

A nonlinear multi-field coupled model for soils

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A nonlinear multi-field coupled model for multi-constituent three-phase soils is derived by using the hybrid mixture theory. The balance equations with three levels (constituents, phases and the whole mixture soil) are set up under the assumption that soil is composed of multi-constituent elastic-plastic solid skeleton (which is different from the linearization method) and viscous liquid and ideal gas. With reasonable constitutive assumptions in such restrictive conditions as the principles of determinism, equipresence, material frame-indifference and the compatible principle in continuum mechanics, a theoretical framework of constitutive relations modeling three-phase soil in both non-equilibrium and equilibrium states is established, thus the closed field equations are formed. In the theoretical framework, the concept of effective generalized thermodynamic forces is introduced, and the nonlinear coupling constitutive relations between generalized dissipation forces and generalized flows within the system at nonequilibrium state are also presented. On such a basis, four special coupling relations, i.e., solid thermal elastic-plastic constitutive relation, liquid visco-elastic-plastic constitutive relation, the generalized Fourier's law, and the generalized Darcy's law are put forward. The generalized or nonlinear results mentioned above can degenerate into the linear coupling results given by Bennethum and Singh. Based on a specific dissipation function, the concrete form of generalized Darcy's law is deduced, which may degenerate into the traditional form of Darcy's law by neglecting the influence of skeleton deformation and temperature. Without considering temperature and other coupling effects, the nonlinear coupled model in this paper can degenerate into a soil elastic-plastic constitutive model.

multi-field coupled model for soils, hybrid mixture theory, non-linear, multi-constituent

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1 Introduction

Soil behaviors, e.g., the deformation of soil skeleton, pore-water seepage, advection and diffusion of pollutants in soil pores, pore-water phase change, etc., are normally controlled by its multi-fields including the stress, seepage, temperature and chemical fields. These behaviors under multi-field differ significantly from those under a single field. The study of soil behaviors under multi-fields is of great demand in many applications, e.g., civil engineering construction, geo-disaster prevention, diffusion and migration of pollutants, and high-efficient exploitation of new

energies (coal-bed methane, natural gas hydrate, etc.). After several decades' research on multi-field coupling theory, great achievements have been made. Most of them are based on intuition, experience, or macroscopic recognition, and are lack of a united and consistent scientific theoretical basis. These empirical theories normally have their own limitations and often fail to describe the behaviors of soils under multi-field coupling conditions strictly and effectively. Therefore, the solutions cannot meet the needs of engineering practice.

Currently, soil mechanics is still in a semi-theoretical and semi-empirical stage. Specifically, theories of seepage and deformation are established according to different assumptions and lack of a unified theoretical basis between the two parts. Empirical formula and methods can be seen every-

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where in soil mechanics. Experience and engineering judgments are still playing important roles [1]. The developments of modern soil mechanics, particularly the critical state soil mechanics, have established the relation between soil deformation and shear strength, and improved the theoretical basis of soil mechanics. However, these developments still have not fundamentally changed the situation mentioned above. Unified and consistent theory of soil mechanics is still desired, in which multi-fields should basically be coupled.

After long-term weathering, rocks on the earth surface break into small particles and transform into soils. Soils are a loose assemblage of such mineral particles with weak connections, hence include soil skeleton formed by the solid particles and voids filled with liquid or gas. Usually, the motions of soil skeleton, pore-liquid and pore-gas are different and there are interactions among them. Because it is too difficult to obtain the specific geometry and shape variation of each pore, we cannot obtain certain description of the motions at each space point for pore-fluids and soil skeleton. In order to overcome the above difficulties, it is necessary to turn to the solution in macro level, which is a rougher and average level. For example, soils are often regarded as continuous homogenous materials in the macro level. That's to say, a macroscopic homogeneous continuum is used to substitute the soil, which is in fact a microscopically heterogeneous porous media. This approach requires that the two kinds of media should have the same macroscopic behaviors. After such treatment, only the macroscopic properties of soils are required, which do not depend on the micro-structure of pores and can be obtained or verified by macro experiments. Therefore, continuum mechanics can be applied to soils. By following this route, the mixture theory [2–5] is established to describe the behavior of the porous media, i.e., soils, on a macroscopic level, as well as the later developed hybrid mixture theory [6–9].

Since 1960, the mixture theory has achieved great development [2–5]. The mixture theory is used to describe the complex interactions between different phases in porous media and their responses to external stress or chemical actions. The mixture theory can be applied to soils, which are typical porous media, and seems to be able to unify the theoretical basis of soil mechanics. Comparing to rock and concrete, soils are of weak connections between the solid phase, i.e., the particles. The liquid phase, i.e., pore-water, and the air phase, i.e., pore-air, have strong effect on the soil deformation and shearing behaviors. Hence, much attention should be paid to the pore-water pressure and the pore-air pressure in soils.

The mixture theory was originally proposed to analyze the multi-constituent gas mixtures [2]. Bowen (1980, 1982)[3, 4] extended the mixture theory to multi-phase porous media and used the volume fractions of different phases as internal variables. Then, equations were established by considering the followed principles: 1) the momentum con-

versation, 2) the energy conversation, 3) the mass conversation, and 4) the principle of entropy increase. After incorporating some constitutive assumptions, constitutive equations can be derived finally. de Boer [5] and his research team set up the mixture theory considering variable volume fraction, and later named it as porous media theory. Morland [10], Goodman and Cowin [11], Bowen [3, 4], Passman [12], Hutter [13, 14], de Boer, et al. [5] were dedicated to the theoretical research on multi-phase porous media using mixture theory. Hassanizadeh and Gray [6–8] established an averaging method in the mixture theory, which led to equivalent equations derived by Bowen (1980, 1982). The mixture theory involving the averaging method was called the hybrid mixture theory (HMT) and further advanced by Achanta and Cushman[9], Hassanizadeh and Gray [15, 16], Bennethum and Cushman, et al. [17, 18]. We believe that the hybrid mixture theory can provide a more reasonable description of soil microstructure and better links between soil micro and macro behaviors. In addition, the hybrid mixture theory can result in the same equations as those obtained using the mixture theory under proper assumptions.

In this paper, the hybrid mixture theory is used to build a unified, theoretical, and thermodynamics-based theory for soils. Further, the continuum porous medium soil mechanics proposed in ref. [1] is used to establish a nonlinear multi-field coupling framework for soils.

Based on the hybrid mixture theory, porous media including unsaturated soils exhibit a hierarchy of scales and there are often distinct separations between different scales. Figure 1 illustrates a three-scale (micro-scale, meso-scale, and macro-scale) system of unsaturated soils [17, 18]. At present, it is believed that only the meso and macro scales have direct influence on the macroscopic properties of soil. According to the volume averaging theory [6–8], porous media contains a number of phases and each phase contains a number of constituents. First, the balance equations and variables for each constituent can be derived on the micro-scale. Second, the balance equations for each phase are established by using the classical continuum mechanics on the meso-scale. Third, the balance equations and macro varia-

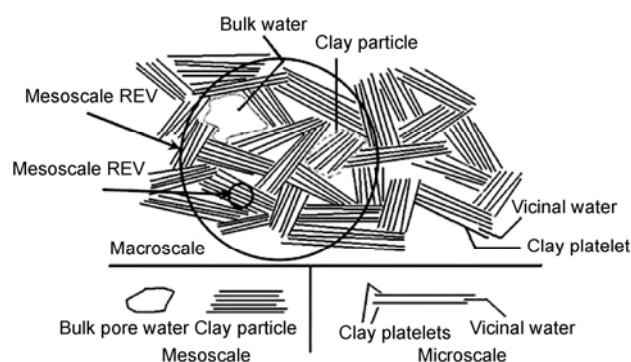


Figure 1 Three scales of unsaturated soils^[17].

bles for the mixture can be derived by volume averaging and the consideration of interactions between different phases.

According to the continuum mechanics, soils are regarded as continuum porous media under multi-field, including the stress, seepage, temperature, and chemical field. Differential equations on a local element are constructed to describe the macro behavior of a continuum medium under multi-fields. Hence, the following assumptions are implied.

1) Representative element volume (REV) should be large enough in the micro-scale. On the micro-scale, the local element analyzed should contain enough solid particles and voids, so that it can be averaged statistically and has meaningful parameters and thermodynamics properties.

2) REV should be small enough in the macro-scale that the local element analyzed can be treated as a point in the macro space. Then, averaged properties can be assigned to the local element and will not induce unacceptable error after integration.

3) Characteristic scale of REV should not change with time and space. Even if there are slight changes of the characteristic scale, the averaged material properties and parameters should still be constant rather than changing with their characteristic scales.

Therefore, under the frame of volume averaging theory, the multi-phase porous media can be defined as:

1) The mixture is composed of α phases and each phase contains the same set of j constituents. If a constituent does not exist in a specific phase, the concentration of the constituent in the phase will be set as zero.

2) The porous media is continuous and the $\alpha \times j$ constituents are overlapping and coexisting at every element in the space. Averaging thermodynamic and mechanical properties on meso-scale can be assigned to each element.

3) The macro parameters of the mixture can be related to and be expressed by the properties on meso-scale.

Pore fluid is usually multi-constituent in many practical engineering, particularly in the pollutants transport system, so it is very important to establish a mixture theory for multi-constituent and multi-phase porous media. Hutter et al. [13, 14] studied multi-field coupling theory of porous media using the classical mixture theory. Bennethum [19] illustrated the use of rational thermodynamics to develop the mathematical multi-field model for multi-constituent swelling porous media. Huang and Zhao [20] established the mixture theory for multi-constituent micropolar porous media by combining the hybrid mixture theory with micropolar continuum theory. However, linearization methods were used to describe the behaviours of the mixtures, and the solid phase was assumed to be elastic (such as a series of works by Bennethum) in all previous works, while the elastic-plastic deformation and the corresponding energy dissipation that is more important for soils were not considered. In addition, the theoretical interpretation of coupling phenomena were also not complete, and the unsaturated

state of soil were seldom considered in these studies.

In this paper, we assume that soil is composed of elastic-plastic solid, viscous liquid and ideal gas. The elastic-plastic constitutive modeling framework for multi-constituent unsaturated soils is established based on the hybrid mixture theory; considering the coupling effects among deformation, seepage, and heat conduction, etc., a nonlinear multi-field coupled model for describing coupling behaviors of multi-constituent and multi-phase porous media is established. Using the averaging theory, the macroscopic balance equations and the entropy inequality equations for each phase and the whole soil are derived. And the constitutive relations in non-equilibrium state are given by Lagrange multiplier method to further process the entropy inequality. Then based on the balance constraints, the constitutive relations at equilibrium are presented. Finally, by dealing with the dissipative parts of entropy inequality based on near-equilibrium thermodynamics, the coupling relations among elastic-plastic deformation, seepage, heat conduction, chemical reaction, diffusion of chemicals and pollutants, etc. are set up, then the theoretical framework of multi-field coupling for unsaturated soils is established. Four special coupling results, that is, solid thermal elastic-plastic constitutive relation, liquid viscous elastic-plastic constitutive relation, generalized Fourier's law and generalized Darcy's law, are also given. Furthermore, the specific form of the generalized Darcy's law is deduced based on the given dissipative function. In addition, it is shown that the non-linear model proposed in this paper could degenerate into soil elastic-plastic constitutive model without considering temperature or other coupling effects.

When analyzing multi-field coupling problems for soils using hybrid mixture theory, the following three aspects need to be considered .

1) Selection of independent state variables. The choice of independent state variables depends on the nature and characteristics of the problems involved, the existing knowledge (including theoretical knowledge and experimental results, etc.), researchers' experience, and so on.

2) Establish all kinds of equations at equilibrium and the corresponding restrictions and constraints with Coleman and Noll(1963)[21]'s method. Note that the balance equations used to solve multi-field coupling problems are universal, which can be used for any substance and problem. So the specialty of coupling phenomena is usually reflected in the corresponding constitutive relations, meanwhile, the established restrictions and constraints directly give the definitions of certain variables and phenomena.

3) Constitutive equations for multi-field coupling problems can be set up based on the specific dissipative functions and the second law of thermodynamics. The selection for dissipative function depends on researchers' experience, theoretical knowledge and test results.

The aspects mentioned above will be discussed in the following relevant parts respectively.

2 Balance equations

2.1 Basic assumptions

For simplicity, the main assumptions for soil are as follows:

1) The soil is composed of the superposition of solid skeleton *s*, liquid *l* and gas *g*.

2) The solid, water and air phases have the same but not constant temperature at the same point (the process is non-isothermal), that is, $T = T_s = T_l = T_g$.

3) Phases are immiscible with each other except steam and gas. Dry air and steam are treated as gas, and the dissolution of gas in liquid is ignored.

4) Materials of phases are non-polar, thus conservation of momentum moment for each phase means that the Cauchy stress tensor of the phase is symmetric.

5) The thermodynamic properties of materials at the interface are ignored.

2.2 Balance equations, entropy inequality and restriction equations

The volume fraction is introduced to describe the internal microstructure of porous media according to the averaging theory. n_s , n_l and n_g are the volume fraction of solid, liquid and gas, respectively; in the equation $n_s = 1 - n$, where n is the porosity of porous media; $n_l = nS_w$, where S_w is the degree of saturation for liquid phase; $n_g = n(1 - S_w)$; $n = n_l + n_g$. Bennethum [19] derived the macroscopic balance equations for two-phase (solid and liquid phases) swelling porous media using the averaging theory. Now we extend it into three-phase (solid, liquid and gas phases) porous media.

(I) Mass conservation

The mass conservation equation of constituent *j* in phase α can be expressed as

$$\frac{D_\alpha^j(n_\alpha \rho_\alpha^j)}{Dt} + n_\alpha \rho_\alpha^j \nabla \cdot \mathbf{v}_\alpha^j = \hat{e}_\alpha^j, \quad (1)$$

$$\alpha = s, l, g, \quad j = 1, 2, \dots, N,$$

where D_α^j/Dt denotes material time derivative following the *j*-th constituent in the α -phase, i.e., $D_\alpha^j(\bullet)/Dt = \partial(\bullet)/\partial t + \mathbf{v}_\alpha^j \cdot \nabla(\bullet) = D_\alpha(\bullet)/Dt + \mathbf{u}_\alpha^j \cdot \nabla(\bullet)$, \mathbf{v}_α^j is the mass averaged velocity of *j*-th constituent in phase α , \mathbf{u}_α^j is the diffusive velocity, $\mathbf{u}_\alpha^j = \mathbf{v}_\alpha^j - \mathbf{v}_\alpha$, \mathbf{v}_α is the velocity of phase α ; ρ_α^j is the averaged mass density of *j*-th constituent in α phase; \hat{e}_α^j is the rate of mass exchange between constituent *j* inside phase α and other constituents outside phase α , where the mass exchange between constitute *j* and other constituents inside phase α is ignored, that is to say, the role of reactive chemical field is not taken into account.

In order to get higher-level macroscopic equations by

constituent conservation equation, Olivella et al. [22, 23] adopted the compositional approach, which used the total balance equation with the same species in different phases superimposed instead of the balance equation with different constituents in the same phase superimposed, so as to establish field equations. The advantage of the approach is that there is no interaction among each phase, which is especially effective in establishing momentum balance equations. The total mixture equation can be derived from the superposition of each total species equation. But, starting with constituent balance equations, we will establish balance equations for each phase and the whole soil in this paper, which will have more general significance and the result is the same as that of Olivella et al. [22, 23].

Summing over all constituents and according to the relations between microscopic and macroscopic quantities, we obtain the mass conservation equation for phase α :

$$\frac{D_\alpha(n_\alpha \rho_\alpha)}{Dt} + n_\alpha \rho_\alpha \nabla \cdot \mathbf{v}_\alpha = \hat{e}_\alpha, \quad \alpha = s, l, g, \quad (2)$$

where $D_\alpha(\bullet)/Dt = \partial(\bullet)/\partial t + \mathbf{v}_\alpha \cdot \nabla(\bullet)$. Taking soil skeleton as the reference system, then the mass average velocity $\mathbf{v}_{\beta,s}$ of fluid phase β (*l*, *g*) relative to solid skeleton *s* is $\mathbf{v}_{\beta,s} = \mathbf{v}_\beta - \mathbf{v}_s$, thus $D_\beta(\bullet)/Dt = D_s(\bullet)/Dt + \mathbf{v}_{\beta,s} \cdot \nabla(\bullet)$; ρ_α is the average mass density of phase α ; \hat{e}_α is the mass exchange rate between phase α and other phases.

In order to get the mass conservation equation of constituent *j*, which is expressed by mass concentration C_α^j (defined as $C_\alpha^j = \rho_\alpha^j / \rho_\alpha$) and diffusion velocity \mathbf{u}_α^j , we subtract C_α^j eq. (2) from eq. (1):

$$n_\alpha \rho_\alpha \frac{D_\alpha C_\alpha^j}{Dt} + \nabla \cdot (n_\alpha \rho_\alpha^j \mathbf{u}_\alpha^j) = \hat{e}_\alpha^j - C_\alpha^j \hat{e}_\alpha, \quad (3)$$

$$\alpha = s, l, g, \quad j = 1, 2, \dots, N.$$

By summing over all phases, the mass conservation equation for the total soil mixture can be derived as follows:

$$\frac{D\rho}{Dt} + \rho \nabla \cdot \mathbf{v} = 0, \quad (4)$$

where ρ is the total mass density of soil; \mathbf{v} is the velocity of soil.

(II) Momentum conservation

The momentum conservation equation for constituent *j* in phase α can be expressed as

$$n_\alpha \rho_\alpha^j \frac{D_\alpha^j \mathbf{v}_\alpha^j}{Dt} - \nabla \cdot (n_\alpha \mathbf{t}_\alpha^j) - n_\alpha \rho_\alpha^j \mathbf{g}_\alpha^j = \hat{\mathbf{T}}_\alpha^j + \hat{\mathbf{i}}_\alpha^j, \quad (5)$$

$$\alpha = s, l, g, \quad j = 1, 2, \dots, N,$$

where \mathbf{t}_α^j is the stress tensor of constituent *j* in phase α ;

\mathbf{g}_α^j is the volume force density of constituent j ; $\hat{\mathbf{T}}_\alpha^j$ is the momentum gained by constituent j in the process of interaction between phase α and other phases; $\hat{\mathbf{i}}_\alpha^j$ is the momentum obtained by constituent j in the process of interaction between constituent j and other constituents.

The momentum conservation equation of phase α can be derived by summing over all constituents:

$$n_\alpha \rho_\alpha \frac{D_\alpha \mathbf{v}_\alpha}{Dt} - \nabla \cdot (n_\alpha \mathbf{t}_\alpha) - n_\alpha \rho_\alpha \mathbf{g}_\alpha = \hat{\mathbf{T}}_\alpha, \quad \alpha = s, l, g, \quad (6)$$

where \mathbf{t}_α is the stress tensor of phase α ; \mathbf{g}_α is the volume force density of phase α ; $\hat{\mathbf{T}}_\alpha$ is the momentum exchange rate between phase α and other phases.

Summing over all phases, the momentum conservation equation for the total soil mixture can be derived as follows

$$\rho \frac{D\mathbf{v}}{Dt} - \nabla \cdot \mathbf{t} - \rho \mathbf{g} = 0, \quad (7)$$

where \mathbf{t} and \mathbf{g} are the stress tensor and volume force density of the total soil mixture, respectively. Generally, \mathbf{g} is the acceleration of gravity.

(III) Energy conservation

The energy conservation equation for constituent j in phase α can be expressed as

$$n_\alpha \rho_\alpha^j \frac{D_\alpha^j E_\alpha^j}{Dt} - n_\alpha \mathbf{t}_\alpha^j : \mathbf{d}_\alpha^j - \nabla \cdot (n_\alpha \mathbf{q}_\alpha^j) - n_\alpha \rho_\alpha^j h_\alpha^j = \hat{Q}_\alpha^j + \hat{E}_\alpha^j, \quad \alpha = s, l, g, j = 1, 2, \dots, N, \quad (8)$$

where E_α^j is the internal energy density of constituent j in phase α ; \mathbf{d}_α^j is the symmetric part of $\nabla \mathbf{v}_\alpha^j$, which is called Euler deformation rate tensor and controls the extension; \mathbf{q}_α^j is the heat flux of constituent j in phase α ; h_α^j is the external heating supply density (generally induced by radiation); \hat{Q}_α^j is the energy exchange between constituent j inside phase α and other phases (due to nonmass transfer interactions); and \hat{E}_α^j is the energy exchange between constituent j and other constituents inside phase α (due to non-chemical or non-mechanical interactions).

The energy conservation equation of phase α is given by

$$n_\alpha \rho_\alpha \frac{D_\alpha E_\alpha}{Dt} - n_\alpha \mathbf{t}_\alpha : \mathbf{d}_\alpha - \nabla \cdot (n_\alpha \mathbf{q}_\alpha) - n_\alpha \rho_\alpha h_\alpha = \hat{Q}_\alpha, \quad \alpha = s, l, g, \quad (9)$$

where E_α , \mathbf{d}_α , \mathbf{q}_α and h_α are the internal energy density, deformation rate tensor, heat flux vector and external heating supply density of phase α , respectively; \hat{Q}_α is the energy

exchange between phase α and other phases.

By summing all constituents, the energy conservation equation for the total soil mixture can be derived as follows:

$$\rho \frac{DE}{Dt} - \mathbf{t} : \mathbf{d} - \nabla \cdot \mathbf{q} - \rho h = 0, \quad (10)$$

where E , \mathbf{d} , \mathbf{q} and h are the internal energy density, deformation rate tensor, heat flux vector and external heating supply density of the total soil mixture, respectively.

(IV) Entropy inequality

According to the second law of thermodynamics, the total entropy generation of the system must be greater than or equal to zero, that is,

$$A = \sum_{\alpha=s,l,g} \sum_{j=1}^N \left[n_\alpha \rho_\alpha^j \frac{D_\alpha^j \eta_\alpha^j}{Dt} - \nabla \cdot \left(\frac{n_\alpha \mathbf{q}_\alpha^j}{T} \right) - n_\alpha \rho_\alpha^j \zeta_\alpha^j - \hat{\omega}_\alpha^j - \hat{\eta}_\alpha^j \right] \geq 0, \quad (11)$$

where η_α^j is the entropy density of constituent j in phase α ; T is absolute temperature; ζ_α^j is external entropy supply density; $\hat{\omega}_\alpha^j$ is entropy exchange between constituent j inside phase α and other phases (due to nonmass transfer interactions); and $\hat{\eta}_\alpha^j$ is entropy exchange between constituent j and other constituents inside phase α (due to nonmass transfer interactions).

(V) Relations and constraints between phases and constituents

The relations between physical quantities of phases and those of the corresponding constituents are as follows:

$$\rho_\alpha = \sum_{j=1}^N \rho_\alpha^j, \hat{e}_\alpha = \sum_{j=1}^N \hat{e}_\alpha^j, \quad (12)$$

$$\mathbf{t}_\alpha = \sum_{j=1}^N (\mathbf{t}_\alpha^j - \rho_\alpha^j \mathbf{u}_\alpha^j \otimes \mathbf{u}_\alpha^j), \mathbf{g}_\alpha = \sum_{j=1}^N C_\alpha^j \mathbf{g}_\alpha^j, \quad \hat{\mathbf{T}}_\alpha = \sum_{j=1}^N (\hat{\mathbf{T}}_\alpha^j + \hat{e}_\alpha^j \mathbf{u}_\alpha^j), \quad (13)$$

$$\mathbf{v}_\alpha = \sum_{j=1}^N C_\alpha^j \mathbf{v}_\alpha^j, \eta_\alpha = \sum_{j=1}^N C_\alpha^j \eta_\alpha^j, A_\alpha = \sum_{j=1}^N C_\alpha^j A_\alpha^j, \quad (14)$$

$$E_\alpha = \sum_{j=1}^N C_\alpha^j \left(E_\alpha^j + \frac{1}{2} \mathbf{u}_\alpha^j \cdot \mathbf{u}_\alpha^j \right), \quad h_\alpha = \sum_{j=1}^N C_\alpha^j (h_\alpha^j + \mathbf{g}_\alpha^j \cdot \mathbf{u}_\alpha^j), \quad (15)$$

$$\mathbf{q}_\alpha = \sum_{j=1}^N \left[\mathbf{q}_\alpha^j + \mathbf{t}_\alpha^j \cdot \mathbf{u}_\alpha^j - \rho_\alpha^j \left(E_\alpha^j + \frac{1}{2} \mathbf{u}_\alpha^j \cdot \mathbf{u}_\alpha^j \right) \mathbf{u}_\alpha^j \right]. \quad (16)$$

The following constraints are also satisfied:

$$\sum_{\alpha=s,l,g} n_\alpha = 1, \sum_{j=1}^N C_\alpha^j = 1, \sum_{j=1}^N \rho_\alpha^j \mathbf{u}_\alpha^j = 0, \quad (17)$$

$$\sum_{\alpha=s,l,g} \hat{e}_\alpha = 0, \quad \sum_{\alpha=s,l,g} \hat{e}_\alpha^j = 0, \quad (18)$$

$$\sum_{j=1}^N \hat{i}_\alpha^j = 0, \quad \sum_{j=1}^N \hat{\eta}_\alpha^j = 0, \quad \sum_{j=1}^N (\hat{E}_\alpha^j + \hat{t}_\alpha^j \cdot \mathbf{u}_\alpha^j) = 0, \quad (19)$$

$$\sum_{\alpha=s,l,g} \left[\hat{Q}_\alpha^j + \hat{\mathbf{T}}_\alpha^j \cdot \mathbf{v}_\alpha^j + \hat{e}_\alpha^j \left(E_\alpha^j + \frac{1}{2} \mathbf{v}_\alpha^j \cdot \mathbf{v}_\alpha^j \right) \right] = 0, \quad (20)$$

$$\sum_{\alpha=s,l,g} (\hat{\mathbf{T}}_\alpha^j + \hat{e}_\alpha^j \mathbf{v}_\alpha^j) = 0, \quad \sum_{\alpha=s,l,g} (\hat{\omega}_\alpha^j + \hat{e}_\alpha^j \eta_\alpha^j) = 0, \quad (21)$$

$j = 1, 2, \dots, N.$

(VI) Relations and constraints between the entire mixture and phases

The relations between physical quantities of the whole soil mixture and those of the corresponding phases are as follows:

$$\rho = \sum_{\alpha=s,l,g} n_\alpha \rho_\alpha, \quad \mathbf{v} = \sum_{\alpha=s,l,g} \frac{\rho_\alpha}{\rho} \mathbf{v}_\alpha, \quad (22)$$

$$\mathbf{t} = \sum_{\alpha=s,l,g} (n_\alpha \mathbf{t}_\alpha - \rho_\alpha \mathbf{u}_\alpha \otimes \mathbf{u}_\alpha), \quad \mathbf{g} = \sum_{\alpha=s,l,g} n_\alpha \mathbf{g}_\alpha, \quad (23)$$

$$\mathbf{q} = \sum_{\alpha=s,l,g} \left[\mathbf{q}_\alpha + \mathbf{t}_\alpha \cdot \mathbf{u}_\alpha - \rho_\alpha \left(E_\alpha + \frac{1}{2} \mathbf{u}_\alpha \cdot \mathbf{u}_\alpha \right) \mathbf{u}_\alpha \right],$$

$$h = \sum_{\alpha=s,l,g} n_\alpha (h_\alpha + \mathbf{g}_\alpha \cdot \mathbf{u}_\alpha), \quad (24)$$

where \mathbf{u}_α is the relative velocity of each phase relative to the entire soil mixture, $\mathbf{u}_\alpha = \mathbf{v}_\alpha - \mathbf{v}$. If soil skeleton is taken as a reference system, then the relative velocity of solid phase is zero, and the relative velocity of fluid phase is $\mathbf{v}_{\beta,s}$.

Different from the static equilibrium case in which seepage and diffusion are not taken into account, the stress \mathbf{t} and heat flux vector \mathbf{q} here are subject to the relative velocity \mathbf{u}_α of each phase relative to the whole solid mixture; see eqs. (23) and (24).

Meanwhile, eqs. (2), (3), (6) and (9) should satisfy the following constraints:

$$\sum \hat{e}_\alpha = 0, \quad \sum \hat{\mathbf{T}}_\alpha = 0, \quad \sum \hat{Q}_\alpha = 0. \quad (25)$$

(VII) Further processing of entropy inequality
Define Helmholtz' free energy function as

$$A = E - T\eta. \quad (26)$$

After substitute eqs. (9) and (26) into eq. (11) and simplification, it follows that

$$A = \sum_{\alpha=s,l,g} \sum_{j=1}^N \left[-\frac{n_\alpha \rho_\alpha^j}{T} \left(\frac{D_\alpha^j A_\alpha^j}{Dt} + \eta_\alpha^j \frac{D_\alpha^j T}{Dt} \right) + \frac{n_\alpha}{T} \mathbf{t}_\alpha^j : \mathbf{d}_\alpha^j \right. \\ \left. + \frac{n_\alpha}{T^2} \mathbf{q}_\alpha^j \cdot \nabla T + \frac{n_\alpha}{T} \rho_\alpha^j h_\alpha^j - n_\alpha \rho_\alpha^j \zeta_\alpha^j \right]$$

$$+ \frac{1}{T} \left(\hat{Q}_\alpha^j + \hat{E}_\alpha^j \right) - \hat{\omega}_\alpha^j - \hat{\eta}_\alpha^j \geq 0. \quad (27)$$

Replace the absolute velocity by diffusion velocity \mathbf{u}_α^j and seepage velocity $\mathbf{v}_{\beta,s}$ which are more important in soil mechanics; the above entropy inequality which is expressed by constituent properties is expressed in terms of phase properties using eqs. (12)–(21) as

$$T\Lambda = \sum_{\alpha=s,l,g} -n_\alpha \rho_\alpha \left(\frac{D_\alpha A_\alpha}{Dt} + \eta_\alpha \frac{D_\alpha T}{Dt} \right) \\ + \sum_{\alpha=s,l,g} n_\alpha \mathbf{d}_\alpha : \left(\mathbf{t}_\alpha + \sum_{j=1}^N \rho_\alpha^j \mathbf{u}_\alpha^j \otimes \mathbf{u}_\alpha^j \right) \\ + \sum_{\alpha=s,l,g} \sum_{j=1}^N n_\alpha (\nabla \mathbf{u}_\alpha^j) : \left(\mathbf{t}_\alpha^j - \rho_\alpha^j A_\alpha^j \mathbf{I} \right) \\ - \sum_{\alpha=s,l,g} \sum_{j=1}^N \mathbf{u}_\alpha^j \cdot \left[\nabla (n_\alpha \rho_\alpha^j A_\alpha^j) + \hat{\mathbf{T}}_\alpha^j + \hat{i}_\alpha^j \right] \\ + \sum_{\alpha=s,l,g} \frac{n_\alpha}{T} \nabla T \cdot \left\{ \mathbf{q}_\alpha + \sum_{j=1}^N \left[\rho_\alpha^j \mathbf{u}_\alpha^j \left(A_\alpha^j + \frac{1}{2} \mathbf{u}_\alpha^j \cdot \mathbf{u}_\alpha^j \right) - \mathbf{t}_\alpha^j \cdot \mathbf{u}_\alpha^j \right] \right\} \\ - \mathbf{v}_{\beta,s} \cdot \hat{\mathbf{T}}_\beta - \hat{e}_\beta \left(A_\beta - A_s + \frac{1}{2} \mathbf{v}_{\beta,s} \cdot \mathbf{v}_{\beta,s} \right) \\ - \sum_{j=1}^N \hat{e}_\beta^j \left(\frac{1}{2} \mathbf{u}_\beta^j \cdot \mathbf{u}_\beta^j - \frac{1}{2} \mathbf{u}_s^j \cdot \mathbf{u}_s^j \right) \\ + \sum_{\alpha=s,l,g} n_\alpha \rho_\alpha h - \sum_{\alpha=s,l,g} n_\alpha \rho_\alpha T \zeta \geq 0. \quad (28)$$

3 Constitutive relations

3.1 Constitutive assumptions

In the above-mentioned balance equations and entropy inequalities, there are $47N+3$ unknown variables:

$$n_\beta \text{-(2)}; \quad T \text{-(1)}; \quad \rho_\alpha \text{-(3)}; \quad C_\alpha^j \text{-(3(N-1))}; \\ \mathbf{v}_\alpha \text{-(3}\times\text{2)}; \quad \mathbf{v}_\alpha^j \text{-(3}\times\text{3(N-1))}, \quad (29)$$

$$A_\alpha \text{-(3)}; \quad A_\alpha^j \text{-(3(N-1))}; \quad \eta_\alpha \text{-(3)}; \quad \eta_\alpha^j \text{-(3N)}; \\ \mathbf{t}_\alpha \text{-(3}\times\text{6)}; \quad \mathbf{t}_\alpha^j \text{-(3(N-1)}\times\text{6)}; \\ \hat{\mathbf{T}}_\alpha \text{-(3}\times\text{2)}; \quad \hat{\mathbf{T}}_\alpha^j \text{-(3(N-1)}\times\text{2)}; \\ \hat{e}_\alpha \text{-(2)}; \quad \hat{e}_\alpha^j \text{-(2(N-1))}; \quad \mathbf{q}_\alpha \text{-(3)}; \quad \mathbf{q}_\alpha^j \text{-(3(N-1))}; \\ \alpha = s, l, g, \quad j = 1, 2, \dots, N-1, \quad (30)$$

where group (29) is constitutive independent variables, and group (30) are constitutive dependent variables. Since only $N-1$ constituents are considered, the above variables are indeed independent where constituent N is non-independent, subject to constraints. Other unknowns can be derived from the kinematic relations, self-definition or constraints among

exchange terms. There are 12N+1 conservation equations for the existing constituents and phases, and 35N+2 equations are absent.

Therefore, general balance equations of previous section must be supplemented with constitutive relations which account for material properties under consideration, and also remove the deficient in the number of equations. Compared with the classical single phase mixture theory, the volume fraction is introduced to describe the change of internal structure. Thus, the unknowns are more than the equations, which cause difficulty in closing the field equations in the above process. Here, we adopt the closure scheme which was first put forward by Bowen[4], that is, close the system by constitutive relation of volume fraction n_α (constraint relations at equilibrium (1)). Bennethum[19] also adopted this method.

According to the principle of equipresence in continuum mechanics and the requirements of the problems needed to study, we assume that each constitutive variable is a function of all the following macroscopic constitutive independent variables:

$$n_\beta, \nabla n_\beta, T, \nabla T, \rho_\alpha, \nabla \rho_\alpha, C_\alpha^j, \nabla C_\alpha^j, v_{\beta,s}, d_\beta, u_\alpha^j, \nabla u_\alpha^j, E_s$$

$$\alpha = s, l, g; \beta = 1, g; j = 1, 2, \dots, N-1. \quad (31)$$

Based on the principle of local action, constitutive variables can be expressed as a function of independent state variables, that is,

$$\mathcal{E} = \mathcal{E} \left\{ n_\beta, \nabla n_\beta, T, \nabla T, \rho_\alpha, \nabla \rho_\alpha, C_\alpha^j, \nabla C_\alpha^j, v_{\beta,s}, d_\beta, u_\alpha^j, \nabla u_\alpha^j, E_s \right\}, \quad (32)$$

where \mathcal{E} is an aggregate function of constitutive variables; $n_\beta, \nabla n_\beta$ describe changes of the internal microstructure of porous media (changes of fluid phase); $T, \nabla T$ describe temperature effect and heat conduction, respectively; $\rho_\alpha, \nabla \rho_\alpha$ describe the compression deformation of each phase (volume change); $C_\alpha^j, \nabla C_\alpha^j$ describe changes of constituent concentration inside phases; $v_{\beta,s}$ describes seepage of fluid relative to solid; d_β is the symmetric part of ∇v_β , which describes the viscosity of fluid phase itself; u_α^j describes diffusion of constituents; ∇u_α^j describes the viscous resistance of fluid phase caused by diffusion of its internal constituents; and E_s describes the deformation of shape changes of soil skeleton.

It should be pointed out that the deformation behavior of porous media is generally expressed by solid deformation gradient tensor F_s . In order to meet the objective requirements, the Lagrange strain tensor E_s ($E_s = 1/2[(F_s)^T F_s - I]$) is selected as an independent state variable in this paper.

Using Lagrange multiplier method and constraints (2),

(3) and (17)-3, and setting $T A_{old} = (28)$, we derive the revised entropy inequality:

$$T A_{new} = T A_{old} + \sum_{\alpha=s,l,g} \lambda_\alpha \left[\frac{D_\alpha(n_\alpha \rho_\alpha)}{Dt} + n_\alpha \rho_\alpha \nabla \cdot v_\alpha - \hat{e}_\alpha \right]$$

$$+ \sum_{\alpha=s,l,g} \sum_{j=1}^N \lambda_\alpha^j \left[n_\alpha \rho_\alpha \frac{D_\alpha C_\alpha^j}{Dt} + \nabla \cdot (n_\alpha \rho_\alpha^j u_\alpha^j) - (\hat{e}_\alpha^j - C_\alpha^j \hat{e}_\alpha) \right] \geq 0. \quad (33)$$

Note that only N-1 constituents are independent in the third term at the left side of the inequality sign in the formula above, and constituent N is subject to the constraint relation $\sum_{j=1}^N C_\alpha^j u_\alpha^j = 0$, therefore, $\lambda_\alpha^N = 0$, while u_α^j and ∇u_α^j , as independent state variables, will be independent when $j = 1, 2, \dots, N$. Therefore, the terms need to be rewritten as independent state variables with $j = 1, 2, \dots, N-1$.

$$\sum_{j=1}^N u_\alpha^j \cdot M_\alpha^j = \sum_{j=1}^{N-1} u_\alpha^j \cdot \left(M_\alpha^j - \frac{C_\alpha^j}{C_\alpha^N} M_\alpha^N \right), \quad (34)$$

$$\sum_{j=1}^N \nabla u_\alpha^j \cdot N_\alpha^j = \sum_{j=1}^{N-1} \nabla u_\alpha^j \cdot \left(N_\alpha^j - \frac{C_\alpha^j}{C_\alpha^N} N_\alpha^N \right) - N_\alpha^N \cdot \sum_{j=1}^{N-1} \nabla \left(\frac{C_\alpha^j}{C_\alpha^N} \right) u_\alpha^j, \quad (35)$$

where vector M_α^j and second-order tensor N_α^j represent the coefficients of u_α^j and ∇u_α^j in the simplified entropy inequality, respectively.

Considering that solid is multi-constituent elastic-plastic material, and fluid is multi-constituent viscous material, we assume that the deformation is infinitesimal and the strain tensor for solid and the volume fraction for fluid can be additively decomposed into an elastic part and plastic part:

$$E_s = E_s^e + E_s^p, \quad n_\beta = n_\beta^e + n_\beta^p, \quad \beta = 1, g. \quad (36)$$

Based on the principle of phase separation[12, 24], Helmholtz free energy function of each phase can be given as

$$A_s = A_s(T, \rho_s, C_s^j, E_s, E_s^p, \chi)$$

$$A_l = A_l(T, \rho_l, C_l^j, n_l, n_l^p, v_l) \quad (37)$$

$$A_g = A_g(T, \rho_g, C_g^j, n_g, n_g^p, v_g)$$

where χ, v_l, v_g are the internal variables of other types of dissipation except plastic deformation E_s^p, n_l^p and n_g^p .

Using the chain rule and the functional forms postulated in eq. (37), the total derivatives of the free energies can be rewritten as partial derivatives which would be substituted

into the entropy inequality (33). Based on eqs. (34), (35) and $D_\alpha^j(\bullet)/Dt = (D_\alpha(\bullet)/Dt) + \mathbf{v}_{j,\alpha} \cdot \nabla(\bullet)$, we can derive the following inequality by ignoring external supply terms of momentum and energy:

$$\begin{aligned}
 T\Lambda_{\text{new}} = & \sum_{\alpha=s,1,g} \frac{D_s \rho_\alpha}{Dt} \left(n_\alpha \lambda_\alpha - n_\alpha \frac{p_\alpha}{\rho_\alpha} \right) \\
 & + \sum_{\alpha=s,1,g} \sum_{j=1}^N \frac{D_s C_\alpha^j}{Dt} \left(n_\alpha \rho_\alpha \lambda_\alpha^j - n_\alpha \rho_\alpha \tilde{\mu}_\alpha^j \right) \\
 & - \sum_{\alpha=s,1,g} n_\alpha \rho_\alpha \frac{D_s T}{Dt} \left(\frac{\partial A_\alpha}{\partial T} + \eta_\alpha \right) \\
 & + \sum_{\beta=1,g} \frac{D_s n_\beta}{Dt} \left(-n_\beta \rho_\beta \frac{\partial A_\beta}{\partial n_\beta} - \lambda_s \rho_s + \lambda_\beta \rho_\beta \right) \\
 & + n_s \mathbf{d}_s : \left(-\mathbf{t}_s^e + \mathbf{t}_s + \rho_s \lambda_s \mathbf{I} + \sum_{j=1}^N \rho_s^j \mathbf{u}_s^j \otimes \mathbf{u}_s^j \right) \\
 & + \sum_{\beta=1,g} n_\beta \mathbf{d}_\beta : \left(\mathbf{t}_\beta + \rho_\beta \lambda_\beta \mathbf{I} + \sum_{j=1}^N \rho_\beta^j \mathbf{u}_\beta^j \otimes \mathbf{u}_\beta^j \right) \\
 & + \sum_{\alpha=s,1,g} \sum_{j=1}^{N-1} \mathbf{u}_\alpha^j \cdot \left\{ \lambda_\alpha^j \nabla(n_\alpha \rho_\alpha^j) + \nabla \left[n_\alpha \rho_\alpha^j (A_\alpha^N - A_\alpha^j) \right] \right. \\
 & \quad \left. - (\hat{\mathbf{T}}_\alpha^j + \hat{\mathbf{i}}_\alpha^j) + \frac{C_\alpha^j}{C_\alpha^N} (\hat{\mathbf{T}}_\alpha^N + \hat{\mathbf{i}}_\alpha^N) - t_\alpha^N \nabla \left(\frac{C_\alpha^j}{C_\alpha^N} \right) \right\} \\
 & + \sum_{j=1}^{N-1} \nabla \mathbf{u}_s^j : \left[n_s \left(\lambda_s^j \rho_s^j \mathbf{I} + \mathbf{t}_s^j - \rho_s^j A_s^j \mathbf{I} - \frac{C_s^j}{C_s^N} \mathbf{t}_s^N + \rho_s^j A_s^N \mathbf{I} \right) \right] \\
 & + \sum_{\beta=1,g} \sum_{j=1}^{N-1} \nabla \mathbf{u}_\beta^j : \left[n_\beta \left(\lambda_\beta^j \rho_\beta^j \mathbf{I} + \mathbf{t}_\beta^j - \rho_\beta^j A_\beta^j \mathbf{I} - \frac{C_\beta^j}{C_\beta^N} \mathbf{t}_\beta^N + \rho_\beta^j A_\beta^N \mathbf{I} \right) \right] \\
 & + \sum_{\alpha=s,1,g} \nabla T \cdot \frac{n_\alpha}{T} \left\{ \mathbf{q}_\alpha + \sum_{j=1}^N \left[\rho_\alpha^j \mathbf{u}_\alpha^j \left(A_\alpha^j + \frac{1}{2} \mathbf{u}_\alpha^j \cdot \mathbf{u}_\alpha^j \right) - \mathbf{t}_\alpha^j \cdot \mathbf{u}_\alpha^j \right] \right\} \\
 & - \sum_{\beta=1,g} \mathbf{v}_{\beta,s} \cdot n_\beta \rho_\beta \left[\left(\frac{\partial A_\beta}{\partial T} + \eta_\beta \right) \nabla T + \frac{p_\beta}{\rho_\beta} \nabla \rho_\beta + \sum_{j=1}^{N-1} \tilde{\mu}_\beta^j \nabla C_\beta^j \right. \\
 & \quad \left. + \frac{\partial A_\beta}{\partial n_\beta} \nabla n_\beta + \frac{\partial A_\beta}{\partial n_\beta^p} \nabla n_\beta^p + \frac{\partial A_\beta}{\partial v_\beta} \nabla v_\beta \right. \\
 & \quad \left. - \frac{1}{\rho_\beta} \lambda_\beta \nabla \rho_\beta - \frac{1}{n_\beta} \lambda_\beta \nabla n_\beta - \sum_{j=1}^{N-1} \lambda_\beta^j \nabla C_\beta^j + \frac{\hat{\mathbf{T}}_\beta}{n_\beta \rho_\beta} \right] \\
 & - \sum_{\beta=1,g} \hat{e}_\beta \left[\lambda_\beta - \lambda_s + \sum_{j=1}^N (C_s^j \lambda_s^j - C_\beta^j \lambda_\beta^j) + A_\beta - A_s \right] \\
 & - \sum_{\beta=1,g} \sum_{j=1}^{N-1} \hat{e}_\beta^j \left[\lambda_\beta^j - \lambda_s^j + \frac{1}{2} (\mathbf{u}_\beta^j \cdot \mathbf{u}_\beta^j + \mathbf{v}_{\beta,s} \cdot \mathbf{v}_{\beta,s} - \mathbf{u}_s^j \cdot \mathbf{u}_s^j) \right] \\
 & - n_s \rho_s \left(\frac{\partial A_s}{\partial \mathbf{E}_s^p} : \dot{\mathbf{E}}_s^p + \frac{\partial A_s}{\partial \boldsymbol{\chi}} \cdot \dot{\boldsymbol{\chi}} \right) \\
 & - \sum_{\beta=1,g} n_\beta \rho_\beta \left(\frac{\partial A_\beta}{\partial n_\beta^p} \dot{n}_\beta^p + \frac{\partial A_\beta}{\partial v_\beta} \dot{v}_\beta \right) \geq 0, \tag{38}
 \end{aligned}$$

where $\alpha = s, 1, g; \beta = 1, g; p_\alpha$ is the thermodynamic force of phase α , $p_\alpha = \rho_\alpha^2 (\partial A_\alpha / \partial \rho_\alpha)$; $\mathbf{t}_s^e = \rho_s \mathbf{F}_s \cdot (\partial A_s / \partial \bar{\mathbf{E}}_s) \cdot \mathbf{F}_s^T$; $\tilde{\mu}_\alpha^j$ is the relative chemical potential of constituent j , $\tilde{\mu}_\alpha^j = \frac{\partial A_\alpha}{\partial C_\alpha^j}$ ($j = 1, 2, \dots, N-1$).

3.2 General non-equilibrium results

As usual, entropy inequality (38) is a linear function of $D_s \rho_\alpha / Dt$, $D_s C_\alpha^j / Dt$, $D_s T / Dt$, \mathbf{d}_s and $\nabla \mathbf{u}_s^j$, which are neither independent state variables nor constitutive dependent variables. In order to satisfy the entropy inequality for all allowable processes, the coefficients of these variables must be identically zero. It yields

$$\lambda_\alpha = \frac{p_\alpha}{\rho_\alpha}, \tag{39}$$

$$\lambda_\alpha^j = \tilde{\mu}_\alpha^j, \tag{40}$$

$$\sum_{\alpha=\beta,s} n_\alpha \rho_\alpha \left(\frac{\partial A_\alpha}{\partial T} + \eta_\alpha \right) = 0, \tag{41}$$

$$\begin{aligned}
 \mathbf{t}_s &= \mathbf{t}_s^e - \rho_s \lambda_s \mathbf{I} - \sum_{j=1}^N \rho_s^j \mathbf{u}_s^j \otimes \mathbf{u}_s^j \\
 &= \mathbf{t}_s^e - p_s \mathbf{I} - \sum_{j=1}^N \rho_s^j \mathbf{u}_s^j \otimes \mathbf{u}_s^j, \tag{42}
 \end{aligned}$$

$$\mathbf{t}_\alpha^j - \frac{C_\alpha^j}{C_\alpha^N} \mathbf{t}_\alpha^N = \rho_\alpha^j (A_\alpha^j - A_\alpha^N - \tilde{\mu}_\alpha^j) \mathbf{I}. \tag{43}$$

The residual entropy inequality is

$$\begin{aligned}
 D &= \sum_{\beta=1,g} \frac{D_s n_\beta}{Dt} \left(-n_\beta \rho_\beta \frac{\partial A_\beta}{\partial n_\beta} - \lambda_s \rho_s + \lambda_\beta \rho_\beta \right) \\
 &+ \sum_{\beta=1,g} n_\beta \mathbf{d}_\beta : \left(\mathbf{t}_\beta + \rho_\beta \lambda_\beta \mathbf{I} + \sum_{j=1}^N \rho_\beta^j \mathbf{u}_\beta^j \otimes \mathbf{u}_\beta^j \right) \\
 &+ \sum_{\alpha=s,1,g} \sum_{j=1}^{N-1} \mathbf{u}_\alpha^j \cdot \left\{ \lambda_\alpha^j \nabla(n_\alpha \rho_\alpha^j) + \nabla \left[n_\alpha \rho_\alpha^j (A_\alpha^N - A_\alpha^j) \right] \right. \\
 & \quad \left. - (\hat{\mathbf{T}}_\alpha^j + \hat{\mathbf{i}}_\alpha^j) + \frac{C_\alpha^j}{C_\alpha^N} (\hat{\mathbf{T}}_\alpha^N + \hat{\mathbf{i}}_\alpha^N) - \mathbf{t}_\alpha^N \cdot \nabla \left(\frac{C_\alpha^j}{C_\alpha^N} \right) \right\} \\
 &+ \sum_{\beta=1,g} \sum_{j=1}^{N-1} \nabla \mathbf{u}_\beta^j : \left[n_\beta \left(\lambda_\beta^j \rho_\beta^j \mathbf{I} + \mathbf{t}_\beta^j - \rho_\beta^j A_\beta^j \mathbf{I} - \frac{C_\beta^j}{C_\beta^N} \mathbf{t}_\beta^N + \rho_\beta^j A_\beta^N \mathbf{I} \right) \right] \\
 &+ \sum_{\alpha=s,1,g} \nabla T \cdot \frac{n_\alpha}{T} \left\{ \mathbf{q}_\alpha + \sum_{j=1}^N \left[\rho_\alpha^j \mathbf{u}_\alpha^j \left(A_\alpha^j + \frac{1}{2} \mathbf{u}_\alpha^j \cdot \mathbf{u}_\alpha^j \right) - \mathbf{t}_\alpha^j \cdot \mathbf{u}_\alpha^j \right] \right\} \\
 &- \sum_{\beta=1,g} \mathbf{v}_{\beta,s} \cdot n_\beta \rho_\beta \left[\left(\frac{\partial A_\beta}{\partial T} + \eta_\beta \right) \nabla T + \frac{p_\beta}{\rho_\beta} \nabla \rho_\beta + \sum_{j=1}^{N-1} \tilde{\mu}_\beta^j \nabla C_\beta^j \right. \\
 & \quad \left. + \frac{\partial A_\beta}{\partial n_\beta} \nabla n_\beta - \frac{1}{\rho_\beta} \lambda_\beta \nabla \rho_\beta - \frac{1}{n_\beta} \lambda_\beta \nabla n_\beta - \sum_{j=1}^{N-1} \lambda_\beta^j \nabla C_\beta^j + \frac{\hat{\mathbf{T}}_\beta}{n_\beta \rho_\beta} \right]
 \end{aligned}$$

$$\begin{aligned}
 & -\sum_{\beta=1,g} \hat{e}_\beta \left[\lambda_\beta - \lambda_s + \sum_{j=1}^N (C_s^j \lambda_s^j - C_\beta^j \lambda_\beta^j) + A_\beta - A_s \right] \\
 & -\sum_{\beta=1,g} \sum_{j=1}^{N-1} \hat{e}_\beta^j \left[\lambda_\beta^j - \lambda_s^j + \frac{1}{2} (\mathbf{u}_\beta^j \cdot \mathbf{u}_\beta^j + \mathbf{v}_{\beta,s} \cdot \mathbf{v}_{\beta,s} - \mathbf{u}_s^j \cdot \mathbf{u}_s^j) \right] \\
 & -n_s \rho_s \frac{\partial A_s}{\partial \mathbf{E}_s^p} : \dot{\mathbf{E}}_s^p - \sum_{\beta=1,g} n_\beta \rho_\beta \left(\frac{\partial A_\beta}{\partial n_\beta^p} \dot{n}_\beta^p + \mathbf{v}_{\beta,s} \cdot \nabla n_\beta^p \right) \\
 & -n_s \rho_s \frac{\partial A_s}{\partial \boldsymbol{\chi}} : \dot{\boldsymbol{\chi}} - \sum_{\beta=1,g} n_\beta \rho_\beta \left(\frac{\partial A_\beta}{\partial v_\beta} \dot{v}_\beta + \mathbf{v}_{\beta,s} \cdot \nabla v_\beta \right) \geq 0, \quad (44)
 \end{aligned}$$

where D represents the total energy dissipation. The first term on the left side of the inequality sign is the dissipation caused by capillary relaxation; the second term is the dissipation caused by viscosity of fluid itself; the third term is the dissipation caused by the constituent diffusion effect; the fourth term is the dissipation due to viscous resistance caused by diffusion of the fluid's internal constituents; the fifth term is the dissipation caused by heat conduction; the sixth term is the dissipation caused by the macroscopic seepage of fluid relative to soil skeleton; the seventh term is the dissipation due to mass exchange between phases, generally caused by phase transition; the eighth term is the dissipation due to mass exchange between constituents inside phases, which is generally caused by chemical reactions (only non-reactive chemical fields are considered in this paper); the ninth and tenth terms are the dissipations caused by the plastic deformation of solid skeleton and the fluid's irreversible changes, respectively; the last two terms are the dissipations caused by other internal variables except plastic deformation inside porous media (such as damages).

3.3 Equilibrium restrictions

According to thermodynamics, the following independent variables equal zero at equilibrium:

$$Y_e = \left\{ \frac{D_s n_\beta}{Dt}, \mathbf{d}_\beta, \mathbf{u}_\alpha^j, \nabla \mathbf{u}_\beta^j, \nabla T, \mathbf{v}_{\beta,s}, \hat{e}_\beta, \hat{e}_\beta^j, \dot{\mathbf{E}}_s^p, \dot{\boldsymbol{\chi}}, \dot{n}_\beta^p, \dot{v}_\beta \right\} = 0$$

$$\alpha = s, l, g; \beta = 1, g; j = 1, 2, \dots, N-1. \quad (45)$$

It is postulated that at equilibrium entropy is the maximum and entropy generation is the minimum at equilibrium. Thus we have $\partial A / \partial x = 0, \partial^2 A / \partial x \partial y \geq 0$, where x, y represent any variables in eq. (45). Therefore, the equations which must be satisfied at equilibrium are given as follows:

$$1) \quad -n_\beta \rho_\beta \frac{\partial A_\beta}{\partial n_\beta} - \lambda_s \rho_s + \lambda_\beta \rho_\beta = 0,$$

that is,
$$p_\beta - p_s = n_\beta \rho_\beta \frac{\partial A_\beta}{\partial n_\beta}. \quad (46)$$

This equation gives the dynamics compatibility condition restricting changes of the pressure difference at the interface

between fluid and solid, thus the suction expression of unsaturated porous media can be derived as

$$p_g - p_l = n_g \rho_g \frac{\partial A_g}{\partial n_g} - n_l \rho_l \frac{\partial A_l}{\partial n_l}. \quad (47)$$

$$2) \quad \mathbf{t}_\beta + \rho_\beta \lambda_\beta \mathbf{I} + \sum_{j=1}^N \rho_\beta^j \mathbf{u}_\beta^j \otimes \mathbf{u}_\beta^j = 0,$$

that is,
$$\mathbf{t}_\beta = -p_\beta \mathbf{I} - \sum_{j=1}^N \rho_\beta^j \mathbf{u}_\beta^j \otimes \mathbf{u}_\beta^j. \quad (48)$$

Eq. (48) is the expression of stress in fluid at equilibrium, where there is only equilibrium part induced by elastic force but no dissipation.

3)

$$\begin{aligned}
 & \tilde{\mu}_\alpha^j \nabla (n_\alpha \rho_\alpha^j) - \nabla [n_\alpha \rho_\alpha^j (A_\alpha^j - A_\alpha^N)] - (\hat{\mathbf{T}}_\alpha^j + \hat{\mathbf{i}}_\alpha^j) \\
 & + \frac{C_\alpha^j}{C_\alpha^N} (\hat{\mathbf{T}}_\alpha^N + \hat{\mathbf{i}}_\alpha^N) - \mathbf{t}_\alpha^N \cdot \nabla \left(\frac{C_\alpha^j}{C_\alpha^N} \right) = 0. \quad (49)
 \end{aligned}$$

Using the momentum conservation eq. (5) of constituents, we can eliminate $\hat{\mathbf{T}}_\alpha^j + \hat{\mathbf{i}}_\alpha^j$ and simplify the above equation into:

$$\nabla \cdot n_\alpha \rho_\alpha^j \left[\tilde{\mu}_\alpha^j \mathbf{I} - (A_\alpha^j - A_\alpha^N) \mathbf{I} + \left(\frac{1}{\rho_\alpha^j} \mathbf{t}_\alpha^j - \frac{1}{\rho_\alpha^N} \mathbf{t}_\alpha^N \right) \right] = n_\alpha \rho_\alpha^j \nabla \tilde{\mu}_\alpha^j. \quad (50)$$

Then, \mathbf{t}_α^j can be eliminated using eq. (43), then it can be derived as

$$\nabla \tilde{\mu}_\alpha^j = 0. \quad (51)$$

The expression shows that the opposite chemical potential is constant at equilibrium.

$$4) \quad \mathbf{t}_\beta^j - \frac{C_\beta^j}{C_\beta^N} \mathbf{t}_\beta^N = \rho_\beta^j (A_\beta^j - A_\beta^N - \tilde{\mu}_\alpha^j) \mathbf{I}. \quad (52)$$

This equation gives the stress tensor expression of constituents of fluid, without dissipation part.

$$5) \quad \mathbf{q}_\alpha = \sum_{j=1}^N \left[\mathbf{t}_\alpha^j \cdot \mathbf{u}_\alpha^j - \rho_\alpha^j \mathbf{u}_\alpha^j \left(A_\alpha^j + \frac{1}{2} \mathbf{u}_\alpha^j \cdot \mathbf{u}_\alpha^j \right) \right]. \quad (53)$$

The equation gives the expression of heat flow vector of phases at equilibrium. We can see that there is no heat flow in or out of porous media, and that the generation of heat is only due to external force and internal diffusion.

$$\begin{aligned}
 6) \quad & \left(\frac{\partial A_\beta}{\partial T} + \eta_\beta \right) \nabla T + \frac{P_\beta}{\rho_\beta^2} \nabla \rho_\beta + \sum_{j=1}^{N-1} \tilde{\mu}_\beta^j \nabla C_\beta^j \\
 & + \frac{\partial A_\beta}{\partial n_\beta} \nabla n_\beta + \frac{\partial A_\beta}{\partial n_\beta^p} \nabla n_\beta^p + \frac{\partial A_\beta}{\partial v_\beta} \nabla v_\beta - \frac{1}{\rho_\beta} \lambda_\beta \nabla \rho_\beta \\
 & - \frac{1}{n_\beta} \lambda_\beta \nabla n_\beta - \sum_{j=1}^{N-1} \lambda_\beta^j \nabla C_\beta^j + \frac{\hat{\mathbf{T}}_\beta}{n_\beta \rho_\beta} = 0. \quad (54)
 \end{aligned}$$

By the conclusions at non-equilibrium state, it can be simplified as

$$\hat{\mathbf{T}}_\beta = \left(p_\beta - n_\beta \rho_\beta \frac{\partial A_\beta}{\partial n_\beta} \right) \nabla n_\beta, \quad (55)$$

$\hat{\mathbf{T}}_\beta$ can be eliminated by substituting the momentum conservation equation of phases (6) with eq. (55), and \mathbf{t}_β can also be eliminated using eq. (48). After ignoring inertia term and high-order term, this yields

$$\nabla p_\beta - \rho_\beta \mathbf{g} = -\rho_\beta \frac{\partial A_\beta}{\partial n_\beta} \nabla n_\beta. \quad (56)$$

Eq. (56) tells us that the traditional relation of hydrostatic pressure $\nabla p_\beta = \rho_\beta \mathbf{g}$ is not satisfied. That is to say, the fluid flow can not be described only by pressure gradient and gravity. The free energy function shows that the fluid flow is related not only to itself (e.g., pressure, density or viscosity, etc.), but also to the environment and boundary properties (e.g., temperature, specific surface area or surface tension, etc.).

$$7) \quad \lambda_\beta - \lambda_s + \sum_{j=1}^{N-1} (C_s^j \lambda_s^j - C_\beta^j \lambda_\beta^j) + A_\beta - A_s = 0. \quad (57)$$

Its simplification is

$$\left(\frac{p_\beta}{\rho_\beta} + A_\beta \right) - \sum_{j=1}^{N-1} (C_\beta^j \tilde{\mu}_\beta^j) = \left(\frac{p_s}{\rho_s} + A_s \right) - \sum_{j=1}^{N-1} (C_s^j \tilde{\mu}_s^j). \quad (58)$$

This equation gives the relations between Gibbs free energy and the total chemical potential.

$$8) \quad \lambda_\beta^j - \lambda_s^j + \frac{1}{2} (\mathbf{u}_\beta^j \cdot \mathbf{u}_\beta^j + \mathbf{v}_{\beta,s} \cdot \mathbf{v}_{\beta,s} - \mathbf{u}_s^j \cdot \mathbf{u}_s^j) = 0. \quad (59)$$

Ignoring the high-order term yields

$$\lambda_\beta^j = \lambda_s^j, \quad \tilde{\mu}_\beta^j = \tilde{\mu}_s^j. \quad (60)$$

This equation states that the chemical potentials of the same constituents in different phases are equal at equilibrium.

$$9) \quad \frac{\partial A_s}{\partial \mathbf{E}_s^p} = 0, \quad \frac{\partial A_s}{\partial \boldsymbol{\chi}} = 0, \quad \frac{\partial A_\beta}{\partial n_\beta^p} = 0, \quad \frac{\partial A_\beta}{\partial v_\beta} = 0. \quad (61)$$

Eq. (61) shows that the free energy function at equilibrium is irrelevant to plastic deformation or internal variables, and there is no dissipation.

Now, all equations of unsaturated soils containing multi-constituent viscous fluid have been established, including the conservation eqs. (1)–(11), the restriction equations at equilibrium (46)–(61), the restriction equations at non-equilibrium (39)–(43), and the general constraints (12)–(25), which constitute a closed system together.

4 Coupling between generalized forces and flows in near-equilibrium state

4.1 Framework of coupling theory

In this paper, $\dot{n}_\beta, \mathbf{d}_\beta, \mathbf{u}_\alpha^j, \nabla \mathbf{u}_\beta^j, \nabla T, \mathbf{v}_{\beta,s}, \hat{e}_\beta, \hat{e}_\beta^j, \dot{\mathbf{E}}_s^p, \dot{\boldsymbol{\chi}}, \dot{n}_\beta^p$, and \dot{v}_β on the left side of the inequality sign of the dissipative inequality (44) can be regarded as thermo-dynamic flows, all of which are unequal to zero in the near-equilibrium state.

The dissipation function on the left side of the inequality sign of the dissipative inequality (44) can be expressed as

$$D = \tilde{\mathbf{X}} \cdot \mathbf{Y}, \quad (62)$$

where $\mathbf{Y} = \{ \dot{n}_\beta, \mathbf{d}_\beta, \mathbf{u}_\alpha^j, \nabla \mathbf{u}_\beta^j, \nabla T, \mathbf{v}_{\beta,s}, \hat{e}_\beta, \hat{e}_\beta^j, \dot{\mathbf{E}}_s^p, \dot{\boldsymbol{\chi}}, \dot{n}_\beta^p, \dot{v}_\beta \}$ is defined as generalized thermodynamic flow. $\tilde{\mathbf{X}}$, which is respectively expressed by $\Psi, \Sigma, \Gamma, Z, \Theta, \Pi, E, \Phi, \Omega, H, M$ and N , is defined as the effective generalized thermodynamic force, and the element $\tilde{\mathbf{X}}$ consists of all kinds of the special thermodynamic forces that couple together with the special corresponding element \mathbf{Y} . At the near-equilibrium state, the generalized flow is not equal to zero, thus by eq. (62), the dissipative inequality (44) can be simply expressed as follows:

$$\begin{aligned} D = & \sum_{\beta=l,g} \dot{n}_\beta \Psi + \sum_{\beta=l,g} \mathbf{d}_\beta : \Sigma + \sum_{\alpha=s,l,g} \sum_{j=1}^{N-1} \mathbf{u}_\alpha^j \cdot \Gamma \\ & + \sum_{\beta=l,g} \sum_{j=1}^{N-1} \nabla \mathbf{u}_\beta^j : \mathbf{Z} + \sum_{\alpha=s,l,g} \frac{\nabla T}{T} \cdot \Theta - \sum_{\beta=l,g} \mathbf{v}_{\beta,s} \cdot \Pi \\ & - \sum_{\beta=l,g} \hat{e}_\beta E - \sum_{\beta=l,g} \sum_{j=1}^{N-1} \hat{e}_\beta^j \Phi - \dot{\mathbf{E}}_s^p : \Omega - \dot{\boldsymbol{\chi}} \cdot \mathbf{H} \\ & - \dot{n}_\beta^p M - \dot{v}_\beta N \geq 0. \end{aligned} \quad (63)$$

In the dissipative inequality (63), the generalized flow \mathbf{Y} is thought to be definite, while the generalized force $\tilde{\mathbf{X}}$ which is coupled with the generalized flow is not a conventional force. It should be the coupling of all kinds of the special thermodynamic forces, which are coupled together with the special corresponding element of \mathbf{Y}_i . (See coefficients of different kinds of generalized flow in dissipative inequality (44)). Accordingly, the generation of a certain generalized flow is driven by all kinds of generalized forces (principle of equipresence), that is to say, in the case that the coupling is taken into account, the change of \mathbf{Y}_i is also driven by other (generalized) forces besides its corresponding forces. Therefore, the real effective driving forces (effective generalized thermodynamic force) which lead to the changes of certain generalized flows must be the results of joint participation of all kinds of generalized forces. Ref. [24] gives a discussion for the effective stress of unsaturated soil about the static problem at the equilibrium state. According to the thermodynamic theory in non-equilibrium

state, the following equation can be obtained:

$$\tilde{X} = \frac{\partial D(Y)}{\partial Y}. \tag{64}$$

Based on the thermodynamics of irreversible processes at non-equilibrium state, we can know that any effective generalized thermodynamic force \tilde{X} and dissipation potential function D can be decomposed into the quantities at equilibrium state $\tilde{X}_e (D_e)$ and $\tilde{X}_n (D_n)$ at non-equilibrium state:

$$\tilde{X} = \tilde{X}_e(Y_e) + \tilde{X}_n(Y), \quad D = D_e(Y_e) + D_n(Y). \tag{65}$$

And the dissipation is zero at the equilibrium state, that is, $\tilde{X}_n(Y_e) = 0, D_n(Y_e) = 0$. \tilde{X} can be expanded at $Y = Y_e$ by using Taylor series, at the same time, $\tilde{X}_n(Y_e) = 0$ and $D_n(Y_e) = 0$ are taken into account, then the first order approximation can be derived as

$$\begin{aligned} \tilde{X}_i(Y) = & A_{i-1} \dot{n}_\beta + A_{i-2} d_\beta + A_{i-3} u_\alpha^j + A_{i-4} \nabla u_\beta^j + A_{i-5} \nabla T + A_{i-6} v_{\beta,s} \\ & + A_{i-7} \hat{e}_\beta + A_{i-8} \hat{e}_\beta^j + A_{i-9} \dot{E}_s^p + A_{i-10} \dot{\chi} + A_{i-11} \dot{n}_\beta^p + A_{i-12} \dot{v}_\beta \\ & i = 1 \sim 12, \end{aligned} \tag{66}$$

where $A_{i-1}(Y_e) = \left. \frac{\partial \tilde{X}}{\partial \dot{n}_\beta} \right|_{Y=Y_e}, A_{i-2}(Y_e) = \left. \frac{\partial \tilde{X}}{\partial d_\beta} \right|_{Y=Y_e}, \dots$

In equation $\tilde{X}_i(Y) = A_{i-12} \cdot Y_i$, when $\tilde{X} = \Psi$ and considering eq. (64), we have

$$A_{i-1}(Y_e) = \frac{\partial^2 D}{\partial \dot{n}_\beta \partial \dot{n}_\beta}. \tag{67}$$

Similarly,

$$\begin{aligned} A_{i-2}(Y_e) &= \frac{\partial^2 D}{\partial \dot{n}_\beta \partial d_\beta}, A_{i-3}(Y_e) = \frac{\partial^2 D}{\partial \dot{n}_\beta \partial u_\alpha^j}, \\ A_{i-4}(Y_e) &= \frac{\partial^2 D}{\partial \dot{n}_\beta \partial \nabla u_\beta^j}, A_{i-5}(Y_e) = \frac{\partial^2 D}{\partial \dot{n}_\beta \partial \nabla T}, \\ A_{i-6}(Y_e) &= \frac{\partial^2 D}{\partial \dot{n}_\beta \partial v_{\beta,s}}, A_{i-7}(Y_e) = \frac{\partial^2 D}{\partial \dot{n}_\beta \partial \hat{e}_\beta}, \\ A_{i-8}(Y_e) &= \frac{\partial^2 D}{\partial \dot{n}_\beta \partial \hat{e}_\beta^j}, A_{i-9}(Y_e) = \frac{\partial^2 D}{\partial \dot{n}_\beta \partial \dot{E}_s^p}, \\ A_{i-10}(Y_e) &= \frac{\partial^2 D}{\partial \dot{n}_\beta \partial \dot{\chi}}, A_{i-11}(Y_e) = \frac{\partial^2 D}{\partial \dot{n}_\beta \partial \dot{n}_\beta^p}, \\ A_{i-12}(Y_e) &= \frac{\partial^2 D}{\partial \dot{n}_\beta \partial \dot{v}_\beta}. \end{aligned} \tag{68}$$

Similarly, when \tilde{X} is equal to $\Sigma, \Gamma, Z, \Theta, \Pi, E, \Phi, \Omega, H, M$ or N , respectively, the coefficients of eq. (66) can be determined according to the above method. Eqs. (66)–(68)

are general expressions of coupling effect among different fields of soils, which contain the term $(\dot{n}_\beta, \dot{E}_s^p, \dot{\chi}, \dot{n}_\beta^p, \dot{v}_\beta)$ directly related to the stress field, the term $(v_{\beta,s}, d_\beta)$ related to the seepage field, the term $(u_\alpha^j, \nabla u_\beta^j)$ relevant to the diffusion field, the term $(\hat{e}_\beta, \hat{e}_\beta^j)$ associated with the chemical field, and the term (∇T) related to the temperature field. Compared with the stress-strain constitutive relations for geotechnical materials derived based on thermodynamics, the above formulas can synthetically consider the coupling effect under various fields, thus the theoretical basis of multi-field coupling of soils can be established. For a specific problem, after making sure which fields should be included, the dissipative inequality can be simplified, eliding dissipation caused by fields which have no effects. While for a specific material, the specific form of dissipation potential function D needs to be determined according to the type, physical meaning, the existing experimental results and the research experience of the problem under treatment. Finally, the coupling relations among different fields are determined using eqs. (66)–(68).

We should note that eq. (64) is correct based on the premise that the generalized fluxes are taken as independent variables in this paper. However, taking generalized forces as independent variables is more convenient in some other cases, hence $Y = \partial D^*(\tilde{X}) / \partial \tilde{X}$ is derived, where $D^*(\tilde{X})$ is the Legendre transform of $D(Y)$. The general expressions of coupling effect among different fields of soils for the latter case can be derived in the same way.

When considering the linear case, the result is the same as that of the linear non-equilibrium thermodynamic theory, which can be obtained by setting eq. (68) equal to different constants. That is to say, the generalized forces in the dissipative inequality can be expressed as the linear combination of all kinds of generalized flows, which makes eqs. (66)–(68) degenerate into the results given by Bennethum[19] and Singh [27].

The followings are some non-linear constitutive equations at non-equilibrium state in special cases which are frequently encountered.

1) Thermal elastic-plastic coupling constitutive equation for solid

The plastic deformation of solid is described by \dot{E}_s^p . Considering the effect of seepage, temperature, and chemical fields on solid stress field, neglecting the influence of other factors, and the dissipation potential function D_1 , the effective generalized stress of solid is

$$\Omega = \omega_M : \dot{E}_s^p + \omega_H \cdot v_{\beta,s} + \omega_T \cdot \nabla T + \omega_C \hat{e}_\beta^j \equiv \tilde{t}_s^D, \tag{69}$$

where \tilde{t}_s^D is defined as the dissipative part of the effective generalized stress of solid; $\omega_M = \partial^2 D_1 / \partial \dot{E}_s^p \otimes \partial \dot{E}_s^p$ represents the strain of solid skeleton caused by load;

$\omega_H = \partial^2 D_1 / \partial \dot{E}_s^p \otimes \partial v_{\beta,s}$ represents the effects of seepage field on stress field, which is called ‘seepage-mechanical coupling coefficient’ of solid; $\omega_T = \partial^2 D_1 / \partial \dot{E}_s^p \otimes \partial \nabla T$ represents the influence of temperature on stress field, which is called ‘thermal-mechanical coupling coefficient’ of solid; and $\omega_C = \partial^2 D_1 / \partial \dot{E}_s^p \partial \hat{e}_\beta^j$ represents the effects of chemical field on stress field, which is called ‘chemical-mechanical coupling coefficient’ of solid.

2) Visco-elastic-plastic coupling constitutive equations for liquid

Considering the effects of seepage, temperature and chemical fields on liquid stress field, neglecting other factors, and setting the dissipation potential function as D_2 , we have

$$M = \xi_M \dot{n}_1^p + \xi_H \cdot v_{1,s} + \xi_T \cdot \nabla T + \xi_C \hat{e}_1^j \equiv \tilde{t}_1^D, \quad (70)$$

where \tilde{t}_1^D is defined as the dissipative part of the generalized stress of liquid; $\xi_M = \partial^2 D_2 / \partial \dot{n}_1^p \partial \dot{n}_1^p$ represents the change of plastic moisture content caused by external loading; $\xi_H = \partial^2 D_2 / \partial \dot{n}_1^p \partial v_{1,s}$ represents the effect of seepage field on stress field, which is called ‘seepage-mechanical coupling coefficient’ of liquid; $\xi_T = \partial^2 D_2 / \partial \dot{n}_1^p \partial \nabla T$ represents the influence of temperature on stress field, which is called ‘thermal-mechanical coupling coefficient’ of liquid; $\xi_C = \partial^2 D_2 / \partial \dot{n}_1^p \partial \hat{e}_1^j$ represents the effect of chemical field on stress field, which is called ‘chemical-mechanical coupling coefficient’ of liquid.

3) Generalized Fourier’s law

Considering the effects of stress, seepage, and chemical fields on heat conduction, neglecting other factors, and setting the dissipation potential function as D_3 , then:

$$\Theta = \zeta_T \cdot \nabla T + \zeta_M : \dot{E}_s^p + \zeta'_M \dot{n}_\beta^p + \zeta_H \cdot v_{\beta,s} + \zeta'_H : d_\beta + \zeta_C \hat{e}_\beta^j \equiv \tilde{q}, \quad (71)$$

where \tilde{q} is defined as generalized heat flow vector; $\zeta_T = \partial^2 D_3 / \partial \nabla T \otimes \partial \nabla T$ represents the heat transfer caused by temperature gradient, which is called ‘generalized thermal conductivity coefficient’; $\zeta_M = \partial^2 D_3 / \partial \nabla T \otimes \partial \dot{E}_s^p$ represents the heat generated in the process of irreversible deformation of solid skeleton; $\zeta'_M = \partial^2 D_3 / \partial \nabla T \partial \dot{n}_\beta^p$ represents the heat generated in the process of irreversible change of fluid content; $\zeta_H = \partial^2 D_3 / \partial \nabla T \otimes \partial v_{\beta,s}$ represents the heat generated during the seepage process of fluid; $\zeta'_H = \partial^2 D_3 / \partial \nabla T \otimes \partial d_\beta$ represents the heat generated by the viscosity of fluid; and $\zeta_C = \partial^2 D_3 / \partial \nabla T \partial \hat{e}_\beta^j$ represents the heat released or absorbed in the process of chemical reaction. Note that the heat generated by the last five rea-

sons is less than that generated by temperature gradient.

4) Generalized Darcy’s law

Considering the effects of stress, temperature and chemical fields on the seepage of liquid, neglecting other factors, and setting the dissipation potential function as D_4 , we have

$$\Pi = \delta_H \cdot v_{\beta,s} + \delta'_H : d_\beta + \delta_M : \dot{E}_s^p + \delta'_M \dot{n}_\beta^p + \delta_T \cdot \nabla T + \delta_C \hat{e}_\beta^j \equiv \tilde{t}, \quad (72)$$

where \tilde{t} is defined as the generalized seepage force; $\delta_H = \partial^2 D_4 / \partial v_{\beta,s} \otimes \partial v_{\beta,s}$ represents seepage caused by hydraulic gradient, which is called ‘general osmotic coefficient’; $\delta'_H = \partial^2 D_4 / \partial v_{\beta,s} \otimes \partial d_\beta$ represents the retarding effect of fluid viscosity on seepage; $\delta_M = \partial^2 D_4 / \partial v_{\beta,s} \otimes \partial \dot{E}_s^p$ represents the impact of the plastic deformation of solid skeleton on seepage field; $\delta'_M = \partial^2 D_4 / \partial v_{\beta,s} \partial \dot{n}_\beta^p$ represents the influence of the irreversible change of fluid content on seepage field; $\delta_T = \partial^2 D_4 / \partial v_{\beta,s} \otimes \partial \nabla T$ represents the effect of temperature field on seepage field; and $\delta_C = \partial^2 D_4 / \partial v_{\beta,s} \partial \hat{e}_\beta^j$ represents the influence of chemical field on the seepage field.

If the linear coupling is considered only, then the dissipation potential function will be expanded by taking the first order, and the coefficients ω , ξ , ζ , and δ of the generalized flows on the right sides of equal formulas (69)–(72) will degenerate into material parameters, thus the above-mentioned nonlinear coupling model degenerates into a linear coupling model proposed by Singh(2003)[27]:

$$\tilde{t}_s^D = a \mathbf{E}_s^{(m)} + b \cdot \nabla T, \quad (73)$$

$$\tilde{t}_1^D = c : d_\beta + d \cdot \nabla T, \quad (74)$$

$$q = e \cdot \nabla T + f \cdot \mathbf{E}_s^{(m)} + g \cdot d_\beta, \quad (75)$$

$$\tilde{t} = h \cdot v_{\beta,s} + i \cdot d_\beta + j \nabla T, \quad (76)$$

where $a, b, c, d, e, f, g, h, i, j$ are material parameters; $\mathbf{E}_s^{(m)}$ is m th order material derivative of \mathbf{E}_s , which is used to describe the viscosity of solid. Note that Singh [27] considered the viscous effects on swelling biopolymeric systems for solid phase, while plasticity which is more important for soils is also taken into account in this paper. If the coupling effect is ignored, the above-mentioned model can further degenerate into the conventional elastic-plastic constitutive model and the classical Fourier’s law and Darcy’s law.

4.2 Application of theoretical models

The determination of dissipation potential function is the key to advance the above-mentioned theory. Obviously,

there is no correct set of dissipation potential functions, however, they can be appropriately chosen in such a way that they meet certain theoretical and practical requirements. Theoretically, the selection for dissipation potential function must satisfy the dissipative inequality, that is, the second law of thermodynamics; meanwhile, the selection for dissipation potential function must also be consistent with the experimental observations. Collins [28] and Li [25, 26] gave the concrete form of the corresponding dissipation potential functions for saturated soil and unsaturated soil, respectively; however, both the two studies failed to consider the multi-field coupling effects of soils. Jussila [29, 30] gave the dissipation potential function describing the thermal-hydro-mechanical coupling of swelling unsaturated bentonite, but only elastic deformation of soils was considered.

For the given problems, variables that are related to the dissipation potential functions can be known with the existing knowledge, thus they can be determined based on the existing theories, experimental results and experience. Then the dissipation potential functions can be expanded by Taylor's series, and the expression of the corresponding constitutive equation can also be given. Next, the above theoretical framework is used to analyze both the two kinds of specific issues.

1) Generalized Darcy's law considering temperature effect

Here the corresponding dissipation potential function is selected as

$$D_4 = D_4(\mathbf{v}_{\beta,s}, \nabla T). \tag{77}$$

Then, its second order expansion is

$$D_4 = \frac{1}{2} \delta^{v_{\beta,s}} \mathbf{v}_{\beta,s} \cdot \mathbf{v}_{\beta,s} + \frac{1}{2} \delta^T \nabla T \cdot \nabla T + \delta^{v_{\beta,s}T} \mathbf{v}_{\beta,s} \cdot \nabla T, \tag{78}$$

where $\delta^{v_{\beta,s}}$ and δ^T are the influence parameters of seepage gradient and temperature gradient, respectively, and $\delta^{v_{\beta,s}T}$ is a coupling parameter.

Substituting it into formula (72) yields

$$\tilde{\mathbf{i}} \equiv \mathbf{II} = \delta^{v_{\beta,s}} \mathbf{v}_{\beta,s} + \delta^{v_{\beta,s}T} \nabla T. \tag{79}$$

According to the dissipative inequality (44), it can be derived as

$$\mathbf{II} = \hat{\mathbf{T}}_{\beta} - \left(p_{\beta} - n_{\beta} \rho_{\beta} \frac{\partial A_{\beta}}{\partial n_{\beta}} \right) \nabla n_{\beta}, \tag{80}$$

so,

$$\hat{\mathbf{T}}_{\beta} = \delta^{v_{\beta,s}} \mathbf{v}_{\beta,s} + \delta^{v_{\beta,s}T} \nabla T + \left(p_{\beta} - n_{\beta} \rho_{\beta} \frac{\partial A_{\beta}}{\partial n_{\beta}} \right) \nabla n_{\beta}. \tag{81}$$

Substituting it into the phase momentum conservation eq. (6) and ignoring the inertia term, we have

$$\begin{aligned} \delta^{v_{\beta,s}} \mathbf{v}_{\beta,s} &= -\nabla \cdot (n_{\beta} \mathbf{t}_{\beta}) - n_{\beta} \rho_{\beta} \mathbf{g}_{\beta} \\ &\quad - \delta^{v_{\beta,s}T} \nabla T - \left(p_{\beta} - n_{\beta} \rho_{\beta} \frac{\partial A_{\beta}}{\partial n_{\beta}} \right) \nabla n_{\beta}. \end{aligned} \tag{82}$$

Without considering fluid viscosity, \mathbf{d}_{β} in the dissipative inequality is neither an independent state nor a constitutively dependent variable, so its coefficient is equal to zero in the non-equilibrium state, that is, $\mathbf{t}_{\beta} = -p_{\beta} \mathbf{I} - \sum_{j=1}^N \rho_{\beta}^j \mathbf{u}_{\beta}^j \otimes \mathbf{u}_{\beta}^j$.

Substituting it into formula (82), gives

$$\begin{aligned} \delta^{v_{\beta,s}} \mathbf{v}_{\beta,s} &= \nabla \cdot \left[n_{\beta} \left(p_{\beta} \mathbf{I} + \sum_{j=1}^N \rho_{\beta}^j \mathbf{u}_{\beta}^j \otimes \mathbf{u}_{\beta}^j \right) \right] \\ &\quad - n_{\beta} \rho_{\beta} \mathbf{g}_{\beta} - \delta^{v_{\beta,s}T} \nabla T - \left(p_{\beta} - n_{\beta} \rho_{\beta} \frac{\partial A_{\beta}}{\partial n_{\beta}} \right) \nabla n_{\beta}, \end{aligned} \tag{83}$$

where the first term on the right side of the equation is the external pressure gradient considering the constituent diffusion effect; the second term is the gravity hydraulic head. The first two terms are the hydraulic gradient terms in the traditional Darcy's law, the third term is the temperature gradient, which reflects the influence of heat conduction on seepage; and the fourth term is the influence of porosity change caused by the elastic deformation of soil skeleton on seepage. When ignoring the latter two effects and considering only the single-constituent fluid, the above-mentioned generalized Darcy's law can degenerate into the general Darcy's law.

$$\mathbf{v}_{\beta,s} = k \left(\nabla p_{\beta} - \rho_{\beta} \mathbf{g}_{\beta} \right), \tag{84}$$

where k is a permeability coefficient.

2) Elastic-plastic constitutive model for soil

The above-mentioned thermal-elastic-plastic constitutive equation of solid (69) is coupled with the influences of seepage, temperature and chemical fields on stress field of solid. When neglecting the impact of other fields, formula (69) can degenerate into the elastic-plastic model.

$$\mathbf{\Omega} = \boldsymbol{\omega}_M : \dot{\mathbf{E}}_s^p \equiv \tilde{\mathbf{t}}_s^D, \boldsymbol{\omega}_M = \frac{\partial^2 D_1}{\partial \mathbf{E}_s^p \otimes \partial \mathbf{E}_s^p}. \tag{85}$$

For isotropic saturated soil, Collins [28] stated that the dissipation created by plastic volumetric strain and plastic shear strain are independent of each other, and there is no coupling. On such a basis, the dissipation potential in incremental form dD and stored energy $d\Psi_2$ can be proposed as

$$dD = dD(\varepsilon_v^p, p'; d\varepsilon_v^p, d\varepsilon_s^p) = \left[(Ad\varepsilon_v^p)^2 + (Bd\varepsilon_s^p)^2 \right]^{1/2}, \tag{86a}$$

$$d\Psi_2 = \frac{1}{2} \gamma p_c d\varepsilon_s^p, \tag{86b}$$

where A and B are the linear functions of \tilde{p}, q, p_c with the same dimensions as the stress, and $A = (1 - \gamma)\tilde{p} + 1/2\gamma p_c$, $B = M[(1 - \alpha)\tilde{p} + 1/2\alpha\gamma p_c]$. \tilde{p}, q are the stress variables of solid under triaxial stress condition; $d\varepsilon_v^p$ and $d\varepsilon_s^p$, are the volumetric strain and the shear strain, respectively, which are related to $\tilde{p}, q; p_c$ is preconsolidation pressure; α is a parameter between zero and one; γ is a variable related to stress ratio, which can be expressed as $\gamma = 2\tilde{p}_{CSL} / \tilde{p}$, and ranges from zero to one. γ actually reflects that the proportion of stored energy in the total plastic work is $\gamma/2$; the smaller γ is, the more plastic work will be dissipated.

Using the dissipation potential function, the dissipative stress is derived as

$$\tilde{\pi} = \frac{\partial(\delta\Phi)}{\partial(d\varepsilon_v^p)} = \frac{A^2 d\varepsilon_v^p}{\delta\Phi}, \tau = \frac{\partial(\delta\Phi)}{\partial(d\varepsilon_s^p)} = \frac{B^2 d\varepsilon_s^p}{\delta\Phi}, \quad (87)$$

where $\tilde{\pi}, \tau$ are the average effective stress and deviator stress in the dissipative stress space, respectively: $\tilde{\pi} = \tilde{p} - p_\alpha$, $\tau = q - q_\alpha$; p_α and q_α are the back stresses under triaxial stress condition, thus the yield equation in dissipative stress space is given as

$$g(\tilde{\pi}, \tau) = \frac{B^2}{A^2} \tilde{\pi}^2 + \tau^2 - B^2 = 0. \quad (88)$$

Using the stored energy $d\Psi_2$, the back stresses are figured out:

$$p_\alpha = \frac{\partial(d\Psi_2)}{\partial(d\varepsilon_v^p)} = \frac{1}{2}\gamma p_c, \quad q_\alpha = \frac{\partial(d\Psi_2)}{\partial(d\varepsilon_s^p)} = 0. \quad (89)$$

The stresses in true stress space are

$$\tilde{p} = \tilde{\pi} + p_\alpha = \tilde{\pi} + \frac{1}{2}\gamma p_c, \quad q = \tau + q_\alpha = \tau. \quad (90)$$

Substituting formula (90) into formula (88) yields the equation in real stress space:

$$f(\tilde{p}, q, p_c) = \frac{B^2}{A^2} (\tilde{p} - \gamma p_c / 2)^2 + q^2 - B^2 = 0. \quad (91)$$

Then, the plastic strain increment in the real stress space is

$$d\varepsilon_v^p = 2 \frac{B^2}{A^2} \left(\tilde{p} - \frac{1}{2} p_c \right) \delta\bar{\lambda}, \quad d\varepsilon_s^p = 2q\delta\bar{\lambda}. \quad (92)$$

By applying the hardening law and the consistency condition $df = \frac{\partial f}{\partial \tilde{p}} d\tilde{p} + \frac{\partial f}{\partial q} dq + \frac{\partial f}{\partial p_c} dp_c = 0$, the plastic factor $\delta\bar{\lambda}$ can be figured out.

The dissipation potential functions that are coupled with the elastic-plastic deformation of soil, seepage and heat

conduction must be given by combination of the above-mentioned theoretical basis with the experimental results. At present, study in this area is still limited, which will be an important issue in further research.

5 Conclusions

In such a complicated surrounding environment (especially in practical engineering), as the construction of repositories of high-level nuclear waste and the municipal landfill, soil is not only affected by a single field but by the multi-field coupling actions. Most of the existing theories started with experience and established the analyzing method for soils under multi-field coupling in testing or numerical methods. In this case, it is difficult to establish a unified, consistent multi-field coupling theory using such approaches. In this paper, soil is treated as porous media, which is composed of elastic-plastic solid skeleton, viscous liquid and ideal gas. By taking the multi-field coupling effects into account, such as deformation, seepage, heat conduction, and so on, the theoretical framework of multi-field coupling issues of multi-constituent and multi-phase soil can be established. Based on the hybrid mixture theory, the constitutive relations of multi-constituent unsaturated soil in the non-equilibrium state (39)–(43), the constitutive relations at equilibrium (46)–(61), the coupling relations of generalized force and the generalized flow in the near-equilibrium state (64)–(72) can also be obtained. The coupling relations (66)–(68) established in this paper are general expressions of multi-field coupling of soils, which can provide a theoretical basis for experimental and numerical method research. Of course, for multi-field coupling issues in specific circumstances, the specific form of the dissipation potential function needs to be determined in combination with theoretical knowledge and experiments, in order to give a method for determining the specific coupling equations and the corresponding parameters.

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