposed (Alonso et al,⁵³ Khalili and Khabbaz,⁵⁶ Gray and Schrefler,⁵⁷ Vlahinić et al,⁵⁸ Dangla, and Pereira²⁹).

The effective stress parameter (Equation 34) obtained here is consistent with the above statements. It cannot be simply replaced by degree of saturation if the interfacial effect is considered. However, because of the inherent limitations of laboratory test, the specific interface area is difficult to measure. At present, the pore network model or lattice-Boltzmann model has been used to estimate the interface area.³³ It is found that the specific interface area is a function of saturation and capillary pressure, which is verified by our work input equation 28 and will be discussed in the next section. Our research may offer a practical method to determine the effective stress value with the aid of relationship among the interfacial area, saturation, and capillary pressure.

4 | CONSTITUTIVE LAW FOR LIQUID PHASE

Equation 28 represents the work input by pore fluids. If the specific interface area is assumed to be a function of saturation ($a^{wg} = a^{wg}(S_r)$), Equation 28 can be rewritten as

$$W_2 = \left[n(p^g - p^w) + \gamma^{wg} \frac{\partial a^{wg}}{\partial S_r} \right] \frac{d^s S_r}{dt} \quad (35)$$

The stress work conjugated to the saturation is

$$\tilde{s} = n[(p^g - p^w) - p^c] \quad (36)$$

where $(p^g - p^w)$ is the macroscale pressure difference, and usually called matric suction. p^c is the macroscale capillary pressure and is expressed as⁴⁸

$$p^c = -\frac{\gamma^{wg} \partial a^{wg}}{n \partial S_r} \quad (37)$$

Equation 37 implies that the capillary depends not only on the saturation but also on the porosity and the specific interfacial area (ie, $p^c = p^c(S_r, n, a^{wg})$).

The macroscale pressure difference $(p^g - p^w)$ depends on the rate of change of saturation.³² Such time-dependent behavior can be attributed to local fluid flow in locally heterogeneity porous media, which plays an important role in simulating nonequilibrium flow in unsaturated soils. A detailed explanation can be found in Wei and Muraleetharan.^{59,60}

The imbalance between macroscale pressure difference $(p^g - p^w)$ and capillary pressure p^c could lead to variation in

saturation, cause the system to reach a new equilibrium state, and reestablish balance between matric suction and capillary pressure. Only at equilibrium, when no change in saturation is occurring, will have the following relation

$$(p^g - p^w)_{eq} = p^c(S_r, n, a^{wg}) \quad (38)$$

At equilibrium, if the specific interfacial area a^{wg} is neglected, Equation 38 will degenerate to traditional SWCC equation including soil porosity effect. Hysteresis is always existent in the equilibrium capillary pressure-saturation relationship. It is pointed out by Hassanizadeh and Gray³¹ that the nonuniqueness in the capillary pressure-saturation relationship is indeed because of the absence of specific interfacial area in the capillarity theory. In other words, a unique specific interfacial area-capillary pressure-saturation relationship (p^c - S_r - a^{wg}) surface may exist for all the imbibitions and drainage process. However, such conjecture of Hassanizadeh and Gray³¹ has not been fully proved currently^{36,61}, and more experiments are required.

5 | EXPERIMENTAL VALIDATION

Results reported in the literature can be used to validate our proposed equations considering the interfacial effects. The soil water characteristic curve proposed by van-Genuchten is used for simulation. The equation reads

$$S_r = S_r^{irr} + (1 - S_r^{irr}) [1 + (\alpha s)^n]^{-(1-1/n)} \quad (39)$$

where S_r^{irr} is the residual degree of saturation and α and n are material coefficients. The maximum saturation is assumed to be 1.

According to Equation 38, the specific interfacial area is a function of saturation and capillary pressure if the soil porosity is not considered. Joekar-Niasar et al³⁷ have used a quadratic polynomial relation to fit the (p^c - S_r - a^{wg}) surface based on pore network model. However, the polynomial equations are not restricted within the physical range of variation. To have a physical-based range of variation, an exponential form relation has been proposed by Joekar-Niasar and Hassanizadeh.⁶¹ Because the equilibrium capillary pressure can be substituted by the degree of saturation through Equation 39, the specific interfacial area is assumed to be a function of degree of saturation as follows:

$$a^{wg} = b S_r^c (1 - S_r)^d \quad (40)$$

where b , c , and d are material coefficients.

Equation 40 implies that the value of specific interfacial area is equal to zero ($a^{wg} = 0$) when soil is completely dry ($S_r = 0$) or saturated ($S_r = 1$). This is because only the capillary-associated interfacial areas are considered here. The total air-water interfacial area comprises contributions from film-associated water and capillary phase water, but the films have not been explicitly accounted for. If the interfacial areas associated with film need to be considered, one can refer to the formulation given by Peng et al.³⁵

5.1 | Verification of proposed relationship of specific interfacial area

The experimental results of Culligan³⁴ are used to validate the proposed Equation 40. The experimental points of the SWCC are depicted in Figure 2. We used the second drainage and imbibition data to calibrate the material coefficients α and n in Equation 39 and b , c , and d in Equation 40. Values of the above coefficients are given in Table 1, which are then adopted to predict the other series of test points.

The relationship between specific interfacial area and saturation is shown in Figure 3. The predicted curve by Equation 40 agrees well with the experimental points. According to the experimental results, the relationship between imbibition and drainage stage is not unique. It is noted that the maximum difference between imbibition and drainage occurs at $S_r = 0.32$, where the specific interfacial area is 0.20 mm^{-1} at imbibition curve and 0.26 mm^{-1} at drainage curve. Because the difference is insignificant, a unique relationship can be assumed if the test data are insufficient.

The relationship between interfacial area and capillary pressure is shown in Figure 4. As pointed by Culligan,³⁴ the small negative interfacial areas observed at the beginning of primary drainage correspond to full saturation are likely because of numerical errors or misidentification of pixels. The simulated results are all positive and in accordance with practice. Because the simulations are conducted for unsaturated soils, predictions for saturated state where the pressure

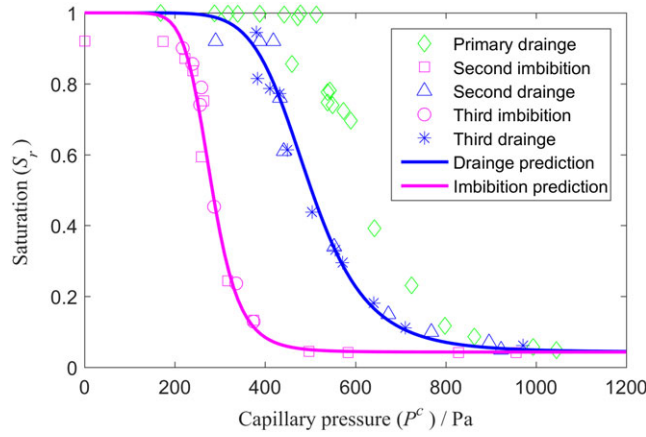


FIGURE 2 Relationship between saturation and capillary pressure [Colour figure can be viewed at wileyonlinelibrary.com]

TABLE 1 Material coefficients used in Figures 2–4

Parameter	S_r^{irr}	α (kPa ⁻¹)	n	b (mm ⁻¹)	c	d
Drainage	0.043	2.06	8.07	0.52	0.49	1.01
Imbibition	0.043	3.63	9.34	0.95	0.65	1.40

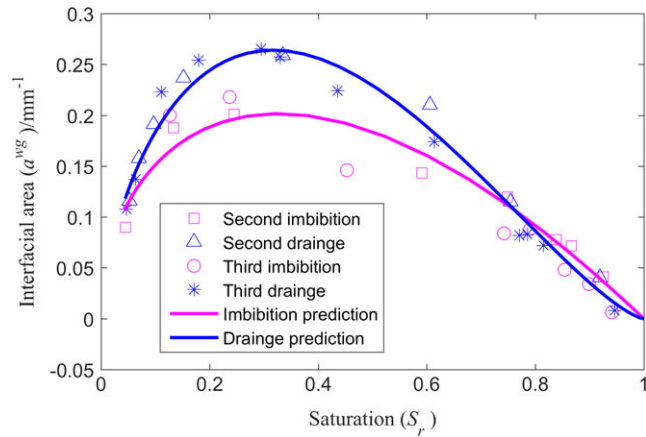


FIGURE 3 Relationship between interfacial area and saturation [Colour figure can be viewed at wileyonlinelibrary.com]

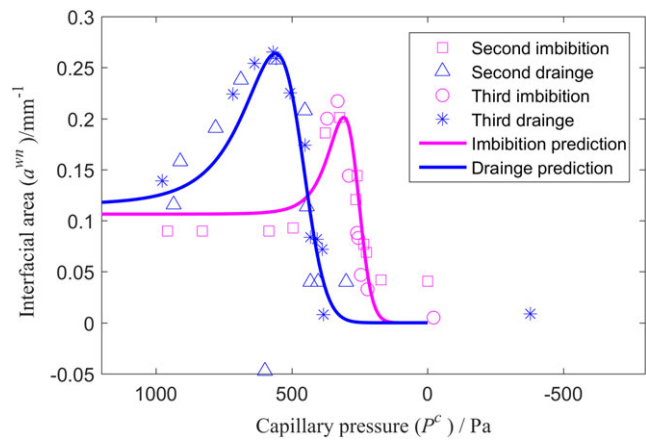


FIGURE 4 Relationship between interfacial area and capillary pressure [Colour figure can be viewed at wileyonlinelibrary.com]

is positive are not depicted in the figure. The simulated results fit the experiment data well. Although the capillary pressure is absent in Equation 40, it has indirect impact on interfacial area by virtue of the SWCC Equation 39.

5.2 | Verification of proposed effective stress equation

The experimental results of Khalili and Zargarbashi⁶² are then used to validate the effective stress given in Equation 33. Two soils are chosen in our simulation: a low plasticity clay from the Bourke region of New South Wales and a mixture of Sydney sand and kaolin. Figure 5 shows the relationship between the effective stress parameter and the saturation, which can be used to predict the material coefficients b , c , and d in Equation 40, of which the values are shown in Table 2. Because the difference between imbibition and drainage is insignificant according to the experimental results, the related parameters for these 2 stages are assumed same in our research. The SWCC parameters α and n given in Table 2 are obtained by fitting drying and wetting data points shown in Figures 6 and 7.

The variations of effective stress parameter with suction for low-plasticity silt and sand-kaolin mixture are shown in Figures 6 and 7, respectively. Predicted curves capture well with the test points. The predictions are consistent with the

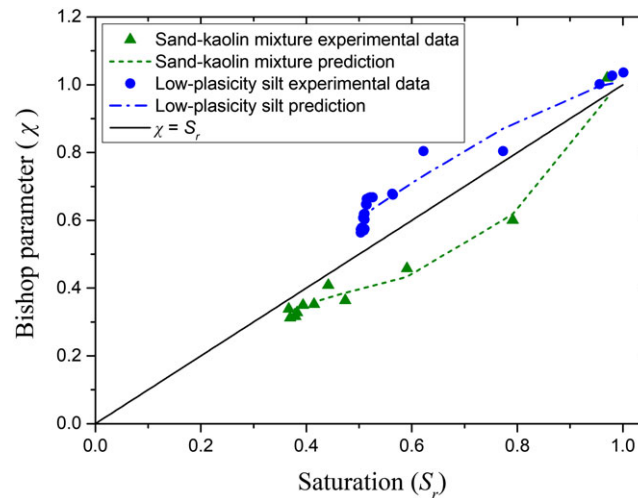


FIGURE 5 Relationship between the effective stress parameter and saturation [Colour figure can be viewed at wileyonlinelibrary.com]

TABLE 2 Material coefficients used in Figures 5–7

Parameter	S_r^{irr}	α (kPa ⁻¹) (dry)	n (dry)	α (kPa ⁻¹) (wet)	n (wet)	b/J	c	d
Low-plasticity silt	0	0.018	1.58	1.51	1.16	-12.79	4.94	2.00
Sand-kaolin mixture	0.4	0.004	3.16	2.23	1.11	0.35	1.03	0.68

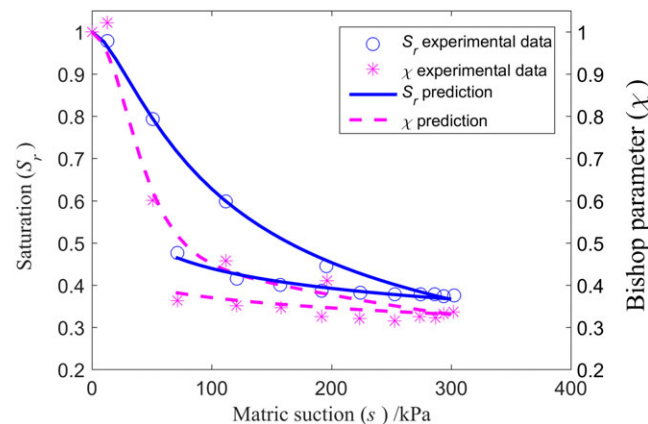


FIGURE 6 Variation of the effective stress parameter and saturation with suction for low-plasticity silt [Colour figure can be viewed at wileyonlinelibrary.com]

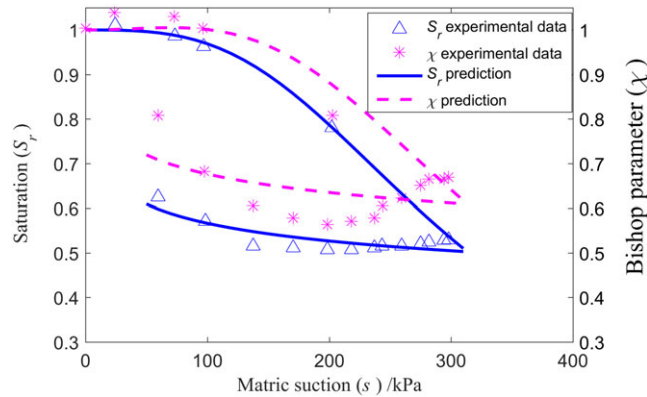


FIGURE 7 Variation of the effective stress parameter and saturation with suction for sand-kaolin mixture [Colour figure can be viewed at wileyonlinelibrary.com]

comparisons given in Figure 5, which indicates that the effective stress parameter is not equal to the degree of saturation. It has to depend on interfacial area as well. The effective stress equation derived from the deformation work here is valid according to the simulation results.

6 | CONCLUSIONS

The choice of stress state variables has always played a central role in the description of unsaturated soil behavior, which should be based on scientific evidence. It is hence better to select the work-conjugate variables contained in the work input equation derived from the thermodynamical energy balance equations. In this paper, the work input for unsaturated soils considering interfacial effects is proposed based on the porous media theory. Accordingly, the conjugate stresses and strain increments compliant with the work input equation can be obtained.

Based on the derived work input equation, the principle of effective stress of unsaturated soils and the constitutive law for liquids are discussed. The effective stress of unsaturated soils, conjugated with the displacement of the soil skeleton, is given in Equation 30. The surface tension is included and assumed to be a function of matric suction. The effective stress can be expressed in Bishop's type. It is shown that the effective stress parameter (Equation 34) is not simply equal to the degree of saturation, but relates to both saturation and the interfacial area.

The constitutive law for liquid phase under dynamic condition is presented based on the work input equation. It is indicated that the matric suction depends on both the history and the rate of change of saturation. Only when a new equilibrium is reached and the saturation does not change can the matric suction be equal to the capillary pressure. At equilibrium, a third variable, interfacial area, is added into the soil water characteristic equation. Traditional SWCC curve is in fact the projection of the p^c - S_r - a^{wsg} surface on the p^c - S_r plane. The interfacial area is very crucial to determine the value of effective stress, which can be calculated from the relationship among interfacial area, saturation, and capillary pressure. Simulation results show that our equations are in good agreement with existing experimental data.

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ORCID

Yan Liu  <http://orcid.org/0000-0001-9909-1763>

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APPENDIX

DERIVATION OF THE WORK INPUT EQUATION

According to Equation 19, the work input in unsaturated soils can be rewritten as follows:

$$W = \sum_{\alpha} \text{tr}(n^{\alpha} \boldsymbol{\sigma}^{\alpha} \cdot \nabla \mathbf{v}^{\alpha}) + \sum_{\alpha\beta} \text{tr}(a^{\alpha\beta} \mathbf{s}^{\alpha\beta} \cdot \nabla \mathbf{v}^{\alpha\beta}) \quad (\text{A1})$$

Substituting Equations 23 and 24 into Equation A1 and making use of the relationship $\text{tr}(\boldsymbol{\delta} \cdot \nabla \mathbf{v}^{fs}) = \nabla \cdot \mathbf{v}^{fs}$, Equation A2 is obtained

$$W = \text{tr}(\boldsymbol{\sigma} \cdot \nabla \mathbf{v}^s) + n^w p^w \nabla \cdot \mathbf{v}^{w,s} + n^g p^g \nabla \cdot \mathbf{v}^{g,s} - \sum_{\alpha\beta} a^{\alpha\beta} \gamma^{\alpha\beta} \nabla \cdot \mathbf{v}^{\alpha\beta,s} \quad (\text{A2})$$

Taking soil skeleton as a reference configuration, the mass balance law Equations 1 and 2 expressed by the volume fraction is

$$n^{\alpha} \nabla \cdot \mathbf{v}^{\alpha,s} = \frac{1}{\rho^{\alpha}} \sum_{\beta \neq \alpha} \widehat{e}_{\alpha\beta}^{\alpha} \frac{d^{\alpha} n^{\alpha}}{dt} - \frac{n^{\alpha} d^{\alpha} \rho^{\alpha}}{\rho^{\alpha} dt} - n^{\alpha} \nabla \cdot \mathbf{v}^s \quad (\text{A3})$$

$$a^{\alpha\beta} \Gamma^{\alpha\beta} \nabla \cdot \mathbf{v}^{\alpha\beta,s} = -\widehat{e}_{\alpha\beta}^{\alpha} - \widehat{e}_{\alpha\beta}^{\beta} + \widehat{e}_{\text{swg}}^{\alpha\beta} - a^{\alpha\beta} \frac{d^{\alpha\beta} \Gamma^{\alpha\beta}}{dt} - \Gamma^{\alpha\beta} \frac{d^{\alpha\beta} a^{\alpha\beta}}{dt} - a^{\alpha\beta} \Gamma^{\alpha\beta} \nabla \cdot \mathbf{v}^s \quad (\text{A4})$$

Substituting Equations A3 and A4 into Equation 25, we get

$$\begin{aligned} W = & \text{tr}(\boldsymbol{\sigma} \cdot \nabla \mathbf{v}^s) + \left(\frac{p^w}{\rho^w} \sum_{\beta \neq \alpha} \widehat{e}_{\alpha\beta}^{\alpha} - p^w \frac{d^w n^w}{dt} - \frac{p^w n^w d^w \rho^w}{\rho^w dt} - n^w p^w \nabla \cdot \mathbf{v}^s \right) \\ & + \left(\frac{p^g}{\rho^g} \sum_{\beta \neq \alpha} \widehat{e}_{\alpha\beta}^{\alpha} - p^g \frac{d^g n^g}{dt} - \frac{p^g n^g d^g \rho^g}{\rho^g dt} - n^g p^g \nabla \cdot \mathbf{v}^s \right) \\ & - \sum_{\alpha\beta} \left(\frac{-\widehat{e}_{\alpha\beta}^{\alpha} - \widehat{e}_{\alpha\beta}^{\beta} + \widehat{e}_{\text{swg}}^{\alpha\beta}}{\Gamma^{\alpha\beta}} - \gamma^{\alpha\beta} \frac{d^{\alpha\beta} \Gamma^{\alpha\beta}}{dt} - \gamma^{\alpha\beta} \frac{d^{\alpha\beta} a^{\alpha\beta}}{dt} - a^{\alpha\beta} \gamma^{\alpha\beta} \nabla \cdot \mathbf{v}^s \right) \end{aligned} \quad (\text{A5})$$

Rearranging Equation A5 yields

$$\begin{aligned} W = & \underbrace{\text{tr}(\boldsymbol{\sigma} \cdot \nabla \mathbf{v}^s)}_I - \underbrace{\left(\frac{p^w n^w d^w \rho^w}{\rho^w dt} + \frac{p^g n^g d^g \rho^g}{\rho^g dt} - \sum_{\alpha\beta} \frac{a^{\alpha\beta} \gamma^{\alpha\beta} d^{\alpha\beta} \Gamma^{\alpha\beta}}{\Gamma^{\alpha\beta} dt} \right)}_{II} \\ & - \underbrace{\left(p^w \frac{d^w n^w}{dt} + p^g \frac{d^g n^g}{dt} - \sum_{\alpha\beta} \gamma^{\alpha\beta} \frac{d^{\alpha\beta} a^{\alpha\beta}}{dt} \right)}_{III} - \underbrace{\left(n^w p_w + n^g p_g - \sum_{\alpha\beta} a^{\alpha\beta} \gamma^{\alpha\beta} \right)}_{IV} \nabla \cdot \mathbf{v}^s \\ & + \underbrace{\left(\frac{p^w}{\rho^w} \sum_{\beta \neq w} \widehat{e}_{w\beta}^w + \frac{p^g}{\rho^g} \sum_{\beta \neq g} \widehat{e}_{g\beta}^g \right)}_V - \sum_{\alpha\beta} \left(\frac{-\widehat{e}_{\alpha\beta}^{\alpha} - \widehat{e}_{\alpha\beta}^{\beta} + \widehat{e}_{\text{swg}}^{\alpha\beta}}{\Gamma^{\alpha\beta}} - \gamma^{\alpha\beta} \right) \end{aligned} \quad (\text{A6})$$

Equation A6 consists of 5 parts: I, II, III, IV, and V. The 5 parts can be simplified and explained below.

The following relationship between volume fraction is used:

$$n^w = nS_r, \quad n^g = (1-n)S_r, \quad n^s = 1-n \quad (\text{A7})$$

Keeping parts I and II constant and substituting Equation A7 into part III yield

$$\begin{aligned} \text{III} &= p^w \frac{d^w n^w}{dt} + p^g \frac{d^g n^g}{dt} - \sum_{\alpha\beta} \gamma^{\alpha\beta} \frac{d^{\alpha\beta} a^{\alpha\beta}}{dt} \\ &= p^w \frac{d^s (nS_r)}{dt} + p^w \nabla n^w \cdot \mathbf{v}^{w,s} + p^g \frac{d^s [n(1-S_r)]}{dt} + p^g \nabla n^g \cdot \mathbf{v}^{g,s} - \sum_{\alpha\beta} \gamma^{\alpha\beta} \frac{d^s a^{\alpha\beta}}{dt} - \sum_{\alpha\beta} \gamma^{\alpha\beta} \nabla a^{\alpha\beta} \cdot \mathbf{v}^{\alpha\beta,s} \\ &= \underbrace{n(p^w - p^g) \frac{d^s S_r}{dt} - \sum_{\alpha\beta} \gamma^{\alpha\beta} \frac{d^s a^{\alpha\beta}}{dt}}_{\text{IIIa}} + \underbrace{[S_r p^w + (1-S_r) p^g] \frac{d^s n}{dt}}_{\text{IIIb}} \\ &\quad + \underbrace{p^w \nabla n^w \cdot \mathbf{v}^{w,s} + p^g \nabla n^g \cdot \mathbf{v}^{g,s} - \sum_{\alpha\beta} \gamma^{\alpha\beta} \nabla a^{\alpha\beta} \cdot \mathbf{v}^{\alpha\beta,s}}_{\text{IIIc}} \end{aligned}$$

Substituting Equations A1 (when $\alpha = s$) and A7 into part IV yields

$$\begin{aligned} \text{IV} &= \left(n^w p^w + n^g p^g - \sum_{\alpha\beta} a^{\alpha\beta} \gamma^{\alpha\beta} \right) \nabla \cdot \mathbf{v}^s = [S_r p^w + (1-S_r) p^g] (1-n^s) \nabla \cdot \mathbf{v}^s - \sum_{\alpha\beta} a^{\alpha\beta} \gamma^{\alpha\beta} \nabla \cdot \mathbf{v}^s \\ &= [S_r p^w + (1-S_r) p^g] \left(\nabla \cdot \mathbf{v}^s + \frac{n^s d^s \rho^s}{\rho^s dt} + \frac{d^s n^s}{dt} \frac{1}{\rho^s} \sum_{\beta \neq s} \hat{e}_{\alpha\beta}^s \right) - \sum_{\alpha\beta} a^{\alpha\beta} \gamma^{\alpha\beta} \nabla \cdot \mathbf{v}^s \\ &= \underbrace{[S_r p^w + (1-S_r) p^g - \sum_{\alpha\beta} a^{\alpha\beta} \gamma^{\alpha\beta}] \nabla \cdot \mathbf{v}^s}_{\text{IVa}} + \underbrace{[S_r p^w + (1-S_r) p^g] \frac{n^s d^s \rho^s}{\rho^s dt}}_{\text{IVb}} \\ &\quad - \underbrace{[S_r p^w + (1-S_r) p^g] \frac{d^s n}{dt}}_{\text{IVc}} - \underbrace{\frac{1}{\rho^s} [S_r p^w + (1-S_r) p^g] \sum_{\beta \neq s} \hat{e}_{\alpha\beta}^s}_{\text{IVd}} \end{aligned}$$

The compressibility of α phase is defined as

$$\beta^\alpha = \frac{1}{\rho^\alpha} \frac{d\rho^\alpha}{dp^\alpha} \quad (\text{A8})$$

Combining part IVa with part I as well as part IVb with part II, canceling part IIIb and part IVc, and substituting Equation A8 into Equation A6 yield

$$\begin{aligned}
W = & \left\{ \underbrace{\text{tr}(\boldsymbol{\sigma} \cdot \nabla \mathbf{v}^s)_I}_{IVa} - \left[S_r p^w + (1-S_r) p^g - \sum_{\alpha\beta} a^{\alpha\beta} \gamma^{\alpha\beta} \right] \nabla \cdot \mathbf{v}^s \right\} - \left\{ \underbrace{n(p^w - p^g) \frac{d^s S_r}{dt} - \sum_{\alpha\beta} \gamma^{\alpha\beta} \frac{d^s a^{\alpha\beta}}{dt}}_{IIIa} \right\} \\
& - \left\{ \underbrace{\left[p^w n^w \beta^w \frac{d^w p^w}{dt} + p^g n^g \beta^g \frac{d^g p^g}{dt} - \sum_{\alpha\beta} \frac{a^{\alpha\beta} \gamma^{\alpha\beta} d^{\alpha\beta} \Gamma^{\alpha\beta}}{\Gamma^{\alpha\beta}} \right]}_{II} + \underbrace{[S_r p^w + (1-S_r) p^g] n^s \beta^s \frac{d^s p^s}{dt}}_{IVb} \right\} \\
& - \left\{ \underbrace{p^w \nabla n^w \cdot \mathbf{v}^{w,s} + p^g \nabla n^g \cdot \mathbf{v}^{g,s} - \sum_{\alpha\beta} \gamma^{\alpha\beta} \nabla a^{\alpha\beta} \cdot \mathbf{v}^{\alpha\beta,s}}_{IIIc} \right\} \\
& + \underbrace{\left[\frac{p^w}{\rho^w} (\hat{e}_{ws}^w + \hat{e}_{wg}^w) + \frac{p^g}{\rho^g} (\hat{e}_{gs}^g + \hat{e}_{gw}^g) \right] - \sum_{\alpha\beta} \left(\frac{-\hat{e}_{\alpha\beta}^{\alpha} - \hat{e}_{\alpha\beta}^{\beta} + \hat{e}_{swg}^{\alpha\beta}}{\Gamma^{\alpha\beta}} \gamma^{\alpha\beta} \right)}_V - \underbrace{\frac{1}{\rho^s} [S_r p^w + (1-S_r) p^g] \sum_{\beta \neq s} \hat{e}_{\alpha\beta}^s}_{IVd}
\end{aligned} \tag{A9}$$

Neglecting mass exchange (ie, $\hat{e}_{\alpha\beta}^{\alpha} = 0$, $\hat{e}_{swg}^{\alpha\beta} = 0$) and the compressibility of solid, liquid, and interfaces, Equation A9 can be simplified as

$$\begin{aligned}
W = & \left\{ \left[\boldsymbol{\sigma} - \left(S_r p^w + (1-S_r) p^g - \sum_{\alpha\beta} a^{\alpha\beta} \gamma^{\alpha\beta} \right) \boldsymbol{\delta} \right] : \mathbf{d}^s \right\} \\
& + \left\{ n(p^g - p^w) \frac{d^s S_r}{dt} + \sum_{\alpha\beta} \gamma^{\alpha\beta} \frac{d^s a^{\alpha\beta}}{dt} \right\} - \left\{ p^g n^g \beta^g \frac{d^g p^g}{dt} \right\} \\
& - \left(p^w \nabla n^w \cdot \mathbf{v}^{w,s} + p^g \nabla n^g \cdot \mathbf{v}^{g,s} - \sum_{\alpha\beta} \gamma^{\alpha\beta} \nabla a^{\alpha\beta} \cdot \mathbf{v}^{\alpha\beta,s} \right)
\end{aligned} \tag{A10}$$