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CONSTITUTIVE RELATION OF UNSATURATED SOIL BY USE OF THE MIXTURE THEORY(I)—NONLINEAR CONSTITUTIVE EQUATIONS AND FIELD EQUATIONS *

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Abstract: *The nonlinear constitutive equations and field equations of unsaturated soils were constructed on the basis of mixture theory. The soils were treated as the mixture composed of three constituents. First, from the researches of soil mechanics, some basic assumptions about the unsaturated soil mixture were made, and the entropy inequality of unsaturated soil mixture was derived. Then, with the common method usually used to deal with the constitutive problems in mixture theory, the nonlinear constitutive equations were obtained. Finally, putting the constitutive equations of constituents into the balance equations of momentum, the nonlinear field equations of constituents were set up. The balance equation of energy of unsaturated soil was also given, and thus the complete equations for solving the thermodynamic process of unsaturated soil was formed.*

Key words: mixture theory; unsaturated soil; entropy inequality; constitutive equations; field equations

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Introduction

Soil is the most commonly used construction material in civil engineering and hydraulic engineering. The characteristics of soil have been investigating for nearly one hundred years. But because of its complex structure, changeable environment and being sensitive to the outside conditions, the soil often shows varied properties^[1, 2]. The main difficulty to the development of geotechnical mechanics is how to set up constitutive equations which could satisfactorily account

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for engineering properties of soil^[3]. Many constitutive models have been formed in the long-time engineering practice, scientific research and theoretical investigation. These models^[4] can be roughly classified as nonlinear elastic models^[5], plastic models^[6], endochronic models^[7], and mixture models^[8]. Up to now, the geotechnical mechanics is still in the state of semi-experience and semi-theory^[9], not only has no fast theory foundation, but also is far from complete theoretical system^[10]. The mixture theory^[11, 12] possesses ability to deal with the constitutive problem of composite medium. Maybe, due to the tedious expression, no attentions from geotechnical engineering has been paid to the ability^[13] of mixture theory, only a few experts analyzed the transport processes in soil with the theory^[14]. Although Chen Zheng-han^[9, 15, 16] proposed the axiom system of the mixture theory for geotechnical mechanics, there are still some principles which need more discussion. A. C. Eringen^[13] is the first scientist who used the mixture theory to do research on the characteristics of unsaturated soil. His study only was the simplification of mixture theory of porous medium and the natures of the unsaturated soil were not involved.

In the article, unsaturated soil is treated as saturated mixture composed of soil solid skeleton and liquid as well as gas in the pores of soil. By combination of material characteristics of three constituents and use of classical mixture theory, the nonlinear constitutive equations, the field equations and the balance equation of energy are derived. The complete equations for solving the thermodynamic process of unsaturated soil are given. Thus the foundation of mixture theory of constitutive relation for unsaturated soil is made.

1 Mixture Theory

Mixing several pure materials with different properties (physical or chemical properties) forms mixture. The mixing maybe homogeneous locally and entirely (e. g. gas mixture and solution), or inhomogeneous locally but homogeneous entirely (e. g. suspension and porous medium). The pure materials, which form mixture, are constituents of the mixture. There could be not only relative motion, but also interaction, even matter transformation (e. g. phase transformation and chemical reaction) between constituents. Mixture theory is a system that investigates the laws of motions, interactions and transformations of constituents, as well as relationships between the motions of mixture and the actions upon it from the outside.

Mixture theory is based on thermodynamics. It is the development of the continuum theory^[17, 18] of single medium and called interaction continuum theory. It is well self-consistent and systematic. In the theory, the mixture is visualized as the fold of continua that represent the constituents, one point in the mixture is occupied simultaneously by the material points of constituents and each constituent only has one material point at that point. Truesdell^[19] (1957) developed the mathematical theory of mixture. The theory has three axioms: 1) All properties of the mixture must be mathematical consequences of properties of the constituents; 2) So as to describe the motion of a constituent, we may in imagination isolate it from the rest of the mixture, provided we allow properly for the actions of the other constituents on it; 3) The motion of the mixture is governed by the same equations as is a single body. In sixties to seventies of 20th century, the mixture theory was studied intensively. Many scientists had made contributions to its development. References [11] and [12] discussed the important works in the period. The

mixture theories for complex media with special structure were also proposed, for example, the mixture theory of materials with microstructure, the mixture theory of immiscible and structured mixture and the mixture theory of composite material etc. Bedford and Drumheller^[20] summed up lots of applications of mixture theory.

To make preparation for the following deduction, here we give a brief introduction to the classical mixture theory.

1.1 Kinematics of mixture

Consider a mixture composed of N continuous media B^a ($a = 1, 2, \dots, N$). Each medium or constituent is assigned a reference configuration. The position of the particle of the a th constituent in its reference configuration is X_a (material coordination). The motions of particles of constituents make up of the motion or deformation of the mixture. The motion equation of a th constituent is

$$\mathbf{x}_a = \mathbf{x}_a(X_a, t), \quad (1)$$

where t is time, \mathbf{x}_a (spatial coordination) is the spatial position occupied at time t by the particle labeled X_a . Eq. (1) is also called deformation function of a th constituent. Assume that the constituents satisfy the axiom of continuity, then a unique inverse of Eq. (1) exists, at least in a neighborhood of \mathbf{x}_a . The inverse of Eq. (1) is

$$X_a = X_a(\mathbf{x}_a, t). \quad (2)$$

The axiom of continuity means the indestructibility and impenetrability of matter. The velocity and acceleration of X_a are defined, respectively, by

$$\mathbf{v}_a = \dot{\mathbf{x}}_a = \frac{\partial}{\partial t} \mathbf{x}_a(X_a, t) = \partial_t \mathbf{x}_a(X_a, t), \quad (3)$$

$$\mathbf{a}_a = \ddot{\mathbf{x}}_a = \frac{\partial^2}{\partial t^2} \mathbf{x}_a(X_a, t) = \partial_t^2 \mathbf{x}_a(X_a, t), \quad (4)$$

where $(\)'_a$ denotes material derivative with respect to the motion of a th constituent. Given Eq. (2), the velocity and acceleration can be regarded as functions of (X_a, t)

$$\mathbf{v}_a = \mathbf{v}_a(\mathbf{x}_a, t), \quad \mathbf{a}_a = \mathbf{a}_a(\mathbf{x}_a, t). \quad (5,6)$$

They represent the velocity and acceleration, respectively, of particle of a th constituent which is at the spatial position \mathbf{x}_a at time t .

The deformation gradient at (X_a, t) is a linear transformation defined by

$$\mathbf{F}_a = \text{GRAD}_a \mathbf{x}_a(X_a, t), \quad \det \mathbf{F}_a \geq 0. \quad (7,8)$$

The linear transformation inverse to \mathbf{F}_a is

$$\mathbf{F}_a^{-1} = \text{grad}_a X_a(\mathbf{x}_a, t) \quad (9)$$

and

$$\mathbf{F}_a \mathbf{F}_a^{-1} = \mathbf{F}_a^{-1} \mathbf{F}_a = \mathbf{I}, \quad (10)$$

where GRAD_a means differentiation with respect to the material coordination X_a , grad_a the spatial position \mathbf{x}_a , \mathbf{I} is unit tensor. The second deformation gradient at X_a is given by

$$\mathbf{G}_a = \text{GRAD}_a \mathbf{F}_a. \quad (11)$$

The velocity gradient for the a th constituent at (\mathbf{x}_a, t) is defined by

$$L_a = \text{grad}_a v_a(x_a, t) \quad (12)$$

and, by the chain rule,

$$L_a = F'_a F_a^{-1}. \quad (13)$$

L_a can also be expressed in the form of deformation rate tensor d_a and spin tensor w_a as

$$L_a = d_a + w_a, \quad (14)$$

in which

$$d_a = \frac{1}{2}(L_a + L_a^T), \quad w_a = \frac{1}{2}(L_a - L_a^T). \quad (15, 16)$$

They are symmetric part and antisymmetric part of tensor L_a , respectively, $(\)^T$ signifies transpose of tensor or matrix.

If ρ_a denotes the density of a th constituent, then the density of mixture is defined by

$$\rho(x, t) = \sum_{a=1}^N \rho_a(x, t). \quad (17)$$

Physically ρ_a represents the mass of the a th constituent per unit volume of mixture. The quantity is sometimes called bulk density as opposed to the true density. The true density for a th constituent is denoted by γ_a and equates the mass of the a th constituent per unit volume of the constituent. The quantity given by

$$\phi_a(x, t) = \rho_a(x, t) / \gamma_a(x, t) \quad (18)$$

is the volume fraction of the a th constituent. Physically ϕ_a represents the volume of the a th constituent per unit volume of the mixture. ϕ_a ($a = 1, 2, \dots, N$) are a rough description of local structure of the mixture. If

$$\sum_{a=1}^N \phi_a = 1, \quad (19)$$

the mixture is saturated. There is no void between the constituents in saturated mixture. If

$$\sum_{a=1}^N \phi_a < 1, \quad (20)$$

the mixture is unsaturated. Voids may exist between the constituents of unsaturated mixture.

The velocity of the mixture at (x, t) is defined by

$$v(x, t) = \frac{1}{\rho} \sum_a \rho_a(x, t) v_a(x, t). \quad (21)$$

The diffusion velocity or barycentric velocity of the a th constituent u_a is the difference of v_a and v

$$u_a(x, t) = v_a(x, t) - v(x, t). \quad (22)$$

It follows from Eqs. (17), (21) and (22) that

$$\sum_a \rho_a u_a = 0. \quad (23)$$

1.2 The balance equations and Clausius-Duhem inequality of mixture

The local balance equations of mass, linear momentum, moment of momentum and energy for the a th constituent are

$$\rho'_a + \rho_a \text{div} v_a = c_a \quad \text{or} \quad (\rho_a | \det F_a |)' = | \det F_a | c_a, \quad (24a, b)$$

$$\rho_a \dot{v}_a + c_a v_a = \text{div} t_a + \rho_a b_a + p_a, \quad (25)$$

$$t_a - t_a^T = M_a, \quad (26)$$

$$\rho_a \dot{\epsilon}_a + c_a \left(\epsilon_a - \frac{1}{2} v_a^2 \right) = \text{tr}(t_a^T L_a) - \text{div} q_a + \rho_a r_a + \hat{\epsilon}_a - p_a \cdot v_a, \quad (27)$$

where c_a is the growth of mass of the a th constituent, t_a is the partial stress tensor, p_a is the momentum supply, it is also call local body force or inner body force, b_a is the partial external body force density, M_a or m_a is the growth of moment of momentum and reflects the couple stress acting on the a th constituent. The relationship between skew-symmetric tensor M_a and vector m_a is

$$M_a x_0 = m_a \times x_0, \quad (28)$$

where x_0 is arbitrary vector. The components of M_a are

$$\begin{cases} M_{a11} = M_{a22} = M_{a33} = 0, M_{a23} = -M_{a32} = m_{a1}, \\ M_{a31} = -M_{a13} = m_{a2}, M_{a12} = -M_{a21} = m_{a3}, \end{cases} \quad (29a - d)$$

ϵ_a is the inner energy density, q_a is the partial heat flux vector, r_a is the heat supply density of and $\hat{\epsilon}_a$ is the energy supply.

The balance equations of mass, linear momentum, moment of momentum and energy for the mixture are

$$\partial_t \rho + \text{div}(\rho v) = 0 \quad \text{or} \quad \sum_a c_a = 0, \quad (30a, b)$$

$$\rho a = \text{div} t + \rho b \quad \text{or} \quad \sum_a p_a = 0, \quad (31a, b)$$

$$t = t^T \quad \text{or} \quad \sum_a M_a = 0, \quad (32a, b)$$

$$\rho \frac{d\epsilon}{dt} = \text{tr}(t^T L) - \text{div} q + \rho r \quad \text{or} \quad \sum_a \hat{\epsilon}_a = 0, \quad (33a, b)$$

where

$$t = \sum_a (t_a - \rho_a u_a \otimes u_a) \quad (34)$$

is the stress tensor for the mixture, \otimes denotes tensor production. The stress tensor t of the mixture defined by Eq. (34) satisfies the relation

$$t - \rho v \otimes v = \sum_a (t_a - \rho_a v_a \otimes v_a). \quad (35)$$

The inner part of the stress tensor of the mixture is

$$t_I = \sum_a t_a. \quad (36)$$

The relationship between external body force b of the mixture and external body force b_a of the a th constituent is

$$\rho b = \sum_a \rho_a b_a. \quad (37)$$

The energy density of the mixture ϵ is defined by

$$\epsilon = \frac{1}{\rho} \sum_a \left(\rho_a \epsilon_a + \frac{1}{2} \rho_a u_a^2 \right) \quad (38)$$

and satisfies

$$\rho \left(\epsilon + \frac{1}{2} v^2 \right) = \sum_a \rho_a \left(\epsilon_a + \frac{1}{2} v_a^2 \right). \quad (39)$$

The inner part of ϵ is expressed as

$$\epsilon_I = \frac{1}{\rho} \sum_a \rho_a \epsilon_a. \quad (40)$$

Here \mathbf{q} is the heat flux vector of the mixture, defined by

$$\mathbf{q} = \mathbf{q}_0 + \frac{1}{2} \sum_a \rho_a u_a^2 \mathbf{u}_a \quad (41)$$

and

$$\mathbf{q}_0 = \sum_a (\mathbf{q}_a - \mathbf{t}_a^T \mathbf{u}_a + \rho_a \epsilon_a \mathbf{u}_a). \quad (42)$$

Here \mathbf{q} meets the equation

$$\mathbf{q} - \mathbf{t}^T \mathbf{v} + \rho \left(\epsilon + \frac{1}{2} v^2 \right) \mathbf{v} = \sum_a \left[\mathbf{q}_a - \mathbf{t}_a^T \mathbf{v}_a + \rho_a \left(\epsilon_a + \frac{1}{2} v_a^2 \right) \mathbf{v}_a \right]. \quad (43)$$

The quantity

$$r = \frac{1}{\rho} \sum_a \rho_a (r_a + \mathbf{b}_a \cdot \mathbf{u}_a) \quad (44)$$

is the heat supply density for the mixture and it has following relationship with r_a

$$\rho (r + \mathbf{b} \cdot \mathbf{v}) = \sum_a \rho_a (r_a + \mathbf{b}_a \cdot \mathbf{v}_a). \quad (45)$$

\mathbf{L} , the velocity gradient for the mixture, is defined by

$$\mathbf{L} = \text{grad} \mathbf{v}(\mathbf{x}, t). \quad (46)$$

It can also be expressed as

$$\mathbf{L} = \frac{1}{\rho} \sum_a (\rho_a \mathbf{L}_a + \mathbf{u}_a \otimes \text{grad} \rho_a). \quad (47)$$

The axiom of dissipation, i. e., Clausius-Duhem inequality or entropy inequality of the mixture system, is

$$\sum_a \left[\rho_a \eta'_a + c_a \eta_a + \text{div} \left(\frac{\mathbf{q}_a}{\theta_a} \right) - \frac{\rho_a r_a}{\theta_a} \right] \geq 0 \quad (48a)$$

or

$$\rho \frac{d\eta}{dt} + \sum_a \text{div} \left(\frac{\mathbf{q}_a}{\theta_a} + \rho_a \eta_a \mathbf{u}_a \right) - \sum_a \frac{\rho_a r_a}{\theta_a} \geq 0, \quad (48b)$$

where $\eta_a(\mathbf{x}, t)$ and $\theta_a(\mathbf{x}, t)$ are entropy density and temperature of the a th constituent, respectively. The entropy density of the mixture η is

$$\eta = \frac{1}{\rho} \sum_a \rho_a \eta_a. \quad (49)$$

Substituting Eq.(27) into Eq.(48a) and eliminating the term $\rho_a r_a$, the reduced entropy inequality of the mixture is obtained

$$\sum_a \frac{1}{\theta_a} \left[\rho_a (\eta'_a \theta_a - \epsilon'_a) + \text{tr}(\mathbf{t}_a^T \mathbf{L}_a) - \frac{\mathbf{q}_a \cdot \text{grad} \theta_a}{\theta_a} + \right]$$

$$\hat{\varepsilon}_a - \mathbf{p}_a \cdot \mathbf{v}_a - c_a \left(\eta_a \theta_a - \varepsilon_a + \frac{1}{2} v_a^2 \right) \geq 0. \quad (50)$$

The partial Helmholtz free energy density for the a th constituent ψ_a is defined by

$$\psi_a = \varepsilon_a - \theta_a \eta_a, \quad (51)$$

Equation (50) is rewritten as

$$\sum_a \frac{1}{\theta_a} \left[-\rho_a (\psi'_a + \eta_a \theta'_a) + \text{tr}(\mathbf{t}_a^T \mathbf{L}_a) - \frac{\mathbf{q}_a \cdot \text{grad} \theta_a}{\theta_a} + \hat{\varepsilon}_a - \mathbf{p}_a \cdot \mathbf{v}_a - c_a \left(\psi_a - \frac{1}{2} v_a^2 \right) \right] \geq 0. \quad (52)$$

When each constituent is constrained to have the same temperature as every other constituents, i. e. ,

$$\theta_a(\mathbf{x}, t) = \theta(\mathbf{x}, t) \quad (a = 1, 2, \dots, N), \quad (53)$$

the material derivative of $\theta(\mathbf{x}, t)$ with respect to the motion of the a th constituent is

$$(\theta)'_a = d\theta/dt + \mathbf{g} \cdot \mathbf{u}_a, \quad (54)$$

where

$$\mathbf{g} = \text{grad} \theta(\mathbf{x}, t). \quad (55)$$

The entropy inequality (52) is simplified as

$$-\sum_a \rho_a \psi'_a - \rho \eta \frac{d\theta}{dt} + \text{tr} \left[\sum_a (\mathbf{t}_a^T \mathbf{L}_a) \right] - \frac{\mathbf{g}}{\theta} \cdot \sum_a (\mathbf{q}_a + \rho_a \eta_a \theta \mathbf{u}_a) - \sum_a \mathbf{p}_a \cdot \mathbf{v}_a - \sum_a c_a \left(\psi_a - \frac{1}{2} v_a^2 \right) \geq 0. \quad (56)$$

The research deals with the mixture of single temperature and no mass transformation exists between constituents, i. e. , $c_a = 0$ ($a = 1, 2, \dots, N$). In the case, the reduced entropy inequality (56) is rewritten as

$$\sum_a \left[-\Psi'_a - \rho_a \eta_a \partial_t \theta - \text{tr}(\rho_a \mathbf{K}_a \mathbf{L}_a) - \frac{\mathbf{g}}{\theta} \cdot (\mathbf{q}_a + \rho_a \eta_a \theta \mathbf{v}_a) - \mathbf{p}_a \cdot \mathbf{v}_a \right] \geq 0, \quad (57)$$

where

$$\Psi_a = \rho_a \psi_a, \quad \rho_a \mathbf{K}_a = \Psi_a \mathbf{I} - \mathbf{t}_a^T, \quad (58, 59)$$

Ψ_a is the free energy of the a th constituent per unit volume of the mixture and \mathbf{K}_a is the chemical potential tensor.

2 Basic Assumptions About Unsaturated Soil Mixture

In order to simplify the discussion, on the basis of soil mechanics^[21], the following assumptions about unsaturated soil mixture are made:

1) The unsaturated soil is saturated mixture composed of solid constituent (solid skeleton made up of soil particles) s , liquid constituent (water, water solution or other liquid in the pores of soil skeleton) l and gas constituent (air, water vapor or mixed gas in the pores of soil skeleton) g ;

2) No transformation of constituent's matter exists in the unsaturated soil mixture, i. e. ,

$c_a = 0 \ (a = s, l, g)$;

3) At one spatial point, the three constituents of unsaturated soil mixture have same temperature;

4) The materials of solid constituent (soil particle) and material of liquid constituent are incompressible, and their true densities $\gamma_b \ (b = s, l)$ are constants. The gas constituent is compressible, and its true density γ_g is variable.

3 The Entropy Inequality of Unsaturated Soil

Saturated mixture is different from usual mixture and unsaturated soil mixture is also different with saturated mixture. In this section, the entropy inequalities for saturated mixture and unsaturated soil mixture are given.

3.1 The entropy inequality of saturated mixture

The unsaturated soil is saturated mixture composed of solid constituent, liquid constituent and gas constituent. The word “unsaturated” in phrase “unsaturated soil” means that gas exists in the pores of soil skeleton and the pores are not completely occupied by liquid constituent. However, the word “saturated” in phrase “saturated mixture” means that the constituent volume fractions $\phi_a \ (a = s, l, g)$ of the mixture satisfy saturate condition (19), i.e.,

$$\phi_s + \phi_l + \phi_g = 1. \quad (60)$$

Its time partial derivative and spatial gradient are

$$\sum_a \partial_t \phi_a = 0, \quad \sum_a \text{grad} \phi_a = \mathbf{0}. \quad (61, 62)$$

Using material derivative, Eq. (61) can be written as

$$\sum_a (\phi'_a - \text{grad} \phi_a \cdot \mathbf{v}_a) = 0. \quad (63)$$

Because of Eq. (63), the inequality (57) is expressed as

$$\begin{aligned} & - \sum_a \Psi'_a - \rho \eta \partial_t \theta - \sum_a \text{tr}(\rho_a \mathbf{K}_a \mathbf{L}_a) - \frac{\mathbf{g}}{\theta} \cdot \sum_a (\mathbf{q}_a + \rho_a \eta_a \theta \mathbf{v}_a) - \\ & \sum_a (\mathbf{p}_a - P \text{grad} \phi_a) \cdot \mathbf{v}_a - P \sum_a \phi'_a \geq 0, \end{aligned} \quad (64)$$

where P is Lagrange's multiplier. Eq. (64) indicates that the interaction between constituents in saturated mixture has one more term $(-P \text{grad} \phi_a)$ than that in mixture which is not constrained by saturate condition, and the increasing rate of entropy density of saturated mixture is affected by material derivatives of constituent volume fractions ϕ'_a .

Free energy of the a th constituent per unit volume of mixture is the function of the independent constitutive variables describing the recoverable energy of mixture system^[13], i.e.,

$$\Psi_a = \Psi_a(\theta, \mathbf{C}_s, \rho_l, \rho_g, \phi_l, \phi_g), \quad (65)$$

where $\mathbf{C}_s = \mathbf{F}_s^T \mathbf{F}_s$ is right Cauchy-Green strain tensor of the solid constituent. Computing the material derivative of Eq. (65) and summing over constituents, we obtain

$$\sum_a \Psi'_a = \frac{\partial \Psi_l}{\partial \theta} \partial_t \theta + \mathbf{g} \cdot \sum_a \left(\frac{\partial \Psi_a}{\partial \theta} \mathbf{v}_a \right) +$$

$$\sum_a \text{tr}(\mathbf{t}_{aR}^T \mathbf{L}_a) + \sum_a \mathbf{k}_a \cdot \mathbf{v}_a + \sum_f \frac{\partial \Psi_1}{\partial \phi_f} \phi_f', \quad (66)$$

where

$$\mathbf{k}_f = \text{grad} \Psi_f - \left(\frac{\partial \Psi_1}{\partial \rho_f} \text{grad} \rho_f + \frac{\partial \Psi_1}{\partial \phi_f} \text{grad} \phi_f + \frac{\partial \Psi_f}{\partial \theta} \mathbf{g} \right) \quad (f = l, g), \quad (67)$$

$$\mathbf{k}_s = - \sum_f \mathbf{k}_f = \text{grad} \Psi_s - \left(\frac{\partial \Psi_1}{\partial \mathbf{C}_s} [\text{grad} \mathbf{C}_s] + \frac{\partial \Psi_s}{\partial \theta} \mathbf{g} \right), \quad (68)$$

$$\mathbf{t}_{sR} = \mathbf{F}_s \left(\frac{\partial \Psi_1}{\partial \mathbf{C}_s} + \left(\frac{\partial \Psi_1}{\partial \mathbf{C}_s} \right)^T \right) \mathbf{F}_s^T = 2 \mathbf{F}_s \left(\frac{\partial \Psi_1}{\partial \mathbf{C}_s} \right) \mathbf{F}_s^T, \quad (69)$$

$$\mathbf{t}_{fR} = - \rho_f \frac{\partial \Psi_1}{\partial \rho_f} \mathbf{I} \quad (f = l, g). \quad (70)$$

$\bar{\Psi}_1 = \sum_a \rho_a \Psi_a$. Given Eq. (66), Eq. (64) becomes

$$\begin{aligned} & - \left(\rho \eta + \frac{\partial \Psi_1}{\partial \theta} \right) \partial_t \theta - \sum_a \text{tr}[(\rho_a \mathbf{K}_a + \mathbf{t}_{aR}^T) \mathbf{L}_a] - \frac{\mathbf{g}}{\theta} \cdot \mathbf{q}_1 - \\ & \sum_a \left[\mathbf{p}_a - P \text{grad} \phi_a + \mathbf{k}_a + \left(\rho_a \eta_a + \frac{\partial \Psi_a}{\partial \theta} \right) \mathbf{g} \right] \cdot \mathbf{v}_a - P \phi_s' - \\ & \sum_f \left(P + \frac{\partial \Psi_1}{\partial \phi_f} \right) \phi_f' \geq 0. \end{aligned} \quad (71)$$

Axiom of frame indifference^[22] needs the velocities of constituents \mathbf{v}_a ($a = s, l, g$) appear in the forms $\mathbf{v}_f - \mathbf{v}_s$ ($f = l, g$). Then the summation of term in the bracket in Eq. (71) over constituents equals zero, i.e.,

$$\sum_a \left[\mathbf{p}_a - P \text{grad} \phi_a + \mathbf{k}_a + \left(\rho_a \eta_a + \frac{\partial \Psi_a}{\partial \theta} \right) \mathbf{g} \right] = \mathbf{0}. \quad (72)$$

From Eqs. (31b), (62) and (68), the above equation is simplified as

$$\eta = - \frac{1}{\rho} \cdot \frac{\partial \Psi_1}{\partial \theta} \quad (73)$$

and entropy inequality (71) as

$$\begin{aligned} & - \sum_a \text{tr}[(\rho_a \mathbf{K}_a + \mathbf{t}_{aR}^T) \mathbf{L}_a] - \frac{\mathbf{g}}{\theta} \cdot \mathbf{q}_1 - \sum_f \mathbf{f}_f \cdot (\mathbf{v}_f - \mathbf{v}_s) - \\ & P \phi_s' - \sum_f \left(P + \frac{\partial \Psi_1}{\partial \phi_f} \right) \phi_f' \geq 0, \end{aligned} \quad (74)$$

where

$$\mathbf{f}_f = \mathbf{p}_f - P \text{grad} \phi_f + \mathbf{k}_f + \left(\rho_f \eta_f + \frac{\partial \Psi_f}{\partial \theta} \right) \mathbf{g}, \quad (75)$$

$$\mathbf{f}_s = - \sum_f \mathbf{f}_f = \mathbf{p}_s - P \text{grad} \phi_s + \mathbf{k}_s + \left(\rho_s \eta_s + \frac{\partial \Psi_s}{\partial \theta} \right) \mathbf{g}. \quad (76)$$

Equation (74) is the entropy inequality of saturated mixture. It illustrates that $\partial_t \theta$ makes no contribution to the increasing rate of entropy density of the mixture system.

3.2 Entropy inequality of unsaturated soil mixture

Considering that the true densities of the solid constituent and liquid constituent are constants, from mass balance equation (24a) and $c_b = 0$ ($b = s, l$), we get

$$\phi'_b = -\phi_b \operatorname{div} \mathbf{v}_b = -\phi_b \operatorname{tr} \mathbf{L}_b \quad (b = s, l). \quad (77)$$

Noting that γ_l is constant and ρ_l is not longer independent constitutive variable, then

$$\mathbf{t}_{lR} = -\phi_l \frac{\partial \Psi_l}{\partial \phi_l} \mathbf{I}, \quad \mathbf{k}_l = \operatorname{grad} \Psi_l - \left(\frac{\partial \Psi_l}{\partial \phi_l} \operatorname{grad} \phi_l + \frac{\partial \Psi_l}{\partial \theta} \mathbf{g} \right). \quad (78, 79)$$

Equation (74) becomes

$$\sum_a \operatorname{tr}(\mathbf{t}_{aD}^T \mathbf{L}_a) - \frac{\mathbf{g}}{\theta} \cdot \mathbf{q}_I - \sum_f \mathbf{f}_f \cdot (\mathbf{v}_f - \mathbf{v}_s) + \sigma_g \phi'_g \geq 0, \quad (80)$$

where

$$\mathbf{t}_{sD}^T = -(\rho_s \mathbf{K}_s + \mathbf{t}_{sR} - P \phi_s \mathbf{I}), \quad (81)$$

$$\mathbf{t}_{lD}^T = -(\rho_l \mathbf{K}_l + \mathbf{t}_{lR} - P \phi_l \mathbf{I}), \quad (82)$$

$$\mathbf{t}_{gD}^T = -(\rho_g \mathbf{K}_g + \mathbf{t}_{gR}), \quad \sigma_g = -\left(P + \frac{\partial \Psi_l}{\partial \phi_g}\right). \quad (83, 84)$$

Here \mathbf{t}_{aD} and \mathbf{t}_{aR} are the dissipative part and the non-dissipative part of partial stress tensor \mathbf{t}_a , respectively. σ_g is the equilibrated interaction force. It follows from Eqs. (81) to (83) and (59), that the partial stresses of constituents are

$$\mathbf{t}_s = \Psi_s \mathbf{I} + \mathbf{t}_{sR} + \mathbf{t}_{sD} - P \phi_s \mathbf{I}, \quad (85)$$

$$\mathbf{t}_l = \Psi_l \mathbf{I} + \mathbf{t}_{lR} + \mathbf{t}_{lD} - P \phi_l \mathbf{I}, \quad (86)$$

$$\mathbf{t}_g = \Psi_g \mathbf{I} + \mathbf{t}_{gR} + \mathbf{t}_{gD}. \quad (87)$$

Equation (80) can be rewritten as

$$\sum_{a, m, n} \operatorname{tr}(\mathbf{t}_{aD}^s)_{mn} (\mathbf{d}_a)_{mn} + \frac{1}{2} \sum_{f, m, n} (\mathbf{M}_{fD})_{mn} (\mathbf{w}_f - \mathbf{w}_s)_{mn} - \frac{\mathbf{g}}{\theta} \cdot \mathbf{q}_I - \sum_f \mathbf{f}_f \cdot (\mathbf{v}_f - \mathbf{v}_s) + \sigma_g \phi'_g \geq 0, \quad (88)$$

where

$$\mathbf{t}_{aD}^s = \frac{1}{2}(\mathbf{t}_{aD} + \mathbf{t}_{aD}^T), \quad \mathbf{M}_{aD} = \mathbf{t}_{aD} - \mathbf{t}_{aD}^T. \quad (89, 90)$$

Here \mathbf{t}_{aD}^s is the symmetric part of \mathbf{t}_{aD} . \mathbf{M}_{aD} is two times of the skew part of \mathbf{t}_{aD} and meets the identity

$$\sum_a \mathbf{M}_{aD} = \mathbf{0}. \quad (91)$$

Equation (88) is the entropy inequality of unsaturated soil mixture.

4 Nonlinear Constitutive Equations and Field Equations of Unsaturated Soil Mixture

4.1 Nonlinear constitutive equations and field equations of unsaturated soil mixture

The independent variable in the entropy inequality (88)

$$Y_0 = \left(d_a, w_f - w_s, \frac{g}{\theta}, v_f - v_s, \phi'_g \right) \quad (92)$$

are called the thermodynamic force of mixture system, the dependent variables

$$J_0 = \left(t_{ad}^a, \frac{1}{2} M_{fd}, -q_l, -f_f, \sigma_g \right) \quad (93)$$

are the thermodynamic fluxes of mixture system. Thus Eq.(88) is shortened as

$$Y_0 \cdot J_0 \geq 0. \quad (94)$$

The dissipative part of constitutive equation turns to

$$J_0 = F(Y_0; Y_{R0}; Y_{I0}), \quad (95)$$

where

$$Y_{R0} = (\theta, C_s, \rho_g, \phi_l, \phi_g), \quad (96)$$

$$Y_{I0} = (G_s, e_g, \text{grad} \phi_l, \text{grad} \phi_g). \quad (97)$$

Y_{I0} could be treated as the inner variable of the mixture system. Edelen^[23] had given the general solution of inequality (94), and it is

$$F = \nabla_{(Y_0)} \Theta_0(Y_0; Y_{R0}; Y_{I0}) + W(Y_0; Y_{R0}; Y_{I0}), \quad (98)$$

where W satisfies

$$W \cdot Y_0 = 0. \quad (99)$$

The dissipative potential function of mixture system $\Theta_0(Y_0; Y_{R0}; Y_{I0})$ is given by

$$\Theta_0(Y_0; Y_{R0}; Y_{I0}) = \int_0^1 Y_0 \cdot F(\tau Y_0; Y_{R0}; Y_{I0}) \frac{d\tau}{\tau}. \quad (100)$$

Using Eqs.(95) and (98), the components of thermodynamic flux (93) are

$$t_{ad}^a = \frac{\partial \Theta_0}{\partial d_a} + W_a, \quad (101)$$

$$\frac{1}{2} M_{fd} = \frac{\partial \Theta_0}{\partial (w_f - w_s)} + W_{Mf} \quad (f = l, g), \quad (102)$$

$$-q_l = \frac{\partial \Theta_0}{\partial (g/\theta)} + W_q, \quad (103)$$

$$-f_f = \frac{\partial \Theta_0}{\partial (v_f - v_s)} + W_{ff} \quad (f = l, g), \quad (104)$$

$$\sigma_g = \frac{\partial \Theta_0}{\partial \phi'_g} + W_{\phi_g}, \quad (105)$$

where

$$W = (W_a, W_{Mf}, W_q, W_{ff}, W_{\phi_g}). \quad (106)$$

Although nonvanishing W provides the explanations for some phenomena, here we assume $W = 0$ for simplification. Eqs.(101) to (105) are reduced to

$$t_{ad}^s = \frac{\partial \Theta_0}{\partial d_a} \quad (a = s, l, g), \quad (107)$$

$$\frac{1}{2} M_{fd} = \frac{\partial \Theta_0}{\partial (w_f - w_s)} \quad (f = l, g), \quad (108)$$

$$-q_l = \frac{\partial \Theta_0}{\partial (g/\theta)}, \quad (109)$$

$$-f_f = \frac{\partial \Theta_0}{\partial (v_f - v_s)} \quad (f = l, g), \quad (110)$$

$$\sigma_g = \frac{\partial \Theta_0}{\partial \phi_g'}. \quad (111)$$

From the above derivation, the nonlinear constitutive equations of unsaturated soil are expressed, in the form of free energy functions Ψ_a ($a = s, l, g$) and dissipative potential function Θ_0 , as

$$\eta = -\frac{1}{\rho} \cdot \frac{\partial \Psi_l}{\partial \theta}, \quad (73)$$

$$q_l = -\frac{\partial \Theta_0}{\partial (g/\theta)}, \quad (109)$$

$$P = -\frac{\partial \Psi_l}{\partial \phi_g} - \frac{\partial \Theta_0}{\partial \phi_g'}, \quad (112)$$

$$p_l = -\text{grad} \Psi_l + \left(P + \frac{\partial \Psi_l}{\partial \phi_l} \right) \text{grad} \phi_l - \rho_l \eta_l g - \frac{\partial \Theta_0}{\partial (v_l - v_s)}, \quad (113)$$

$$p_g = -\text{grad} \Psi_g + \left(P + \frac{\partial \Psi_l}{\partial \phi_g} \right) \text{grad} \phi_g + \frac{\partial \Psi_l}{\partial \rho_g} \text{grad} \rho_g - \rho_g \eta_g g - \frac{\partial \Theta_0}{\partial (v_g - v_s)}, \quad (114)$$

$$p_s = - (p_l + p_g) = -\text{grad} \Psi_s + P \text{grad} \phi_s + \frac{\partial \Psi_l}{\partial C_s} [\text{grad} C_s] -$$

$$\rho_s \eta_s g + \sum_f \frac{\partial \Theta_0}{\partial (v_f - v_s)}, \quad (115)$$

$$t_s = (\Psi_s - P \phi_s) \mathbf{I} + 2F_s \left(\frac{\partial \Psi_l}{\partial C_s} \right) F_s^T + \frac{\partial \Theta_0}{\partial d_s} - \sum_f \frac{\partial \Theta_0}{\partial (w_f - w_s)}, \quad (116)$$

$$t_l = \left[\Psi_l - \left(P + \frac{\partial \Psi_l}{\partial \phi_l} \right) \phi_l \right] \mathbf{I} + \frac{\partial \Theta_0}{\partial d_l} + \frac{\partial \Theta_0}{\partial (w_l - w_s)}, \quad (117)$$

$$t_g = \left(\Psi_g - \rho_g \frac{\partial \Psi_l}{\partial \rho_g} \right) \mathbf{I} + \frac{\partial \Theta_0}{\partial d_g} + \frac{\partial \Theta_0}{\partial (w_g - w_s)}. \quad (118)$$

Equation (113) is obtained from Eqs.(75), (79) and (110), Eq.(114) from Eqs.(75), (67) and (110), Eq.(112) from Eqs.(84) and (111), Eq.(115) from Eqs.(31), (113), (114), (62) and (73), Eq.(116) from Eqs.(85), (69), (107), (108) and (112), Eq.(117) from Eqs.(86), (78), (107), (108) and (112), and Eq.(118) from Eqs.(87), (70), (107),

(108) and (112).

Using the constitutive equations of \mathbf{p}_a and \mathbf{t}_a Eqs.(113) to (115) and Eqs.(116) to (118) in the balance equations of momentum (25), the field equations of three constituents of unsaturated soil are

$$\begin{aligned} \rho_g \mathbf{v}_g' = & -\rho_g \text{grad} \left(\frac{\partial \Psi_1}{\partial \rho_g} \right) + \text{div} \left[\frac{\partial \Theta_0}{\partial \mathbf{d}_g} + \frac{\partial \Theta_0}{\partial (\mathbf{w}_g - \mathbf{w}_s)} \right] + \rho_g \mathbf{b}_g + \\ & \left(P + \frac{\partial \Psi_1}{\partial \phi_g} \right) \text{grad} \phi_g - \rho_g \eta_g \mathbf{g} - \frac{\partial \Theta_0}{\partial (\mathbf{v}_g - \mathbf{v}_s)}, \end{aligned} \quad (119)$$

$$\begin{aligned} \rho_l \mathbf{v}_l' = & -\phi_l \text{grad} \left(\frac{\partial \Psi_1}{\partial \phi_l} \right) + \text{div} \left[\frac{\partial \Theta_0}{\partial \mathbf{d}_l} + \frac{\partial \Theta_0}{\partial (\mathbf{w}_l - \mathbf{w}_s)} \right] + \rho_l \mathbf{b}_l - \\ & \phi_l \text{grad} P - \rho_l \eta_l \mathbf{g} - \frac{\partial \Theta_0}{\partial (\mathbf{v}_l - \mathbf{v}_s)}, \end{aligned} \quad (120)$$

$$\begin{aligned} \rho_s \mathbf{v}_s' = & \text{div} \left\{ 2\mathbf{F}_s \left(\frac{\partial \Psi_1}{\partial \mathbf{C}_s} \right) \mathbf{F}_s^T + \frac{\partial \Theta_0}{\partial \mathbf{d}_s} - \sum_f \frac{\partial \Theta_0}{\partial (\mathbf{w}_f - \mathbf{w}_s)} \right\} + \rho_s \mathbf{b}_s - \\ & \phi_s \text{grad} P + \frac{\partial \Psi_1}{\partial \mathbf{C}_s} [\text{grad} \mathbf{C}_s] - \rho_s \eta_s \mathbf{g} + \sum_f \frac{\partial \Theta_0}{\partial (\mathbf{v}_f - \mathbf{v}_s)}. \end{aligned} \quad (121)$$

The summation of above three equations is

$$\sum_a \rho_a \mathbf{v}_a' = \text{div} \mathbf{t}_1 + \rho \mathbf{b}, \quad (122)$$

where

$$\mathbf{t}_1 = \left(\Psi_1 - \rho_g \frac{\partial \Psi_1}{\partial \rho_g} - \phi_l \frac{\partial \Psi_1}{\partial \phi_l} \right) \mathbf{I} + 2\mathbf{F}_s \frac{\partial \Psi_1}{\partial \mathbf{C}_s} \mathbf{F}_s^T + \sum_a \frac{\partial \Theta_0}{\partial \mathbf{d}_a}. \quad (123)$$

Constitutive Eqs.(112) to (118), field equations (119) to (121), balance equations of mass (24) and (77), balance equation of energy (33), saturate condition Eq.(60) and constitutive equation of entropy density (73) form complete equations for the thermodynamic system of unsaturated soil mixture. Combining with boundary conditions and initial conditions, the deformation functions $\mathbf{x}(X_a, t)$, the partial stress tensors \mathbf{t}_a , the momentum supplies of constituents \mathbf{p}_a , the temperature distribution $\theta(\mathbf{x}, t)$ and the heat flux vector \mathbf{q}_1 can be obtained. Thus the thermodynamic process of the mixture system is completely decided.

4.2 The balance equation of energy and thermodynamic equilibrium state of unsaturated soil mixture

After using the constitutive equations of unsaturated soil mixture, the energy balance equation of the mixture system (33) is

$$\begin{aligned} \theta \left[\partial_t (\rho \eta) + \sum_a \text{div} (\rho_a \eta_a \mathbf{v}_a) \right] = \\ \sum_a \text{tr} (\mathbf{t}_{aD}^T \mathbf{L}_a) - \text{div} \mathbf{q}_1 - \sum_a \rho_a r_a - \sum_f \mathbf{f}_f \cdot (\mathbf{v}_f - \mathbf{v}_s) + \sigma_g \phi_g'. \end{aligned} \quad (124)$$

The distribution and change of temperature of the mixture $\theta(\mathbf{x}, t)$ could be decided from the balance equation of energy.

The entropy inequality (88) shows that the thermodynamic equilibrium state of the mixture system is

$$d_a = 0, w_f = w_s, g = 0, v_f = v_s, \phi'_g = 0 \quad (a = s, l, g; f = l, g). \quad (125)$$

In the state, the entropy of system does not change and thermodynamic flux (93) equals zero^[11], i.e.,

$$J_0(Y_0 = 0; Y_{R0}; Y_{I0}) = 0. \quad (126)$$

Thus, when know the free energy functions $\Psi_a(a = s, l, g)$ and the dissipative potential function Θ_0 of the unsaturated soil mixture, the constitutive equations, the field equations and the balance equation of energy can be derived, and the complete equations for the thermodynamic process of the unsaturated soil mixture is formed. The function $\Psi_a(a = s, l, g)$ and Θ_0 must meet constraints of axiom of frame indifference, and should be the functions of invariants of vectors and tensors in independent constitutive variables Y_0 , Y_{R0} and Y_{I0} .

5 Conclusion

The constitutive relation of unsaturated soil is studied by use of mixture theory. The nonlinear constitutive equation, the nonlinear field equations and the balance equation of energy are given, and the complete equations for the thermodynamic process of unsaturated soil mixture is constructed. The framework of the mixture theory for unsaturated soil is set up preliminarily. The work provides some help for developing the constitutive theory of unsaturated soil.

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