

微极性多组分多孔介质材料的混合物理论^{*}

黄璐, 赵成刚

(北京交通大学 土木建筑工程学院, 北京 100044)

(陈正汉推荐)

摘要: 将描述多组分系统的复合混合物理论与微极性连续介质力学理论相结合, 建立了描述微极性多组分多孔介质材料的混合物理论. 假定系统由多组分的微极性弹性固体和多组分微极性粘性流体组成. 给出由混合物理论建立的系统的平衡方程. 依据热力学第二定律以及本构假设建立了系统的本构方程, 并使场方程闭合. 为考虑固相的压缩性, 在液相自由能函数中引入液相体积分量作为内变量, 得到动力相容条件, 用以限制固、液两相界面压力差的变化. 最后, 基于线性化理论得到线性化的本构方程和场方程, 建立了考虑介质微极性的热-水力-力学组分运输模型. 此理论框架可以运用到可变形多孔介质中污染物、药物以及农药运输等问题中. 所得到的微极性多组分多孔介质系统的闭合场方程经退化后, 可变为固、流相都为单一组分的多孔介质系统场方程, 它与 Eringen 得到的结果一致.

关键词: 复合混合物理论; 微极性; 多组分; 可变形多孔介质

中图分类号: O33 **文献标识码:** A

DOI: 10.3879/j.issn.1000-0887.2009.05.008

引 言

可变形多孔介质中多组分流体的输运过程是一个多组分多相系统中多作用、多场耦合的热力学过程. 目前, 这类问题大多数是采用半理论、半经验的方法进行分析和处理. 而混合物理论可从理论上统一、科学地描述可变形多孔介质和其中流体的渗流、扩散以及热传导等现象. 近年来, 经典的混合物理论^[1-2]已被运用于研究三相非饱和土的性状^[3-7]. 为研究可混溶多组分流体在可变形多孔介质中的运动, Hassanizadeh^[8]利用混合物理论, 并通过平均化方法建立固相、流相以及流相组分的质量、动量、能量和熵的宏观平衡方程; 由熵不等式及本构假设, 发展了本构方程, 得到一般性的 Darcy 定律和 Fick 定律. Achanta 和 Cushman^[9]称这种把平均化理论和经典混合物理论相结合的理论为复合混合物理论. Achanta 和 Cushman^[9], Murad 和 Cushman^[10-11]以及 Bennethum 等^[12-17]采用复合混合物理论研究多组分可膨胀性多孔介质的多场耦合问题, 总结了针对膨胀性多孔介质的 Darcy 定律、Fick 定律、Fourier 定律以及 Terzaghi 有效应力原理, 得到了多组分无粘性流体饱和的膨胀性多孔介质的两尺度(微观尺度和细观尺度)和三尺度(微观尺度、细观尺度和宏观尺度)的分析方法. Singh^[18-20]在上述工作的基础上考

* 收稿日期: 2008-09-11; 修订日期: 2009-04-07

基金项目: 国家自然科学基金资助项目(50778013); 北京市自然科学基金资助项目(8082020)

作者简介: 黄璐(1982-), 女, 四川人, 博士生(联系人, E-mail: huanglu600@163.com).

虑了流体的粘性,提出了描述多组分粘性流体饱和的粘弹性可膨胀性多孔材料的方法. 以上的研究成果都没有考虑介质的转动自由度. 但实际上很多工程材料(如土、岩石及粒状材料等)都具有微极性,即其质点不仅发生平动还可能会发生旋转. 而具有质点旋转自由度的微极性材料,忽略其质点的旋转自由度就会带来一定的误差^[21]. 为此,Eringen^[22-23],Nowacki^[24]以及戴天民^[25-26]建立了微极性连续统理论,用于研究微极性连续统中的耦合作用问题. 但要将此理论运用到多相系统中则需与混合物理论相结合. 因此,Diebels^[27]在微极性连续介质理论的基础上结合经典混合物理论得到了由微极性弹性不可压缩固相和粘性流相组成的多孔介质的本构关系. Eringen^[21]也建立描述由弹性固体和粘性流体组成的多孔介质的微极性混合物理论,得到了闭合的线性化场方程,并给出初始和边界条件. 但这两位研究者得到的结果都是针对单一组分的流体. 而质量输运系统中,尤其是污染物输运系统中,孔隙流体通常为多组分流体. 因此有必要建立关于微极性多孔介质材料中多组分流体输运的混合物理论. 本文假定质量输运系统是由多组分的微极性弹性固体和多组分微极性粘性流体组成,在复合混合物理论的基础上,考虑组分的微极性,建立了描述微极性多组分多孔介质材料的复合混合物理论.

1 运动学和平衡方程

1.1 运动学

将多孔介质看作固相和流相组成的两相混合物,固相 s 形成多孔介质的可变形骨架;流相 f 可在其中运动并发生相互作用. 假设两相都由 N 种组分组成. 若某相中不含组分 j ,则相中与此组分相关的各物理量都为 0. 由平均化理论, α 相(s 相或 f 相)的平均单位体积质量 ρ^α 以及 α 相中组分 j 的质量分数 c_j^α 分别表示如下:

$$\rho^\alpha = \sum_{j=1}^N \rho_j^\alpha, \quad c_j^\alpha = \frac{\rho_j^\alpha}{\rho^\alpha}, \quad \sum_{j=1}^N c_j^\alpha = 1, \quad (1)$$

其中, ρ_j^α 代表组分 α_j 的体积平均真实密度. 各相有各自的存在空间,若多孔介质的孔隙率为 n ,即流相在单位体积的多孔介质中所占有的体积,也称流相的体积分数 n^f . 因此固相的体积分数 n^s 为 $1 - n$.

为将连续介质力学运用其中,混合物理论假设多孔介质各组分随机分布在控制空间上,为相互重叠的连续介质. 因此,可将 α 相的运动函数定义为: $x_k = X_k^\alpha(X_k^\alpha, t)$, 其中 α 代表 s 相或 f 相, X_k^α 表示 α 相质点的参考位置; x_k 为质点在 t 时的空间位置. 假设 $X_k^\alpha(X_k^\alpha, t)$ 可逆且可微,则 α 相在 t 时刻的速度 v_k^α 、加速度 a_k^α 及变形梯度 F_{kl}^α 各定义为

$$v_k^\alpha(x_k, t) = \frac{\partial X_k^\alpha(X_k^\alpha, t)}{\partial t}, \quad a_k^\alpha(x_k, t) = \frac{\partial^2 X_k^\alpha(X_k^\alpha, t)}{\partial t^2}, \quad F_{kl}^\alpha = \frac{\partial X_k^\alpha}{\partial X_l^\alpha}, \quad (2)$$

函数对时间的物质导数定义为: $d(\bullet)/dt = \partial(\bullet)/\partial t + v_k(\bullet)_{,k}$, 则相对于 f 相、 s 相以及组分 α_j 对时间的物质导数 d^s/dt , d^f/dt 和 d^{α_j}/dt 之间存在以下关系:

$$\frac{d^f(\bullet)}{dt} = \frac{d^s(\bullet)}{dt} + v_k^{f,s}(\bullet)_{,k}, \quad \frac{d^{\alpha_j}(\bullet)}{dt} = \frac{d^s(\bullet)}{dt} + u_k^{\alpha_j}(\bullet)_{,k}, \quad (3)$$

其中, $v_k^{f,s} = v_k^f - v_k^s$, $u_k^{\alpha_j} = v_k^{\alpha_j} - v_k^s$, $v_k^{\alpha_j}$ 为组分 α_j 的速度, $v_k^{f,s}$ 和 $u_k^{\alpha_j}$ 分别表示流相相对于固相及 α 相中组分 α_j 相对于此相的速度,也可分别称为渗流速度和扩散速度.

对于微极性材料,其运动由变形向量 w_k 和转动向量 ϕ_k 控制. 根据微极性连续介质力学理论微极性材料小变形条件下 α 相的线性应变张量 ϵ_{kl}^α 、线性旋转梯度张量 χ_{kl}^α 、应变率张量 $\dot{\epsilon}_{kl}^\alpha$ 和旋转率梯度张量 $\dot{\chi}_{kl}^\alpha$ 分别定义为^[21]

$$\mathfrak{E}_{kl}^{\alpha} = w_{l,k}^{\alpha} + \mathfrak{E}_{km} \mathfrak{Q}_m^{\alpha}, \quad \mathfrak{V}_{kl}^{\alpha} = \mathfrak{Q}_{k,l}^{\alpha}, \quad a_{kl}^{\alpha} = \mathfrak{E}_{kl}^{\alpha} = v_{l,k}^{\alpha} + \mathfrak{E}_{km} \mathfrak{Q}_m^{\alpha}, \quad b_{kl}^{\alpha} = \mathfrak{V}_{kl}^{\alpha} = \mathfrak{U}_{k,l}^{\alpha}, \quad (4)$$

其中, \mathfrak{E}_{km} 为 Eddington 张量, $w_{l,k}^{\alpha} = \partial w_l^{\alpha} / \partial x_k$, $\mathfrak{Q}_{k,l}^{\alpha} = \partial \mathfrak{Q}_k^{\alpha} / \partial x_l$; \mathfrak{U}_k^{α} 为微转动速度. 定义流相相对于固相和组分相对于所在相的微转动速度 \mathfrak{U}_k^s 和 r_k^{α} 分别为 $\mathfrak{U}_k^s = \mathfrak{U}_k^s - \mathfrak{U}_k^s$, $r_k^{\alpha} = \mathfrak{U}_k^{\alpha} - \mathfrak{U}_k^s$.

1.2 平衡定律

本节给出各相和相中各组分的质量、动量、动量矩以及能量守恒方程. 各相中存在 N 种组分, 但只有 $N-1$ 种组分的守恒方程相互独立^[8]. 假设组分为微观各向同性的微极性材料, 即其惯性矩为一个不变标量. 此外, 通常认为各组分总能达到热平衡状态, 因此只需考虑组分所在相的能量平衡方程.

质量守恒方程

$$\frac{d^{\alpha}(n^{\alpha} \rho^{\alpha})}{dt} + n^{\alpha} \rho^{\alpha} v_{l,l}^{\alpha} = \hat{e}^{\alpha}, \quad \alpha = s, f, \quad (5)$$

$$n^{\alpha} \rho^{\alpha} \frac{d^{\alpha} c_i^{\alpha}}{dt} + (n^{\alpha} \rho^{\alpha} u_{l,i}^{\alpha})_{,l} = \hat{e}^{\alpha_i} - c_i^{\alpha} \hat{e}^{\alpha}, \quad \alpha = s, f; \quad i = 1, \dots, N-1, \quad (6)$$

其中, \hat{e}^{α} (\hat{e}^{α_i}) 为 α 相(组分 α_i) 的质量交换率. 满足限制条件:

$$\begin{cases} \rho^{\beta} = c^{\beta} \rho^{\alpha}, \quad \rho^{\beta} = \sum_{j=1}^N \rho^{\beta_j}, \quad \hat{e}^{\alpha} = \sum_{j=1}^N \hat{e}^{\beta_j}, \\ \sum_{\alpha=s,f} \hat{e}^{\alpha} = 0, \quad \sum_{\alpha=s,f} \sum_{j=1}^N \hat{e}^{\beta_j} = 0, \quad \sum_{j=1}^N c^{\alpha_j} u_{l,j}^{\alpha} = 0. \end{cases} \quad (7)$$

动量守恒方程

$$n^{\alpha} \rho^{\alpha} \frac{d^{\alpha} v_l^{\alpha}}{dt} - (n^{\alpha} t_{kl}^{\alpha})_{,k} - n^{\alpha} \rho^{\alpha} g_l^{\alpha} = \hat{T}_l^{\alpha}, \quad (8)$$

$$\begin{aligned} n^{\alpha} \rho^{\alpha} c^{\alpha} \left(\frac{d^{\alpha} v_l^{\alpha}}{dt} - \frac{d^{\alpha_N} v_l^{\alpha_N}}{dt} \right) - (n^{\alpha} t_{kl}^{\alpha})_{,k} + \frac{c^{\alpha}}{c^{\alpha_N}} (n^{\alpha} t_{kl}^{\alpha_N})_{,k} - n^{\alpha} \rho^{\alpha} c^{\alpha} (g_l^{\alpha} - g_l^{\alpha_N}) = \\ \hat{T}_l^{\alpha} - \frac{c^{\alpha}}{c^{\alpha_N}} \hat{T}_l^{\alpha_N}, \end{aligned} \quad (9)$$

其中, t_{kl}^{α} , g_l^{α} 和 \hat{T}_l^{α} ($t_{kl}^{\alpha_i}$, $g_l^{\alpha_i}$ 和 $\hat{T}_l^{\alpha_i}$ 及 $t_{kl}^{\alpha_N}$, $g_l^{\alpha_N}$ 和 $\hat{T}_l^{\alpha_N}$) 表示 α 相(组分 α 及组分 α_N) 的平均应力张量、体积力密度以及动量交换率; c^{α_N} 和 $v_l^{\alpha_N}$ 为组分 α_N 的浓度和速度. 满足限制条件:

$$\begin{cases} \rho^{\alpha} v_l^{\alpha} = \sum_{j=1}^N \rho^{\beta_j} v_l^{\beta_j} = \rho^{\alpha} \sum_{j=1}^N c^{\beta_j} v_l^{\beta_j}, \quad t_{kl}^{\alpha} = \sum_{j=1}^N (t_{kl}^{\beta_j} - \rho^{\beta_j} u_k^{\beta_j} u_l^{\beta_j}), \\ \rho^{\alpha} g_l^{\alpha} = \sum_{j=1}^N \rho^{\beta_j} g_l^{\beta_j}, \quad \hat{T}_l^{\alpha} = \sum_{j=1}^N (\hat{T}_l^{\beta_j} + \hat{e}^{\beta_j} u_l^{\beta_j}), \quad \sum_{\alpha=s,f} \sum_{j=1}^N (\hat{T}_l^{\beta_j} + \hat{e}^{\beta_j} v_l^{\beta_j}) = 0. \end{cases} \quad (10)$$

动量矩守恒方程

$$n^{\alpha} \rho^{\alpha} \pi^{\alpha} \frac{d^{\alpha} \mathfrak{U}^{\alpha}}{dt} - \mathfrak{E}_{mn} (n^{\alpha} t_{mn}^{\alpha}) - (n^{\alpha} m_{kl}^{\alpha})_{,k} - n^{\alpha} \rho^{\alpha} l_l^{\alpha} = \hat{M}_l^{\alpha}, \quad (11)$$

$$\begin{aligned} n^{\alpha} \rho^{\alpha} c^{\alpha} \pi^{\alpha} \left(\frac{d^{\alpha} \mathfrak{U}^{\alpha}}{dt} - \frac{d^{\alpha_N} \mathfrak{U}^{\alpha_N}}{dt} \right) - \mathfrak{E}_{mn} \left(n^{\alpha} t_{mn}^{\alpha} - \frac{c^{\alpha} \pi^{\alpha}}{c^{\alpha_N} \pi^{\alpha_N}} n^{\alpha} t_{mn}^{\alpha_N} \right) - \\ (n^{\alpha} m_{kl}^{\alpha})_{,k} + \frac{c^{\alpha} \pi^{\alpha}}{c^{\alpha_N} \pi^{\alpha_N}} (n^{\alpha} m_{kl}^{\alpha_N})_{,k} - n^{\alpha} \rho^{\alpha} c^{\alpha} (l_l^{\alpha} - l_l^{\alpha_N}) = \\ \hat{M}_l^{\alpha} - \frac{c^{\alpha} \pi^{\alpha}}{c^{\alpha_N} \pi^{\alpha_N}} \hat{M}_l^{\alpha_N}, \end{aligned} \quad (12)$$

其中, π^{α} , m_{kl}^{α} , l_l^{α} 和 \hat{M}_l^{α} (π^{α_i} , $m_{kl}^{\alpha_i}$, $l_l^{\alpha_i}$ 和 $\hat{M}_l^{\alpha_i}$ 及 π^{α_N} , $m_{kl}^{\alpha_N}$, $l_l^{\alpha_N}$ 和 $\hat{M}_l^{\alpha_N}$) 分别为 α 相(组分 α 及组分 α_N) 的惯性矩、偶应力、体积偶应力密度以及动量矩交换率. 给出限制条件:

$$\begin{cases} \rho^\alpha \pi^\alpha \psi^\alpha = \sum_{j=1}^N \rho^\beta \pi^\beta \psi^\beta = \rho^\alpha \sum_{j=1}^N c^{\alpha\beta} \pi^\beta \psi^\beta, & \rho^\alpha l_l^\alpha = \sum_{j=1}^N \rho^\beta l_l^\beta, \\ \sum_{j=1}^N c^{\alpha\beta} \pi^\beta r_l^\beta = 0, & m_{kl}^\alpha = \sum_{j=1}^N (m_{kl}^{\alpha\beta} - \rho^\beta \pi^\beta r_k^\beta r_l^\alpha), \\ \dot{M}_l^\alpha = \sum_{j=1}^N \dot{M}_l^{\alpha\beta} + \hat{e}^{\alpha\beta} \pi^\beta r_l^\alpha, & \sum_{\alpha=s,f} \sum_{j=1}^N (\dot{M}_l^{\alpha\beta} + \hat{e}^{\alpha\beta} \pi^\beta \psi^\beta) = 0. \end{cases} \quad (13)$$

能量守恒方程

$$n^\alpha \rho^\alpha \frac{dE^\alpha}{dt} - n^\alpha t_{kl}^\alpha a_{kl}^\alpha - n^\alpha m_{kl}^\alpha b_{kl}^\alpha + (n^\alpha q_l^\alpha)_{,l} + n^\alpha \rho^\alpha h^\alpha = \hat{Q}^\alpha, \quad (14)$$

其中, E^α , q_l^α , h^α 和 \hat{Q}^α 分别表示 α 相的平均内能密度、热量通量、热量供给以及净能量交换率.

满足以下限制条件:

$$E^\alpha = \sum_{j=1}^N c^{\alpha\beta} \left[E^\beta + \frac{1}{2} u_l^\beta u_l^\beta + \frac{1}{2} \pi^\beta r_l^\beta r_l^\beta \right], \quad (15a)$$

$$h^\alpha = \sum_{j=1}^N c^{\alpha\beta} (h^\beta + g_l^\beta u_l^\beta + l_l^\beta r_l^\beta), \quad (15b)$$

$$q_l^\alpha = \sum_{j=1}^N \left[q_l^\beta - t_{lk}^\beta u_k^\alpha - m_{lk}^{\alpha\beta} + \rho^\beta \left(E^\beta + \frac{1}{2} u_k^\beta u_k^\beta + \frac{1}{2} \pi^\beta r_k^\beta r_k^\beta \right) u_l^\beta + \frac{1}{2} \rho^\beta \pi^\beta u_k^\beta \psi_k^\beta \psi_l^\beta \right], \quad (15c)$$

$$\hat{Q}^\alpha = \sum_{j=1}^N \left[\hat{Q}^\beta + \hat{T}_k^\beta u_k^\alpha + \hat{M}_k^\beta r_k^\alpha + \hat{e}^{\alpha\beta} \left(E^\beta - E^\alpha + \frac{1}{2} u_k^\beta u_k^\beta + \frac{1}{2} \pi^\beta r_k^\beta r_k^\beta \right) \right], \quad (15d)$$

$$\sum_{\alpha=s,f} \sum_{j=1}^N \left[\hat{Q}^\beta + \hat{T}_k^\beta u_k^\alpha + \hat{M}_k^\beta \psi_k^\alpha + \hat{e}^{\alpha\beta} \left(E^\beta + \frac{1}{2} v_k^\beta v_k^\beta + \frac{1}{2} \pi^\beta \psi_k^\beta \psi_k^\beta \right) \right] = 0, \quad (15e)$$

其中, E^α , q_l^α , h^α 和 \hat{Q}^α 为组分 α 的平均内能密度、热量通量、热量供给和净能量交换率.

2 本构方程

2.1 熵不等式

根据热力学第二定律(系统熵的净增长率大于等于0),将能量守恒方程及 Helmholtz 自由能函数 A (定义为: $A = E - \theta \eta$, E , θ 和 η 分别表示内能、绝对温度和熵)代入其中,得到受多组分流体饱和的多孔介质系统的熵不等式:

$$\begin{aligned} \Lambda = \sum_{\alpha=s,f} \sum_{j=1}^N \frac{1}{\theta^\alpha} & \left[-n^\alpha \rho^\alpha \left(\frac{dA^\alpha}{dt} + \eta^\alpha \frac{d\theta^\alpha}{dt} \right) + n^\alpha t_{kl}^\alpha a_{kl}^\alpha + n^\alpha m_{kl}^\alpha b_{kl}^\alpha - \right. \\ & \left. \frac{n^\alpha}{\theta^\alpha} q_k^\alpha \theta_{,k}^\alpha + \hat{Q}^\alpha - \theta^\alpha \hat{\eta}^\alpha \right] \geq 0, \end{aligned} \quad (16)$$

上式中自由能、熵以及熵交换率之间满足以下限制条件:

$$\begin{cases} A^\alpha = \sum_{j=1}^N c^{\alpha\beta} A^\beta, & \eta^\alpha = \sum_{j=1}^N c^{\alpha\beta} \eta^\beta, \\ \hat{\eta}^\alpha = \sum_{j=1}^N \hat{\eta}^{\alpha\beta} + \hat{e}^{\alpha\beta} (\eta^\beta - \eta^\alpha), & \sum_{\alpha=s,f} \sum_{j=1}^N \hat{\eta}^{\alpha\beta} + \hat{e}^{\alpha\beta} \eta^\beta = 0, \end{cases} \quad (17)$$

其中, a_{kl}^α 和 b_{kl}^α 分别为组分 α 的应变率和旋转率张量; Λ , A^α , θ^α , $\hat{\eta}^\alpha$ 和 $\hat{\eta}^{\alpha\beta}$ 分别为熵的净增长率、组分 α 的自由能、相 α 的绝对温度、相 α 和组分 α 的熵交换率. 假设混合物各组分温度相同且各组分间无质量交换. 将式(7)、(10)、(13)、(15)和(17)代入式(16)中,并由相和组分自

由能函数的物质导数之间的关系:

$$\sum_{j=1}^N n^{\alpha} \rho^{\beta} \frac{d^{\alpha} A^{\beta}}{dt} = n^{\alpha} \rho^{\alpha} \frac{d^{\alpha} A^{\alpha}}{dt} + \sum_{j=1}^N (n^{\alpha} c^{\alpha} \rho^{\alpha} A^{\alpha} u_l^{\alpha})_{,l}, \quad (18)$$

可将熵不等式转换为以下由相的物理量表示的形式:

$$\begin{aligned} \theta \Lambda = & \sum_{\alpha=s,f} - n^{\alpha} \rho^{\alpha} \left(\frac{d^{\alpha} A^{\alpha}}{dt} + \eta^{\alpha} \frac{d^{\alpha} \theta}{dt} \right) + \sum_{\alpha=s,f} n^{\alpha} \left(t_{kl}^{\alpha} + \sum_{j=1}^N \rho^{\beta} u_k^{\alpha} u_l^{\beta} \right) a_{kl}^{\alpha} + \\ & \sum_{\alpha=s,f} n^{\alpha} \left(m_{kl}^{\alpha} + \sum_{j=1}^N \rho^{\beta} \mathbb{T} r_k^{\alpha} u_l^{\beta} \right) b_{lk}^{\alpha} - \hat{T}_k^f v_k^{f,s} - \hat{M}_k^f \mathcal{U}_k^{f,s} + \sum_{\alpha=s,f} \sum_{i=1}^{N-1} n^{\alpha} (t_{kl}^{\alpha} - \rho^{\alpha} c^{\alpha} \delta_{kl}) u_{l,k}^{\alpha} + \\ & \sum_{\alpha=s,f} \sum_{i=1}^{N-1} n^{\alpha} m_{kl}^{\alpha} r_{l,k}^{\alpha} - \sum_{\alpha=s,f} \sum_{i=1}^{N-1} \left[n^{\alpha} t_{kl}^{\alpha} \left(\frac{c^{\alpha}}{c^{\alpha_N}} \right)_{,l} + \tilde{T}_k^{\alpha} + (n^{\alpha} \rho^{\alpha} c^{\alpha} A^{\alpha})_{,k} \right] u_k^{\alpha} + \\ & \sum_{\alpha=s,f} \sum_{j=1}^N \left[n^{\alpha} \left(\mathcal{E}_{kmnlm}^{\alpha} - \frac{c^{\alpha} \mathbb{T}^{\alpha}}{c^{\alpha_N} \mathbb{T}^{\alpha_N}} \mathcal{E}_{kmnlm}^{\alpha_N} \right) - \tilde{M}_k^{\alpha} - n^{\alpha} m_{kl}^{\alpha_N} \left(\frac{c^{\alpha} \mathbb{T}^{\alpha}}{c^{\alpha_N} \mathbb{T}^{\alpha_N}} \right)_{,l} \right] r_k^{\alpha} - \\ & \sum_{\alpha=s,f} \left[\frac{n^{\alpha} q_k^{\alpha}}{\theta} - \sum_{j=1}^N \frac{n^{\alpha}}{\theta} (t_{kl}^{\alpha} u_l^{\beta} + m_{kl}^{\alpha} r_l^{\beta} - \rho^{\alpha} c^{\alpha} A^{\alpha} u_k^{\beta} + \Delta^2) \right] \theta_{,k} \geq 0, \quad (19) \end{aligned}$$

其中 δ_{kl} 为 Kronecker 符号; $A^{\alpha_i} = A^{\alpha} - A^{\alpha_N}$, $t_{kl}^{\alpha_i} = t_{kl}^{\alpha} - (c^{\alpha}/c^{\alpha_N}) t_{kl}^{\alpha_N}$, $m_{kl}^{\alpha_i} = m_{kl}^{\alpha} - c^{\alpha} \mathbb{T}^{\alpha}/(c^{\alpha_N} \mathbb{T}^{\alpha_N}) m_{kl}^{\alpha_N}$, $\tilde{T}_k^{\alpha_i} = \hat{T}_k^{\alpha} - (c^{\alpha}/c^{\alpha_N}) \hat{T}_k^{\alpha_N}$, $\tilde{M}_k^{\alpha_i} = \hat{M}_k^{\alpha} - (c^{\alpha} \mathbb{T}^{\alpha}/(c^{\alpha_N} \mathbb{T}^{\alpha_N})) \hat{M}_k^{\alpha_N}$, 分别定义为组分 α 的相对自由能密度、相对应力张量、相对偶应力张量、相对动量交换率以及相对动量矩交换率; A^{α_N} 为组分 α_N 的自由能; 符号 Δ^2 为

$$\Delta^2 = - \frac{1}{2} \rho^{\beta} u_l^{\alpha} u_l^{\alpha} u_k^{\alpha} - \frac{1}{2} \rho^{\beta} \pi^{\beta} r_l^{\alpha} r_l^{\alpha} u_k^{\alpha} - \frac{1}{2} \rho^{\beta} \pi^{\beta} u_l^{\alpha} \psi^{\beta} \psi^{\beta}.$$

2.2 本构假设

熵不等式限制了系统物理量的发展方向, 对建立本构关系起到关键性作用. 根据上述的平衡方程和熵不等式, 可知系统中存在以下未知量:

$$\begin{aligned} n, \rho^{\alpha}, c^{\alpha_i}, v_k^{\alpha}, \mathcal{U}_k^{\alpha}, u_k^{\alpha_i}, r_k^{\alpha_i}, \theta, A^{\alpha}, A^{\alpha_i}, \eta^{\alpha}, \eta^{\alpha_i}, t_{kl}^{\alpha}, t_{kl}^{\alpha_i}, \hat{T}_k^{\alpha}, \tilde{T}_k^{\alpha_i}, \\ m_{kl}^{\alpha}, m_{kl}^{\alpha_i}, \hat{M}_k^f, \tilde{M}_k^{\alpha_i}, q_k^{\alpha}, \hat{Q}^{\alpha}, \quad (20) \end{aligned}$$

可知系统未知数个数大于方程个数, 为使系统闭合, 需根据热力学第二定律和本构假设补充相关变量与独立变量之间的本构关系. 根据所模拟的多孔介质的性质, 假定相关变量为以下独立变量的函数, 其形式如下:

$$\begin{aligned} \Psi = \Psi(n, \rho^{\alpha}, c^{\alpha_i}, \mathcal{E}_{kl}^s, \mathcal{V}_{kl}^s, a_{kl}^f, b_{kl}^f, \theta, n, k, \rho^{\alpha}, c^{\alpha_i}, \mathcal{E}_{kl}^s, m, \\ \mathcal{V}_{kl}^s, m, \theta, k, v_k^{f,s}, \mathcal{U}_k^s, u_k^{\alpha_i}, r_k^{\alpha_i}, u_{k,l}^f, r_{k,l}^f), \quad (21) \end{aligned}$$

为略去繁琐的推导过程, 根据已有研究成果^[15,20,27-28]可知: 针对此系统的自由能函数与独立变量 $a_{kl}^f, b_{kl}^f, n, k, \rho^{\alpha}, c^{\alpha_i}, \mathcal{E}_{kl}^s, \mathcal{V}_{kl}^s, \theta, k, v_k^{f,s}, \mathcal{U}_k^s, u_k^{\alpha_i}, r_k^{\alpha_i}, u_{k,l}^f$ 及 $r_{k,l}^f$ 无关. 同时由相分离原理^[29], 即各相的自由能密度只与此相的状态变量有关, 假设固相和流相的自由能函数分别定义为

$$A^s = A^s(\rho^s, c^{s_i}, \mathcal{E}_{kl}^s, \mathcal{V}_{kl}^s, \theta), \quad A^f = A^f(n, \rho^f, c^{f_i}, \theta). \quad (22)$$

2.3 本构关系

根据本构假设式(22), 可通过多元复合函数的求导法则将熵不等式中的任何微分项展开, 并将质量守恒方程(5)和(6), 物质导数之间的关系式(3)以及式(4)代入到各相自由能函数的求导展开式中, 最后代入到熵不等式(19)中, 整理得到:

$$\theta \Lambda = n^s \left[t_{kl}^s - \rho^s \frac{\partial A^s}{\partial \mathcal{E}_{kl}^s} + p^s \delta_{kl} + \sum_{j=1}^N \rho^{\beta} u_k^s u_l^{\beta} \right] a_{kl}^s +$$

$$\begin{aligned}
& n^s \left(m_{kl}^s - \rho^s \frac{\partial A^s}{\partial y_{lk}^s} + \sum_{j=1}^N \sigma^j \pi^j r_k^s u_l^j \right) b_{lk}^s + \left(p^f - p^s - n^f \rho^f \frac{\partial A^f}{\partial n} \right) \frac{d^s n}{dt} - \\
& \left(\rho^m \Gamma^m + n^s \rho^s \frac{\partial A^s}{\partial \theta} + n^f \rho^f \frac{\partial A^f}{\partial \theta} \right) \frac{d^s \theta}{dt} + n^f \left(t_{kl}^f + p^f \delta_{kl} + \sum_{j=1}^N \rho^j u_k^f u_l^j \right) a_{kl}^f + \\
& n^f \left(m_{kl}^f + \sum_{j=1}^N \rho^j \pi^j r_k^f u_l^j \right) b_{lk}^f + \left(p^f n_{,k}^f - n^f \rho^f \frac{\partial A^f}{\partial n} n_{,k} - n^f \rho^f \Gamma^f \theta_{,k} - \right. \\
& \left. n^f \rho^f \frac{\partial A^f}{\partial \theta} \theta_{,k} - T_k^f \right) v_k^{fs} - \hat{M}_k^f v_k^{fs} + \sum_{\alpha=s,f} \sum_{i=1}^{N-1} n^\alpha \left(t_{kl}^{\alpha} - \rho^\alpha c^{\alpha} A^{\alpha} \delta_{kl} + \rho^\alpha c^{\alpha} \mu^{\alpha} \delta_{kl} \right) u_{l,k}^{\alpha} + \\
& \sum_{\alpha=s,f} \sum_{i=1}^{N-1} n^\alpha m_{kl}^{\alpha} r_{l,k}^{\alpha} + \sum_{\alpha=s,f} \sum_{i=1}^{N-1} \left[\mu^{\alpha} (n^{\alpha} \rho^{\alpha} c^{\alpha})_{,k} - (n^{\alpha} \rho^{\alpha} c^{\alpha} A^{\alpha})_{,k} - n^{\alpha} t_{kl}^{\alpha} \left(\frac{c^{\alpha}}{c^{\alpha N}} \right)_{,l} - \right. \\
& \left. \tilde{T}_k^{\alpha} \right] u_k^{\alpha} + \sum_{\alpha=s,f} \sum_{i=1}^{N-1} \left[n^\alpha \left(\mathcal{E}_{\alpha m l n i}^{\alpha} - \frac{c^{\alpha} \pi^{\alpha}}{c^{\alpha N} \pi^{\alpha N}} \mathcal{E}_{\alpha m n i}^{\alpha} \right) - \tilde{M}_k^{\alpha} - n^{\alpha} m_{kl}^{\alpha N} \left(\frac{c^{\alpha} \pi^{\alpha}}{c^{\alpha N} \pi^{\alpha N}} \right)_{,l} \right] r_k^{\alpha} - \\
& \sum_{\alpha=s,f} \left[\frac{n^{\alpha} q_k^{\alpha}}{\theta} - \sum_{j=1}^N \frac{n^{\alpha}}{\theta} (t_{kl}^{\alpha} u_l^j + m_{kl}^{\alpha} v_l^j - \rho^j A^j u_k^j + \Delta^2) \right] \theta_{,k} \geq 0, \quad (23)
\end{aligned}$$

其中, p^α 和 μ^α 分别是 α 相热力学力和组分 α_i 的相对化学势, 定义为

$$p^\alpha = (\rho^\alpha)^2 \frac{\partial A^\alpha}{\partial \rho^\alpha}, \quad \mu^\alpha = \frac{\partial A^\alpha}{\partial c^{\alpha}}. \quad (24)$$

因本构函数与 a_{kl}^s , b_{lk}^s , u_l^i , $r_{l,k}^i$ 和 $d^s \theta / dt$ 无关, 为满足限制热力学过程可发生性的熵不等式, 需使不等式中以上变量相应的系数项为 0, 因此得到:

$$\begin{cases} t_{kl}^s = \rho^s \frac{\partial A^s}{\partial \mathcal{E}_{kl}^s} - p^s \delta_{kl} - \sum_{j=1}^N \rho^j u_k^s u_l^j, & m_{kl}^s = \rho^s \frac{\partial A^s}{\partial y_{lk}^s} - \sum_{j=1}^N \rho^j \pi^j r_k^s u_l^j, \\ \rho^m \Gamma^m = n^s \rho^s \Gamma^s + n^f \rho^f \Gamma^f = -n^s \rho^s \frac{\partial A^s}{\partial \theta} - n^f \rho^f \frac{\partial A^f}{\partial \theta}, \\ t_{kl}^s = \rho^s c^s (A^s - \mu^s) \delta_{kl}, & m_{kl}^s = 0, \end{cases} \quad (25)$$

若不考虑毛细松弛效应, 则

$$n^f \rho^f \frac{\partial A^f}{\partial n} = (\rho^f)^2 \frac{\partial A^f}{\partial \rho^f} - (\rho^f)^2 \frac{\partial A^s}{\partial \rho^f} = p^f - p^s, \quad (26)$$

此式即为限制固、流相界面处压力差变化的动力相容条件^[4,30]. 由于流体具有粘性, 其应力张量由平衡部分和耗散部分组成, 偶应力只由耗散部分组成:

$$\begin{cases} t_{kl}^f = -p^f \delta_{kl} + D^f t_{kl}^f - \sum_{j=1}^N \rho^j u_k^f u_l^j, & m_{kl}^f = D m_{kl}^f - \sum_{j=1}^N \rho^j \pi^j r_k^f u_l^j, \\ t_{kl}^f = \rho^f c^f (A^f - \mu^f) \delta_{kl} + D t_{kl}^f, & m_{kl}^f = D m_{kl}^f. \end{cases} \quad (27)$$

因此, 熵不等式的剩余项为

$$\begin{aligned}
D = & J_{kl}^f a_{kl}^f + J_{kl}^f b_{lk}^f + \sum_{i=1}^{N-1} J_{kl}^f u_l^i u_k^i + \sum_{i=1}^{N-1} J_{kl}^f r_k^i r_{l,k}^i + J_k^f v_k^{fs} + J_k^f v_k^{fs} + \\
& \sum_{\alpha=s,f} \sum_{i=1}^{N-1} J_k^{\alpha} u_k^{\alpha} + \sum_{\alpha=s,f} \sum_{i=1}^{N-1} J_k^{\alpha} r_k^{\alpha} + J_k^0 \theta_{,k} \geq 0, \quad (28)
\end{aligned}$$

其中, D 即代表总的能量耗散. 不等式左边的前 4 项是由流体的粘性引起的耗散, 第 5 项和第 6 项分别为流相相对于固相流动和转动引起的耗散, 第 7 项和第 8 项是由于组分扩散和组分相对所在相的转动引起的耗散, 最后 1 项即由热传导引起的耗散. 忽略与扩散速度有关的高阶项, 则各通量表示为

$$\left\{ \begin{aligned} J_{kl}^a &= n^f D t_{kl}^f, J_{kl}^b = n^f D m_{kl}^f, J_{kl}^{\cdot u^i} = n^f D t_{kl}^f, J_{kl}^{\cdot r^i} = n^f D m_{kl}^f, \\ J_k^{v^{f,s}} &= p^f n_{,k}^f - n^f \rho^f \frac{\partial A^f}{\partial n_{,k}} - \hat{T}_k^f, J_k^{u^i} = -\hat{M}_k^i, \\ J_k^{u^{\alpha_i}} &= u^{\alpha_i} (n^{\alpha_i} \rho^{\alpha_i} c^{\alpha_i})_{,k} - (n^{\alpha_i} \rho^{\alpha_i} A^{\alpha_i})_{,k} - n^{\alpha_i} t_{kl}^{\alpha_i} \left(\frac{c^{\alpha_i}}{c^{\alpha_i N}} \right)_{,l} - \hat{T}_k^{\alpha_i}, \\ J_k^{r^{\alpha_i}} &= n^{\alpha_i} \left(\varepsilon_{kmnl}^{\alpha_i} - \frac{c^{\alpha_i} \mathcal{T}^{\alpha_i}}{c^{\alpha_i N} \mathcal{T}^{\alpha_i N}} \varepsilon_{kmnl}^{\alpha_i} \right) - n^{\alpha_i} m_{kl}^{\alpha_i} \left(\frac{c^{\alpha_i} \mathcal{T}^{\alpha_i}}{c^{\alpha_i N} \mathcal{T}^{\alpha_i N}} \right)_{,l} - \hat{M}_k^{\alpha_i}, \\ J_k^\theta &= \sum_{\alpha=s,f} n^{\alpha} \frac{q_k^{\alpha}}{\theta}. \end{aligned} \right. \quad (29)$$

当系统达到平衡状态时, 广义力 a_{kl}^f , b_{kl}^f , $u_{l,k}^f$, $r_{l,k}^f$, $v_k^{f,s}$, u_k^i , $u_k^{\alpha_i}$, $r_k^{\alpha_i}$ 以及 $\theta_{,k}$ 消失, 系统的熵到达最大值, 熵增量为最小. 处于非平衡态时, 剩余的熵不等式 (28) 可表示为热力学广义力和热力学广义通量相乘的形式, 则各广义通量为

$$\left\{ \begin{aligned} J_{kl}^a &= \frac{\partial D}{\partial a_{kl}^f}, J_{kl}^b = \frac{\partial D}{\partial b_{kl}^f}, J_{kl}^{\cdot u^i} = \frac{\partial D}{\partial u_{l,k}^f}, J_{kl}^{\cdot r^i} = \frac{\partial D}{\partial r_{l,k}^f}, J_k^{v^{f,s}} = \frac{\partial D}{\partial v_k^{f,s}}, \\ J_k^{u^i} &= \frac{\partial D}{\partial u_k^i}, J_k^{u^{\alpha_i}} = \frac{\partial D}{\partial u_k^{\alpha_i}}, J_k^{r^{\alpha_i}} = \frac{\partial D}{\partial r_k^{\alpha_i}}, J_k^\theta = \frac{\partial D}{\partial \theta_{,k}}. \end{aligned} \right. \quad (30)$$

为发展线性本构关系, 假定系统的初始状态为均匀的、平衡的、各向同性的, 表示如下:

$$\left\{ \begin{aligned} &\left\{ n, \rho^f, c^{\alpha_i}, \theta, \varepsilon_{kl}^s, \gamma_{kl}^s, a_{kl}^f, b_{kl}^f, v_k^{f,s}, u_k^i, u_k^{\alpha_i}, r_k^{\alpha_i}, u_{l,k}^f, r_{l,k}^f \right\} = \\ &\left\{ n^0, \rho^0, c^{\alpha_i 0}, \theta^0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0 \right\}, \end{aligned} \right. \quad (31)$$

在微小扰动下 (小变形, 温度、相的密度以及组分的浓度变化很小), 多孔介质到达一种新的状态 (近平衡状态):

$$\left\{ n^0 + n, \rho^0 + \rho^f, c^{\alpha_i 0} + c^{\alpha_i}, \theta^0 + \theta, \varepsilon_{kl}^s, \gamma_{kl}^s, a_{kl}^f, b_{kl}^f, v_k^{f,s}, u_k^i, u_k^{\alpha_i}, r_k^{\alpha_i}, u_{l,k}^f, r_{l,k}^f \right\}, \quad (32)$$

从此处开始 n , ρ^f , c^{α_i} , θ , ε_{kl}^s , γ_{kl}^s , a_{kl}^f , b_{kl}^f , $v_k^{f,s}$, u_k^i , $u_k^{\alpha_i}$, $r_k^{\alpha_i}$, $u_{l,k}^f$ 和 $r_{l,k}^f$ 为对应物理量的增量.

根据自由能函数和耗散函数的本构假设, 可将自由能和耗散能通过 Taylor 展开式展开^[4]:

$$\begin{aligned} n^{s0} \rho^{s0} A^s &= \frac{1}{2} n^{s0} A_{klmn}^s \varepsilon_{kl}^s \varepsilon_{mn}^s + \frac{1}{2} n^{s0} B_{klmn}^s \gamma_{kl}^s \gamma_{mn}^s - \frac{1}{2} n^{s0} C^s \theta^2 + \\ &\frac{1}{2} n^{s0} K^s \left(\frac{\rho^s}{\rho^0} \right)^2 + \frac{1}{2} n^{s0} \sum_{i=1}^{N-1} L^s (c^s)^2 + n^{s0} R_{klmn}^{s \gamma s} \varepsilon_{kl}^s \gamma_{mn}^s - \\ &n^{s0} R_{kl}^{\theta \gamma s} \theta \gamma_{kl}^s + n^{s0} R_{kl}^{\rho \gamma s} \frac{\rho^s}{\rho^0} \gamma_{kl}^s - n^{s0} R_{kl}^{\theta \varepsilon s} \theta \varepsilon_{kl}^s + n^{s0} R_{kl}^{\rho \varepsilon s} \frac{\rho^s}{\rho^0} \varepsilon_{kl}^s - \\ &n^{s0} \lambda^{\rho 0 s} \frac{\rho^s}{\rho^0} \theta + \sum_{i=1}^{N-1} n^{s0} R_{kl}^{c_i \gamma s} c^s \gamma_{kl}^s + \sum_{i=1}^{N-1} n^{s0} R_{kl}^{c_i \varepsilon s} c^s \varepsilon_{kl}^s + \\ &\sum_{i=1}^{N-1} n^{s0} \lambda^{\rho c_i s} \frac{\rho^s}{\rho^0} c^s - \sum_{i=1}^{N-1} n^{s0} \lambda^{\theta c_i s} \theta c^s + \sum_{m=1, m \neq i}^{N-1} n^{s0} \lambda_{c_i c_m s}^s c^s c^m, \end{aligned} \quad (33)$$

$$\begin{aligned} n^{f0} \rho^{f0} A^f &= \frac{1}{2} n^{f0} K^f \left(\frac{\rho^f}{\rho^0} \right)^2 + \frac{1}{2} n^{f0} \Theta^f n^2 - \frac{1}{2} n^{f0} C^f \theta^2 + \frac{1}{2} n^{f0} \sum_{i=1}^{N-1} L^f (c^f)^2 - \\ &n^{f0} \lambda^{\rho 0 f} \frac{\rho^f}{\rho^0} \theta - n^{f0} \lambda^{\theta 0 f} n \theta + n^{f0} \lambda^{n \rho f} n \frac{\rho^f}{\rho^0} + \sum_{i=1}^{N-1} n^{f0} \lambda^{\rho c_i f} \frac{\rho^f}{\rho^0} c^f + \\ &\sum_{i=1}^{N-1} n^{f0} \lambda^{n c_i f} n c^f + \sum_{m=1, m \neq i}^{N-1} n^{f0} \lambda_{c_i c_m f}^f c^f c^m - \sum_{i=1}^{N-1} n^{f0} \lambda^{\theta c_i f} \theta c^f, \end{aligned} \quad (34)$$

其中, A^s 和 A^f 代表该物理量的增量. A_{klmn}^s 和 B_{klmn}^s 为固相的微极性弹性常数; K^s 和 C^s 分别

为 α 相的体积模量和常体积比热系数; Θ^f 和 L^{α_i} 分别代表体积分数和浓度变化影响的参数; χ^{ba} , R_{kl}^{ba} 和 R_{klmn}^{aba} 分别代表在相 α 中因素 a 和 b 耦合的作用参数. 通常, 将耗散能分为两部分展开^[21]

$$D_1 = \frac{1}{2} n^{f0} M_{klmn}^f u_{kl}^f u_{mn}^f + \frac{1}{2} \sum_{i=1}^{N-1} n^{f0} M_{klmn}^i u_{k,l}^i u_{m,n}^i + \frac{1}{2} \xi^v v_k^f v_k^f + \frac{1}{2} \sum_{\alpha=s,f} \sum_{i=1}^{N-1} \xi^u u_k^{\alpha_i} u_k^{\alpha_i} + \frac{1}{2} \xi^{\theta} \theta_{,k} \theta_{,k} + \sum_{\alpha=s,f} \sum_{i=1}^{N-1} \zeta^v v_k^f v_k^f u_k^{\alpha_i} + \sum_{\alpha=s,f} \sum_{i=1}^{N-1} \zeta^u u_k^{\alpha_i} \theta_{,k} + \zeta^v v_k^f v_k^f \theta_{,k}, \quad (35)$$

$$D_2 = \frac{1}{2} n^{f0} N_{klmn}^f b_{kl}^f b_{mn}^f + \frac{1}{2} \sum_{i=1}^{N-1} n^{f0} N_{klmn}^i r_{k,l}^i r_{m,n}^i + \frac{1}{2} \xi^v v_k^f v_k^f + \frac{1}{2} \sum_{\alpha=s,f} \sum_{i=1}^{N-1} \zeta^r r_k^{\alpha_i} r_k^{\alpha_i}, \quad (36)$$

其中, 耗散能 D_1 和 D_2 也都代表对应物理量的增量. M_{klmn}^f , N_{klmn}^f , M_{klmn}^i 和 N_{klmn}^i 为微极性粘性流体常数; ξ^a 为因素 a 的影响参数; ζ^{ab} 代表因素 b 和 d 耦合的作用参数. 为满足材料的稳定性条件以及物理过程的可发生性, 其自由能函数和耗散函数应非负, 则其系数组成的矩阵为半正定矩阵, 即须使系数矩阵的各阶顺序主子式大于等于 0.

当为各向同性材料时, 材料常数如下:

$$\left\{ \begin{array}{l} R_{kl}^{\rho \epsilon s} = \lambda^{\rho \epsilon s} \delta_{kl}, \quad R_{kl}^{\theta \epsilon s} = \lambda^{\theta \epsilon s} \delta_{kl}, \quad R_{kl}^{\epsilon c_i s} = \lambda^{\epsilon c_i s} \delta_{kl}, \\ R_{klmn}^{\epsilon v s} = 0, \quad R_{kl}^{\rho v s} = R_{kl}^{\theta v s} = R_{kl}^{\epsilon c_i s} = 0, \\ A_{klmn}^s = \lambda^s \delta_{kl} \delta_{mn} + (\mu^s + \kappa^s) \delta_{km} \delta_{ln} + \mu^s \delta_{kn} \delta_{lm}, \\ B_{klmn}^s = \alpha^s \delta_{kl} \delta_{mn} + \beta^s \delta_{kn} \delta_{lm} + \gamma^s \delta_{km} \delta_{ln}, \\ M_{klmn}^f = \lambda^f \delta_{kl} \delta_{mn} + (\mu^f + \kappa^f) \delta_{km} \delta_{ln} + \mu^f \delta_{kn} \delta_{lm}, \\ N_{klmn}^f = \alpha^f \delta_{kl} \delta_{mn} + \beta^f \delta_{kn} \delta_{lm} + \gamma^f \delta_{km} \delta_{ln}, \\ M_{klmn}^i = \lambda^i \delta_{kl} \delta_{mn} + (\mu^i + \kappa^i) \delta_{kn} \delta_{lm} + \mu^i \delta_{km} \delta_{ln}, \\ N_{klmn}^i = \alpha^i \delta_{kl} \delta_{mn} + \beta^i \delta_{kn} \delta_{lm} + \gamma^i \delta_{km} \delta_{ln}. \end{array} \right. \quad (37)$$

将式 (33) ~ (36) 代入到本构关系式 (24)、(25a, b) 和 (26) 中, 并根据式 (37) 得到由多组分可压缩弹性固体和多组分粘性流体组成的各向同性微极性多孔介质的本构方程, 分别如下:

$$p^s = K^s \frac{\rho^s}{\rho^{s0}} + \lambda^{\rho \epsilon s} \epsilon_{mm}^s + \sum_{i=1}^{N-1} \lambda^{\rho c_i s} c^s_i - \lambda^{\rho \theta s} \theta, \quad (38a)$$

$$p^f = K^f \frac{\rho^f}{\rho^{f0}} + \lambda^{\rho f} n + \sum_{i=1}^{N-1} \lambda^{\rho c_i f} c^f_i - \lambda^{\rho \theta f} \theta, \quad (38b)$$

$$\rho^{s0} \mu^s_i = L^s c^s_i + \lambda^{\rho c_i s} \frac{\rho^s}{\rho^{s0}} + \sum_{m=1, m \neq i}^{N-1} \chi_i c^m s c^s_m + \lambda^{\epsilon c_i s} \epsilon_{nm}^s - \lambda^{\theta c_i s} \theta, \quad (38c)$$

$$\rho^{f0} \mu^f_i = L^f c^f_i + \lambda^{\rho c_i f} \frac{\rho^f}{\rho^{f0}} + \sum_{m=1, m \neq i}^{N-1} \chi_i c^m f c^f_m + \lambda^{\rho c_i f} n - \lambda^{\theta c_i f} \theta, \quad (38d)$$

$$t_{kl}^s = \left[(\lambda^s + \lambda^{\rho \epsilon s}) \epsilon_{mm}^s + (\lambda^{\rho \theta s} - \lambda^{\theta \epsilon s}) \theta - (K^s - \lambda^{\rho \epsilon s}) \frac{\rho^s}{\rho^{s0}} + \sum_{i=1}^{N-1} (\lambda^{\epsilon c_i s} - \lambda^{\rho c_i s}) c^s_i \right] \delta_{kl} + \mu^s \epsilon_{,k}^s + (\mu^s + \kappa^s) \epsilon_{,k}^s, \quad (38e)$$

$$t_{kl}^f = \left[\lambda^f c^f_{mm} + \lambda^{\rho \theta f} \theta - K^f \frac{\rho^f}{\rho^{f0}} - \lambda^{\rho f} n - \sum_{i=1}^{N-1} \lambda^{\rho c_i f} c^f_i \right] \delta_{kl} +$$

$$\mu^f a_{lk}^f + (\mu^f + \kappa^f) a_{kl}^f, \quad (38f)$$

$$m_{kl}^s = \alpha^s \gamma_{mm}^s \delta_{kl} + \beta^s \gamma_{kl}^s + \gamma^s \gamma_{lk}^s, \quad m_{kl}^f = \alpha^f b_{mn}^f \delta_{kl} + \beta^f b_{kl}^f + \gamma^f b_{lk}^f, \quad (38g, h)$$

$$\rho^{n0} \Gamma^n = \sum_{\alpha=s,f} n^{\alpha 0} C^{\alpha \theta} + \sum_{\alpha=s,f} n^{\alpha 0} \lambda^{\rho \theta \alpha} \frac{\rho^{\theta}}{\rho^{\alpha 0}} + \sum_{\alpha=s,f} \sum_{i=1}^{N-1} n^{\alpha 0} \lambda^{\theta c_i} c^{\alpha_i} + n^{s0} \lambda^{\theta \varepsilon s} \varepsilon_{mm}^s + n^{f0} \lambda^{\theta n f} n, \quad (38i)$$

$$p^f - p^s = n^{f0} \Theta^f n - n^{f0} \lambda^{\theta n f} \theta + n^{f0} \lambda^{\theta \rho f} \frac{\rho^f}{\rho^{f0}} + \sum_{i=1}^{N-1} n^{f0} \lambda^{\theta c_i f} c^f_i, \quad (38j)$$

$$t_{kl}^f - \rho^f c^f_i (A^f_i - \mu^f_i) \delta_{kl} = \lambda^f_i u_{m,m}^f \delta_{kl} + (\mu^f_i + \kappa^f_i) u_{l,k}^f + \mu^f_i u_{k,l}^f, \quad (38k)$$

$$m_{kl}^f = \alpha^f r_{m,m}^f \delta_{kl} + \beta^f r_{kl}^f + \gamma^f r_{l,k}^f, \quad (38l)$$

$$\hat{T}_k^f = p^f n_{,k}^f - n^f \rho^f \frac{\partial A^f}{\partial \rho^f} n_{,k} - \xi^f v_{k,s}^f - \sum_{\alpha=s,f} \sum_{i=1}^{N-1} \zeta^f v_{k,s}^f u_k^{\alpha_i} - \zeta^f v^{f,s} \theta_{,k}, \quad (38m)$$

$$\hat{M}_k^f = -\xi^f v_{k,s}^f, \quad (38n)$$

$$\tilde{T}_k^{\alpha_i} = \mu^{\alpha_i} (n^{\alpha} \rho^{\alpha} c^{\alpha_i})_{,k} - (n^{\alpha} \rho^{\alpha} c^{\alpha} A^{\alpha_i})_{,k} - n^{\alpha} t_{kl}^{\alpha N} \left(\frac{c^{\alpha_i}}{c^{\alpha N}} \right)_{,l} - \xi^{\alpha_i} u_k^{\alpha_i} - \zeta^{\alpha_i} v_{k,s}^{\alpha_i} - \zeta^{\alpha_i} \theta_{,k}, \quad (38o)$$

$$\tilde{M}_k^{\alpha_i} = n^{\alpha} \left(\varepsilon_{kmn} t_{mn}^{\alpha_i} - \frac{c^{\alpha_i} \Pi^{\alpha_i}}{c^{\alpha N} \Pi^{\alpha N}} \varepsilon_{kmn} t_{mn}^{\alpha N} \right) - n^{\alpha} m_{kl}^{\alpha N} \left(\frac{c^{\alpha_i} \Pi^{\alpha_i}}{c^{\alpha N} \Pi^{\alpha N}} \right)_{,l} - \xi^{\alpha_i} r_{k,s}^{\alpha_i}, \quad (38p)$$

$$\sum_{\alpha=s,f} \frac{n^{\alpha} q_k^{\alpha}}{\theta} = -\xi^{\theta} \theta_{,k} - \sum_{\alpha=s,f} \sum_{i=1}^{N-1} \zeta^{\alpha_i} \theta_{,k} u_k^{\alpha_i} - \zeta^{\alpha_i} v_{k,s}^{\alpha_i}. \quad (38q)$$

3 场方程

将式(25d, e) 以及以上本构关系(38) 对应代入到守恒方程(5)、(6)、(8)、(9)、(11)、(12) 和(14) 中, 建立闭合的场方程系统. 因假设各相温度相同, 则可将能量守恒方程(14) 合并为混合物总体的能量守恒方程. 对场方程线性化, 去除系统中的非线性项, 并由变形向量 w_l^{α} 和转动向量 φ_l^{α} 来表示速度和微转动速度项, 分别得到

$$n^{\alpha 0} \rho^{\alpha 0} (w_{,l}^{\alpha})_{,l} + n^{\alpha 0} \rho^{\alpha} \varphi_{,l}^{\alpha} + \rho^{\alpha 0} n_{,l}^{\alpha} = 0, \quad c_{,l}^{\alpha_i} + (w_{,l}^{\alpha_i} - w_{,l}^{\alpha})_{,l} = 0, \quad (39a, b)$$

$$n^{s0} \rho^{s0} \dot{w}_{,l}^s + n^{s0} (K^s - \lambda^{\rho \varepsilon s}) \frac{\rho^s}{\rho^{s0}} + \sum_{i=1}^{N-1} n^{s0} (\lambda^{\rho c_i s} - \lambda^{\varepsilon c_i s}) c_{,l}^s_i - (n^{s0} \lambda^{\rho \theta s} - n^{s0} \lambda^{\varepsilon \theta s} + \zeta^f v^{f,s} \theta) \theta_{,l} - n^{s0} (\mu^s + \kappa^s) w_{l,kk}^s - n^{s0} (\lambda^s + \mu^s + \lambda^{\rho \varepsilon s}) w_{k,lk}^s - n^{s0} \kappa^s \varepsilon_{lkm} \varphi_{m,k}^s - \xi^f v^f (w_{,l}^f - w_{,l}^s) - \sum_{\alpha=s,f} \sum_{i=1}^{N-1} \zeta^f v^f u^{\alpha_i} (w_{,l}^{\alpha_i} - w_{,l}^{\alpha}) - n^{s0} \rho^{s0} g_l^s = 0, \quad (39c)$$

$$n^{f0} \rho^{f0} \dot{w}_{,l}^f + n^{f0} K^f \frac{\rho^f}{\rho^{f0}} + n^{f0} \lambda^{\theta \rho f} n_{,l} + \sum_{i=1}^{N-1} n^{f0} \lambda^{\theta c_i f} c_{,l}^f_i - (n^{f0} \lambda^{\theta \rho f} - \zeta^f v^{f,s} \theta) \theta_{,l} - n^{f0} (\mu^f + \kappa^f) w_{,l,kk}^f - n^{f0} (\lambda^f + \mu^f) w_{k,lk}^f - n^{f0} \kappa^f \varepsilon_{lkm} \varphi_{m,k}^f + \xi^f v^f (w_{,l}^f - w_{,l}^s) + \sum_{\alpha=s,f} \sum_{i=1}^{N-1} \zeta^f v^f u^{\alpha_i} (w_{,l}^{\alpha_i} - w_{,l}^{\alpha}) - n^{f0} \rho^{f0} g_l^f = 0, \quad (39d)$$

$$n^{s0} \rho^{s0} c^{s0} (\dot{w}_{,l}^s - \dot{w}_{,l}^N) + n^{s0} c^{s0} L^s c_{,l}^s_i + n^{s0} c^{s0} \lambda^{\rho c_i s} \frac{\rho^s}{\rho^{s0}} + \sum_{m=1, m \neq i}^{N-1} n^{s0} c^{s0} \lambda^{\rho c_m s} c_{,l}^s_m + n^{s0} c^{s0} \lambda^{\varepsilon c_i s} w_{k,kl}^s + \xi^s v^s (w_{,l}^s - w_{,l}^f) +$$

$$\zeta^{v^f s} u^{s_i} (w_{l_i}^f - w_{l_i}^s) - (n^{s0} c^{s_i 0} \lambda^{0c_i s} - \zeta^{\theta} u^{s_i}) \theta_{,l} = 0, \quad (39e)$$

$$\begin{aligned} n^{f0} \rho^{f0} c^{f_i 0} (\ddot{w}_{l_i}^f - \dot{w}_{l_i}^{fN}) + n^{f0} c^{f_i 0} L^f c_{,l_i}^f + n^{f0} c^{f_i 0} \lambda^{0c_i f} \frac{\rho_{,l_i}^f}{\rho^{f0}} + \sum_{m=1}^{N-1} n^{f0} c^{f_i 0} \chi_{i, c_m^f} c_{,l_i}^f + \\ n^{f0} c^{f_i 0} \lambda^{nc_i f} n_{,l_i} + \xi^{u^f} (w_{l_i}^f - w_{l_i}^s) + \zeta^{v^f s} u^{f_i} (w_{l_i}^f - w_{l_i}^s) - \\ n^{f0} (\lambda^f + \mu^f) (w_{k, lk}^f - w_{k, lk}^s) - n^{f0} (\mu^f + \kappa^f) (w_{l, kk}^f - w_{l, kk}^s) - \\ (n^{f0} c^{f_i 0} \lambda^{0c_i f} - \zeta^{\theta} u^{f_i}) \theta_{,l} = 0, \end{aligned} \quad (39f)$$

$$\begin{aligned} \rho^{s0} \pi^s \varphi_{l_i}^s - \kappa^s (\mathfrak{E}_{mn} w_{n, m}^s - 2\mathfrak{F}_{l_i}^s) - (\alpha^s + \beta^s) \varphi_{k, lk}^s - \gamma^s \varphi_{l, kk}^s - \\ \rho^{s0} l_{l_i}^s + \frac{\xi^{v^f s}}{n^{s0}} (\mathfrak{F}_{l_i}^f - \mathfrak{F}_{l_i}^s) = 0, \end{aligned} \quad (39g)$$

$$\begin{aligned} \rho^{f0} \pi^f \varphi_{l_i}^f - \kappa^f (\mathfrak{E}_{mn} w_{n, m}^f - 2\mathfrak{F}_{l_i}^f) - (\alpha^f + \beta^f) \varphi_{k, lk}^f - \gamma^f \varphi_{l, kk}^f - \\ \rho^{f0} l_{l_i}^f - \frac{\xi^{v^f s}}{n^{f0}} (\mathfrak{F}_{l_i}^f - \mathfrak{F}_{l_i}^s) = 0, \end{aligned} \quad (39h)$$

$$\rho^{s0} c^{s_i 0} \pi_{i, l_i}^s (\varphi_{l_i}^s - \varphi_{l_i}^{sN}) - \rho^{s0} c^{s_i 0} (l_{l_i}^s - l_{l_i}^{sN}) + \frac{\xi^{r^s}}{n^{s0}} r_{l_i}^s = 0, \quad (39i)$$

$$\begin{aligned} \rho^{f0} c^{f_i 0} \pi_{i, l_i}^f (\varphi_{l_i}^f - \varphi_{l_i}^{fN}) - (\alpha^f + \beta^f) (\varphi_{k, lk}^f - \varphi_{k, lk}^s) - \gamma^f (\varphi_{l, kk}^f - \varphi_{l, kk}^s) - \\ \rho^{f0} c^{f_i 0} (l_{l_i}^f - l_{l_i}^{fN}) + \frac{\xi^{r^f}}{n^{f0}} (\mathfrak{F}_{l_i}^f - \mathfrak{F}_{l_i}^s) = 0, \end{aligned} \quad (39k)$$

$$\begin{aligned} \sum_{a=s, f} n^{a0} C^{a\theta} + \sum_{a=s, f} n^{a0} \lambda^{00a} \frac{\mathfrak{G}}{\rho^{a0}} + \sum_{a=s, f} \sum_{i=1}^{N-1} n^{a0} \lambda^{0c_i a} c_{,l_i}^a + (n^{s0} \lambda^{0\mathfrak{E}s} - n^{f0} \rho^{f0} \eta^{f0}) w_{k, k}^s + \\ n^{f0} \lambda^{0nf} \eta_{,k}^f + n^{f0} \rho^{f0} \eta^{f0} w_{k, k}^f + \xi^{\theta} \theta_{,kk} + \zeta^{v^f s} (w_k^f - w_k^s)_{,k} + \\ \sum_{a=s, f} \sum_{i=1}^{N-1} \zeta^{0u^a} (w_k^a - w_k^s)_{,k} - \frac{\rho^{m0} h^m}{\theta^0} = 0, \end{aligned} \quad (39l)$$

其中, $\rho^{m0} h^m = n^{s0} \rho^{s0} h^s + n^{f0} \rho^{f0} h^f$, $(\dot{\cdot}) = \partial(\cdot)/\partial t$, $(\ddot{\cdot}) = \partial^2(\cdot)/\partial t^2$. 到此, 受多组分粘性流体饱和的微极性热弹性多孔介质系统的控制方程已经全部给出. 场方程(39), 本构方程(38a, b, j)以及扩散速度限制方程(7f)和(13c)形成闭合系统. 此系统的未知量为 $\{n, \rho^f, c^a, w_k^a, w_k^s, \varphi_k^a, \varphi_k^s, \theta, p^a\}$, 共含有 $14N + 16$ 个未知数和 $14N + 16$ 个方程. 要注意的是组分的质量守恒方程去除非线性项 $c_{,k}^a w_k^a$ 后, 可知线性化得到(39b)式与污染物对流-弥散运输方程对比, 忽略了对流作用对组分输运的影响, 因此只适用渗流速度很小的情况. 而对于固相的动量矩守恒方程(39i), 若各组分的外部偶应力体密度相等, 即 $l_{l_i}^s = l_{l_i}^{sN}$, 则组分的相对旋转速率只与该组分惯性矩的相对变化率有关. 若各组分惯性矩变化率也可忽略时, 则组分的相对微转动速度 $r_{l_i}^s = 0$, 这说明组分的相对旋转与组分的浓度梯度、混合物的温度梯度及压缩性等无关. 当组分惯性矩变化率可忽略且若各组分的外部偶应力体密度相等时, 场方程(39i)可不考虑. 另外, 由于本构方程(38a, b, j)可合并为一个含有独立变量的 $\{n, \rho^f, c^a, \theta\}$ 方程, 并且 w_k^a (φ_k^a) 和 w_k^s (φ_k^s) 中只有 N 个量独立, 因此, 最终可简化以独立变量 $\{n, \rho^f, c^a, w_k^a, w_k^s, \varphi_k^a, \varphi_k^s, \theta\}$ 为未知量, 含有 $11N + 5$ 个未知数和方程的闭合系统.

当固相、流相都为单组分时, 以上场方程退化为含有未知量 $\{n, \rho^f, \rho^f, w_k^a, \varphi_k^a, \theta\}$ 的系统, 共 16 个未知数和 16 个方程, 因此系统闭合. 所得到的结果与 Eringen^[21]得到的结果一致, 区别在于本文引入了体积分数以描述多孔介质中固、流相的分布.

4 结 论

当多组分流体在可变形多孔介质中输运时,其中的质点不仅发生平动还会旋转.为考虑这一作用,本文基于微极性连续介质力学以及复合混合物理论研究了多组分粘性流体饱和的微极性多孔介质系统,建立了微极性复合混合物理论.对于可压缩多孔介质,引入体积分数作为内变量,发展了动力相容条件,用以限制可压缩固、流相界面处压力差的变化.此理论框架可运用到多孔介质中污染物、药物以及农药输运等问题中.当系统退化为固、流相为单一组分的微极性多孔介质材料时,得到的场方程与 Eringen 的结果基本是一致的.

另外,多组分输运过程中各组分之间往往还会发生生物化学反应,即存在质量交换作用,将来的研究应考虑这种作用和影响.

[参 考 文 献]

- [1] Bowen R M. Incompressible porous media models by use of the theory of mixtures[J]. *Int J Eng Sci*, 1980, **18**(9): 1129– 1148.
- [2] Bowen R M. Compressible porous media models by use of the theory of mixtures[J]. *Int J Eng Sci*, 1982, **20**(6): 697– 735.
- [3] 陈正汉,谢定义,刘祖典.非饱和土固结的混合物理论(I) [J]. *应用数学和力学*, 1993, **14**(2): 127 – 137.
- [4] Wei C F, Muraleetharan K K. A continuum theory of porous media saturated by multiple immiscible fluids. I. Linear poroelasticity[J]. *Int J Eng Sci*, 2002, **40**(16): 1807– 1833.
- [5] WEI Chang-fu. Static and dynamic behavior of multiphase porous media: governing equations and finite element implementation[D]. Norman, Oklahoma University of Oklahoma, 2001.
- [6] Li X S. Thermodynamics – based constitutive framework for unsaturated soils. 1: theory [J]. *Geotechnique*, 2007, **57**(5): 411– 422.
- [7] Li X S. Thermodynamics – based constitutive framework for unsaturated soils—2: a basic triaxial model[J]. *Geotechnique*, 2007, **57**(5): 423– 435.
- [8] Hassanzadeh S M. Derivation of basic equations of mass transport in porous media, part 2: generalized Darcy's and Fick's law[J]. *Adv Water Res*, 1986, **9**(4): 207– 222.
- [9] Achanta S, Cushman J H. On multicomponent, multiphase thermomechanics with interfaces[J]. *Int J Eng Sci*, 1994, **32**(11): 1717– 1738.
- [10] Murad M A, Cushman J H. Multiscale flow and deformation in hydrophilic swelling porous media[J]. *Int J Eng Sci*, 1996, **34**(3): 313– 338.
- [11] Murad M A, Cushman J H. Thermomechanical model of hydration swelling in smectitic clays — I : two-scale mixture – theory approach[J]. *Int J Numer Anal Methods Geomech*, 1999, **23**(7): 673– 696.
- [12] Bennethum L S, Cushman J H. Multiscale, hybrid mixture theory for swelling systems — I : balance laws[J]. *Int J Eng Sci*, 1996, **34**(2): 125– 145.
- [13] Bennethum L S, Cushman J H. Multiscale, hybrid mixture theory for swelling systems — II : constitutive theory[J]. *Int J Eng Sci*, 1996, **34**(2): 147– 169.
- [14] Bennethum L S, Cushman J H. Clarifying mixture theory and the macroscale chemical potential for porous media[J]. *Int J Eng Sci*, 1996, **34**(14): 1611– 1621.
- [15] Bennethum L S, Murad M A, Cushman J H. Macroscale thermodynamics and the chemical potential for swelling porous media[J]. *Transport in Porous Media*, 2000, **39**(2): 187– 225.
- [16] Bennethum L S, Murad M A, Cushman J H. Modified Darcy's law, Terzaghi's effective stress principle and Fick's law for swelling clay soils[J]. *Computers and Geotechnics*, 1997, **20**(3/4): 245– 266.

- [17] Bennethum L S, Cushman J H. Coupled solvent and heat transport of mixture of swelling porous particles and fluids: Single time- scale problem[J]. *Transport in Porous Media*, 1999, **36**(2): 211– 244.
- [18] Singh P P, Cushman J H, Maier D F. Thermomechanics of swelling biopolymeric systems[J]. *Transport in Porous Media*, 2003, **53**(1): 1– 24.
- [19] Singh P P, Cushman J H, Maier D E. Multiscale fluid transport theory for swelling biopolymers[J]. *Chemical Eng Sci*, 2003, **58**(11): 2409– 2419.
- [20] Singh P P, Cushman J H, Maier D E. Three scale thermomechanical theory for swelling biopolymeric systems[J]. *Chemical Eng Sci*, 2003, **58**(17): 4017– 4035.
- [21] Eringen A C. Micropolar mixture theory of porous media[J]. *J Appl Phys*, 2003, **94**(6): 4184– 4190.
- [22] Eringen A C. *Microcontinuum Field Theories* [M]. New York: Springer- Verlag, 1998.
- [23] 爱林根 A C, 卡法达 C B. 微极场论[M]. 戴天民译. 南京: 江苏科学技术出版社, 1982.
- [24] Nowacki W. *Theory of Asymmetric Elasticity* [M]. Oxford: Pergamon Press, 1986.
- [25] 戴天民. 微极连续统的耦合场理论的再研究(I) —— 微极热弹性理论[J]. *应用数学和力学*, 2002, **23**(2): 111– 118.
- [26] 戴天民. 微极连续统的耦合场理论的再研究(II) —— 微极热压电弹性理论和电磁热弹性理论[J]. *应用数学和力学*, 2002, **23**(3): 229– 238.
- [27] Diebels S. A micropolar theory of porous media: constitutive modelling[J]. *Transport in Porous Media*, 1999, **34**(1/3): 193– 208.
- [28] Hutter K, Jü hnk K. *Continuum Methods of Physical Modeling* [M]. Heidelberg: Springer- Verlag, 2004.
- [29] Passman S T. A theory of multiphase mixtures[A]. In: Trusdell C, Ed. *Rational Thermodynamics* [C]. New York: Springer- Verlag, 1984, 286– 325.
- [30] Wilmanski K. Lagrangean model of two- phase porous material[J]. *J Non - Equilibrium Thermodynamics*, 1995, **20**(1): 50– 77.

Micropolar Mixture Theory of Multicomponent Porous Media

HUANG Lu, ZHAO Cheng- gang

(School of Civil Engineering and Architecture, Beijing Jiaotong University,
Beijing 100044, P. R. China)

Abstract: A mixture theory is developed for multicomponent micropolar porous media by combination of the hybrid mixture theory and micropolar continuum theory. This system was modeled as multicomponent micropolar elastic solids saturated with multicomponent micropolar viscous fluids. Balance equations were given through the mixture theory. Constitutive equations were developed based on the second law of thermodynamic and constitutive assumptions. For taking account of compressibility of solid phase, volume fraction of fluid as an independent state variable was introduced in free energy function, and the dynamic compatibility condition was obtained to restrict the change of pressure difference on solid and fluid interface. The constructed constitutive equations were used to close the field equations. The linear field equations were obtained with the linearization procedure, and the micropolar thermo- hydro- mechanical component transport model was established finally. This model can be applied to some practical problems, such as contaminant, drug and pesticide transport. When the proposed model is supposed to be the porous media, including both fluid and solid are single- component, it will almost agree with Eringen's model.

Key words: hybrid mixture theory; micropolar; multicomponent; deforming porous media