

Multicomponent, Multiphase Thermodynamics of Swelling Porous Media with Electroquasistatics: II. Constitutive Theory

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Abstract

In Part I macroscopic field equations of mass, linear and angular momentum, energy, and the quasistatic form of Maxwell's equations for a multiphase, multicomponent medium were derived. Here we exploit the entropy inequality to obtain restrictions on constitutive relations at the macroscale for a 2-phase, multiple-constituent, polarizable mixture of fluids and solids. Specific emphasis is placed on charged porous media in the presence of electrolytes. The governing equations for the stress tensors of each phase, flow of the fluid through a deforming medium, and diffusion of constituents through such a medium are derived. The results have applications in swelling clays (smectites), biopolymers, biological membranes, pulsed electrophoresis, chromatography, drug delivery, and other swelling systems.

Key words: porous media, mixture theory, electrodynamics, swelling, constitutive equations

1 Introduction

We continue our investigation into the form of the governing equations for a multiple-component, multiple-phase, polarizable, swelling porous medium with charged particles subject to an electric field. In Part I of this series we derived the macroscopic field equations in which it is the total electric field which affects the species' conservation of momentum and energy. In this paper, we exploit the entropy inequality in the sense of Coleman and Noll [14] in order to obtain restrictions on constitutive equations in terms of *macroscopic* variables. This approach differs from classical averaging [29, 30, 31, 35, 36] or

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homogenization [10, 16, 32] where both the field equations and microscopic constitutive equations are upscaled to obtain macroscale equations in terms of microscale geometry and microscale constitutive coefficients. The advantage of homogenization and averaging is that *if* one knows the microscale constitutive equations and geometry, then one can obtain to first-order (and second-order...) constitutive equations (including the coefficients) at the macroscale in terms of microscopic variables. The HMT approach assumes only the variables upon which constitutive variables may depend, and produces restrictions of the form of constitutive equations in terms of *macroscopic* variables. HMT does not assume any microscale constitutive relations nor any specific microscale geometry, which in such complex media as considered here are not satisfactorily known. This point is of significant import for natural media such as geophysical environs or polymeric systems, which are never well-characterized geometrically at the microscale.

For simplicity we consider only a liquid-solid system. The mixture is charge neutral, although neither the phases nor species face this requirement individually. We assume that interfacial properties such as excess mass density, free charge on interfaces, and interface currents are negligible; although the present theory can be extended to explicitly incorporate these effects [19]. However, it should be noted that for many practical materials where the ratio of surface area to volume of the solid phase remains constant, interfacial characteristics can be accounted for in this theory. This is because in the case where surface to volume ratio is constant, charge per unit mass of the solid phase is directly proportional to charge per unit surface area. Likewise the theory presented here also applies to materials in which the charge of the solid itself changes. This theory would *not* apply to materials in which the charge of the solid phase and of the interface vary independently. So, for example, the theory applies to clay minerals, which has a charge associated only with its surface, and to polymers which has a charge associated with the polymer but not with its surface if a surface can be defined.

In deriving restrictions on the form of the constitutive equations, we follow [17, 18] and view fluxes as constitutive. In earlier work, Eringen [18] considered constituent electric fields throughout for a non-swelling porous medium; Huyghe and Janssen [23] considered a single electric field in a deformable two-phase porous medium with no exchange terms in the conservation equations; and Gu et al. [20] considered a charged swelling medium with no electric field.

2 Constitutive Assumptions and the Entropy Inequality

The full entropy inequality which is exploited in subsequent sections is presented in Appendix B. The basic notation is found in Part I so only new terms are defined herein. We assume the medium consists of a liquid phase (denoted by $\alpha = l$), and a solid phase, (denoted by $\alpha = s$), and that the medium is macro-

scopically neutrally charged, however charges may move between constituents and phases.

We assume that entropy generation must be non-negative for the total body, i.e.

$$\rho \widehat{\Lambda} = \sum_{\alpha} \sum_j \varepsilon^{\alpha} \rho^{\alpha_j} \widehat{\Lambda}^{\alpha_j} \geq 0. \quad (1)$$

Further we assume a form of local equilibrium wherein there is one temperature for all constituents and all phases, i.e. $T^{\alpha_j}(\mathbf{x}, t) = T(\mathbf{x}, t)$ for all constituents j and all phases α . This effectively states that the rate of heat transfer between constituents is much faster than the time scales of interest to the problem.

To couple the entropy and energy equations, it is necessary to relate the fluxes and sources of entropy to the fluxes and sources of heat. We assume the processes are simple in the sense of [17]. In this sense several possible relations are admissible. Among these are:

$$\phi^{\alpha_j} = \frac{\mathbf{q}^{\alpha_j}}{T} \quad b^{\alpha_j} = \frac{h^{\alpha_j}}{T} \quad (2)$$

$$\phi^{\alpha} = \frac{\mathbf{q}^{\alpha}}{T} \quad b^{\alpha} = \frac{h^{\alpha}}{T} \quad (3)$$

$$\sum_{\alpha} \varepsilon^{\alpha} \phi^{\alpha} = \sum_{\alpha} \frac{\varepsilon^{\alpha} \mathbf{q}^{\alpha}}{T} \quad \sum_{\alpha} \varepsilon^{\alpha} b^{\alpha} = \sum_{\alpha} \frac{\varepsilon^{\alpha} h^{\alpha}}{T}. \quad (4)$$

The expressions in (4) have been used in [18], and the relations in (2) have been used in [1, 2, 4, 22]. More general expressions which simplify to the above are used in extended thermodynamics [24, 26]. The question is whether the processes governing the behavior of the constituents themselves, the individual phases, or the bulk material are simple. The assumption of any one of these does not imply any other due to microscale/macroscale relationships between heat fluxes and heat sources [5]. This problem is complicated further because the macroscale definition of the heat flux depends on how one incorporates microscale fluctuations (see Part I, [5]). The differences manifest themselves explicitly in the constitutive relations obtained for diffusive fluxes and the chemical potential. For example, if the relations in (4) are used then it can be shown that the chemical potentials of two ‘‘different’’ species at equilibrium must be equal, which is inconsistent with Gibbsian thermostatics [13]. To the authors’ knowledge, the relations in (2) do not result in any physical inconsistencies in near-equilibrium processes, and these are the relations used herein.

Define the Helmholtz free energy for the species and the internal Helmholtz free energy for the bulk phase as

$$A^{\alpha_j} = e^{\alpha_j} - T \eta^{\alpha_j} \quad A^{\alpha} = \sum_{j=1}^N C^{\alpha_j} A^{\alpha_j} \quad (5)$$

and introduce a modified Helmholtz free energy as

$$\tilde{A}^{\alpha_j} = e^{\alpha_j} - T\eta^{\alpha_j} - \frac{1}{\rho^{\alpha_j}} \mathbf{E}_T \cdot \mathbf{P}^{\alpha_j} \quad \tilde{A}^\alpha = \sum_{j=1}^N C^{\alpha_j} \tilde{A}^{\alpha_j}, \quad (6)$$

where C^{α_j} is the mass fraction of constituent j in phase α given by $C^{\alpha_j} = \rho^{\alpha_j} / \rho^\alpha$. The purpose of introducing the modified Helmholtz potential is to reduce the amount of manipulations required to obtain the entropy inequality, as either \mathbf{P}^{α_j} or \mathbf{E}_T must be constitutive (dependent) variables. With this notation, eliminating ϕ^{α_j} , b^{α_j} , $\hat{Q}_\beta^{\alpha_j}$, \hat{Q}^{α_j} , $\hat{\Phi}_\beta^{\alpha_j}$, and $\hat{\eta}^{\alpha_j}$ from the entropy balance and re-writing it in terms of bulk-phase variables one obtains

$$\begin{aligned} \sum_{\alpha} \varepsilon^{\alpha} \rho^{\alpha} T \hat{\Lambda}^{\alpha} &= - \sum_{\alpha} \varepsilon^{\alpha} \rho^{\alpha} \left(\frac{D^{\alpha} \tilde{A}^{\alpha}}{Dt} + \eta^{\alpha} \frac{D^{\alpha} T}{Dt} \right) + \sum_{\alpha} \varepsilon^{\alpha} \mathcal{J}^{\alpha} \cdot \mathbf{E}_T \\ &+ \sum_{\alpha} \left[\varepsilon^{\alpha} \mathbf{t}^{\alpha} + \varepsilon^{\alpha} \mathbf{P}^{\alpha} \cdot \mathbf{E}_T \mathbf{I} + \sum_{j=1}^N \varepsilon^{\alpha} \rho^{\alpha_j} \left(\tilde{A}^{\alpha_j} \mathbf{I} + \mathbf{v}^{\alpha_j, \alpha} \mathbf{v}^{\alpha_j, \alpha} \right) \right] : \nabla \mathbf{v}^{\alpha} \\ &+ \sum_{\alpha} \sum_{j=1}^N \left[\varepsilon^{\alpha} \mathbf{t}^{\alpha_j} + \varepsilon^{\alpha} \mathbf{P}^{\alpha_j} \cdot \mathbf{E}_T \mathbf{I} \right] : \nabla \mathbf{v}^{\alpha_j, \alpha} \\ &+ \sum_{\alpha} \dot{\varepsilon}^{\alpha} \left[\frac{1}{2} \varepsilon_o \mathbf{E}_T \cdot \mathbf{E}^{\alpha} + \mathbf{E}_T \cdot \mathbf{P}^{\alpha} + \rho^{\alpha} A^{\alpha} \right] \\ &+ \sum_{\alpha} \frac{\varepsilon^{\alpha}}{T} \nabla T \cdot \left\{ \mathbf{q}^{\alpha} + \sum_{j=1}^N \left[\rho^{\alpha_j} \mathbf{v}^{\alpha_j, \alpha} \left(\tilde{A}^{\alpha_j} + \frac{1}{2} \mathbf{v}^{\alpha_j, \alpha} \cdot \mathbf{v}^{\alpha_j, \alpha} \right) - \mathbf{t}^{\alpha_j} \cdot \mathbf{v}^{\alpha_j, \alpha} \right] \right\} \\ &+ \sum_{\alpha} \sum_{j=1}^N \varepsilon^{\alpha} \frac{D^s \rho^{\alpha_j}}{Dt} \left[\frac{1}{\rho^{\alpha_j}} \mathbf{E}_T \cdot \mathbf{P}^{\alpha_j} + A^{\alpha_j} \right] - \sum_{\alpha} \varepsilon^{\alpha} \dot{\mathbf{E}}_T \cdot \mathbf{P}^{\alpha_j} \\ &+ \mathbf{v}^{l, s} \cdot \left[-\varepsilon^l \rho^l \hat{\mathbf{T}}_s^l + \sum_{j=1}^N \left(A^{l_j} \nabla (\varepsilon^l \rho^{l_j}) + \frac{1}{\rho^{l_j}} \mathbf{E}_T \cdot \mathbf{P}^{l_j} \nabla (\varepsilon^l \rho^{l_j}) \right. \right. \\ &\quad \left. \left. - \varepsilon^l \nabla \mathbf{E}_T \cdot \mathbf{P}^{l_j} + \frac{1}{2} \varepsilon_o \mathbf{E}_T \cdot \mathbf{E}^{l_j} \nabla \varepsilon^l \right) \right] \\ &+ \sum_{\alpha} \sum_{j=1}^N \mathbf{v}^{\alpha_j, \alpha} \cdot \left[-\varepsilon^{\alpha} \rho^{\alpha_j} \left(\hat{\mathbf{i}}^{\alpha_j} + \sum_{\beta \neq \alpha} \hat{\mathbf{T}}_{\beta}^{\alpha_j} \right) - \varepsilon^{\alpha} \rho^{\alpha_j} \nabla \tilde{A}^{\alpha_j} - \varepsilon^{\alpha} q_e^{\alpha_j} \mathbf{E}_T \right. \\ &\quad \left. + \frac{1}{\rho^{\alpha_j}} \mathbf{E}_T \cdot \mathbf{P}^{\alpha_j} \nabla (\varepsilon^{\alpha} \rho^{\alpha_j}) - \varepsilon^{\alpha} \nabla \mathbf{E}_T \cdot \mathbf{P}^{\alpha_j} + \frac{1}{2} \varepsilon_o \mathbf{E}_T \cdot \mathbf{E}^{\alpha_j} \nabla \varepsilon^{\alpha} \right] \\ &- \sum_{\alpha} \sum_{j=1}^N \sum_{\beta \neq \alpha} \varepsilon^{\alpha} \rho^{\alpha_j} \hat{c}_{\beta}^{\alpha_j} \left[\frac{1}{\rho^{\alpha_j}} \mathbf{E}_T \cdot \mathbf{P}^{\alpha_j} + \tilde{A}^{\alpha_j} + \tilde{A}^{\alpha} + \frac{1}{2} (\mathbf{v}^{\alpha, s})^2 + \frac{1}{2} (\mathbf{v}^{\alpha_j, \alpha})^2 \right] \\ &+ \sum_{\alpha} \sum_{j=1}^N \varepsilon^{\alpha} \rho^{\alpha_j} \hat{r}^{\alpha_j} \left[-\frac{1}{2} (\mathbf{v}^{\alpha_j, \alpha})^2 - \tilde{A}^{\alpha_j} - \frac{1}{\rho^{\alpha_j}} \mathbf{E}_T \cdot \mathbf{P}^{\alpha_j} \right] \geq 0, \quad (7) \end{aligned}$$

where a comma in the superscript denotes difference (e.g. $\mathbf{v}^{\alpha,s} = \mathbf{v}^\alpha - \mathbf{v}^s$), a superimposed dot denotes the material time derivative with respect to the solid phase (e.g. $\dot{\varepsilon}^\alpha = \partial\varepsilon^\alpha/\partial t + \mathbf{v}^s \cdot \nabla \varepsilon^\alpha$), \mathbf{I} is the identity matrix, and the contraction operator $A : B$ is, in indicial notation, $A_{ij}B_{ij}$.

We enforce many of the balance laws weakly using the Lagrange Multiplier approach [25]. The equations and their associated Lagrange multipliers are listed below.

Lagrange Mult.	Equation from [5]	Lagrange Mult.	Equation from [5]
$\lambda_\rho^{\alpha_j}$	Continuity Eqn α_j , (42)	$\lambda_D^{\alpha_j}$	Gauss' Law (49)
$\Lambda_E^{\alpha_j}$	Faraday's Law (55)	$\lambda_{q_e}^{\alpha_j}$	Conserv. of Charge (70)
Λ	$\frac{D^s}{Dt}(\varepsilon^l q_e^l + \varepsilon^s q_e^s) = 0$		

Ampère's law is derivable from the conservation of charge and Gauss' law and so is not enforced directly. The expression corresponding to the Lagrange multiplier Λ enforces *charge neutrality* locally. This restriction alone implies that the total charge could vary in space. However we have in mind that the mixture is charge neutral initially everywhere so that it is assumed the time scale at which imbalances may occur is small compared to the time scale involved with other processes.

The unknowns in this system include:

$$\varepsilon^l, \rho^{\alpha_j}, \mathbf{v}^{\alpha_j}, T, \mathbf{E}^{\alpha_j}, q_e^{\alpha_j}, \quad (8)$$

$$\widehat{e}_\beta^{\alpha_j}, \widehat{r}^{\alpha_j}, \mathbf{t}^{\alpha_j}, \mathbf{t}^\alpha, \widehat{\mathbf{T}}_\beta^{\alpha_j}, \widehat{\mathbf{T}}_\beta^\alpha, \widehat{\mathbf{i}}^{\alpha_j}, \quad (9)$$

$$A^{\alpha_j}, \mathbf{q}^{\alpha_j}, \eta^{\alpha_j}, \quad (10)$$

$$\mathbf{P}^{\alpha_j}, \widehat{\mathbf{d}}^{\alpha_j}, \widehat{\mathbf{d}}_\beta^{\alpha_j}, \widehat{\sigma}^{\alpha_j}, \widehat{\sigma}_\beta^{\alpha_j}, \mathcal{J}^{\alpha_j}, \widehat{q}^{\alpha_j}, \widehat{\mathbf{Z}}_\beta^{\alpha_j}. \quad (11)$$

The variables in the first row, (8), are the primary unknowns. The remaining variables, (9–11), are considered constitutive and are a function of *constitutive independent variables*. In order to close the system, one additional equation is needed, which corresponds to the unknown ε^l . This is known as the closure problem, and it arises from the homogenization of the microscopic geometry. To close the system we follow [1, 9, 12] and view the time rate of change of the volume fraction $D\varepsilon^l/Dt$ as a constitutive variable.

The choice of constitutive independent variables is made based on knowledge of the system being modeled. Here we assume the fluid may behave as a Newtonian fluid and the solid as an elastic solid, hence we include the rate of deformation tensor, \mathbf{d}^l , and the strain tensor, \mathcal{E}^s . Since the solid phase may be disconnected, the macroscale strain tensor is not the average of the microscale strain, but is defined in terms of the deformation gradient $\mathbf{F} = \nabla_o \mathbf{x}$, $\mathcal{E}^s = \frac{1}{2}(\mathbf{F}_s^T \mathbf{F}_s - \mathbf{I})$, where ∇_o denotes differentiation with respect to the macroscopic material particle. Thus the strain tensor is a measure of the geometry of the solid phase. Further, we are particularly interested in modeling materials in which the solid and fluid phases have electro-chemical interactions, so that

the behavior of the liquid phase may strongly depend upon its proximity to the solid phase. Thus we incorporate the volume fraction, ε^l , as an independent variable. The independent variables which are used to define the constitutive variables include:

$$\begin{aligned} &\varepsilon^l, T, \rho^{\alpha_j}, \mathbf{v}^{l,s}, \mathbf{v}^{\alpha_j,\alpha}, \boldsymbol{\mathcal{E}}^s, \mathbf{E}_T, z^{\alpha_j}, \\ &\nabla\varepsilon^l, \nabla T, \nabla\rho^{\alpha_j}, \mathbf{d}^l, \boldsymbol{\omega}^\alpha, \nabla\mathbf{v}^{l_j,l}, \nabla\boldsymbol{\mathcal{E}}^s, \nabla\mathbf{E}_T, \\ & \hspace{15em} j = 1, \dots, N, \quad \alpha = l, s \end{aligned} \quad (12)$$

where because the liquid phase may be polarizable and may depend strongly on the geometry of the solid phase [5], we have also included the vorticity tensor, $\boldsymbol{\omega}^l = (\nabla\mathbf{v} - (\nabla\mathbf{v})^T)$. Note that we have incorporated the total electric field as an independent variable, as opposed to the electric fields of each constituent or each phase. This is because it is assumed that all constitutive variables are measured with respect to the total electric field.

The charge of a species, z^{α_j} , has units of charge of α_j per unit mass of α_j . This results in terms such as $\frac{\partial A^\alpha}{\partial z^{\alpha_j}}$ which is evaluated holding all other independent variables in (12), such as volume fraction and densities, fixed. This allows for disassociation of ions, or changes in the charge density of the solid phase, either through the change in surface charge density or through charge density of the bulk phase, but not both (see the introduction).

To simplify the results we relax the Principle of Equipresence [34] and assume that the modified Helmholtz potential energies \tilde{A}^α are a function of a subset of the above constitutive independent variables:

$$\begin{aligned} \tilde{A}^l = \tilde{A}^l(\varepsilon^l, T, \rho^{l_j}, \mathbf{v}^{l,s}, \mathbf{v}^{l_j,l}, \boldsymbol{\mathcal{E}}^s, \mathbf{E}_T, z^{l_j}, \\ \nabla T, \nabla\rho^{l_j}, \mathbf{d}^l, \boldsymbol{\omega}^l, \nabla\mathbf{v}^{l_j,l}) \end{aligned} \quad (13)$$

$$\begin{aligned} \tilde{A}^s = \tilde{A}^s(\varepsilon^l, T, \rho^{s_j}, \mathbf{v}^{s_j,s}, \boldsymbol{\mathcal{E}}^s, \mathbf{E}_T, z^{s_j}, \\ \nabla T, \nabla\rho^{s_j}, \boldsymbol{\omega}^s). \end{aligned} \quad (14)$$

We note that including the additional independent variables does not change the results if one modifies the definitions of pressure, chemical potential, etc. see e.g. [4]. The entropy inequality is now expanded in the traditional manner [9, 17, 21] and is presented in Appendix B.

3 Non-Equilibrium Constitutive Restrictions

The following variables are neither constitutive nor independent,

$$\frac{D^s \rho^{\alpha_j}}{Dt}, \frac{D^s z^{\alpha_j}}{Dt}, \dot{T}, \dot{\mathbf{E}}_T, \mathbf{d}^s, \nabla\mathbf{v}^{s_j,s}, \nabla\dot{T}, \quad (15)$$

$$\dot{\mathbf{v}}^{\alpha_j,\alpha}, \nabla\left(\frac{D^s \rho^{\alpha_j}}{Dt}\right), \dot{\mathbf{v}}^{l,s}, \dot{\mathbf{d}}^l, \dot{\boldsymbol{\omega}}^l, \nabla\dot{\mathbf{v}}^{l_j,l}, \quad (16)$$

$$\nabla \times \mathbf{E}^{\alpha_j}, \nabla \cdot \mathbf{E}^{\alpha_j}, \quad (17)$$

where $j = 1, \dots, N$ for all variables not containing $\mathbf{v}^{\alpha_j, \alpha}$, since $\sum_{j=1}^N \rho^{\alpha_j} \mathbf{v}^{\alpha_j, \alpha} = \mathbf{0}$. Thus for example, $\mathbf{v}^{s_j, s}$ is indexed from $j = 1, \dots, N-1$ in order to keep the list of variables functionally independent. Since these terms appear linearly in the entropy inequality, their coefficients must be zero. This results in the following restrictions (corresponding directly with the terms in (15)):

$$\lambda_{\rho^{\alpha_j}}^{\alpha_j} = \rho^{\alpha_j} \frac{\partial \tilde{A}^{\alpha_j}}{\partial \rho^{\alpha_j}} - \tilde{A}^{\alpha_j} - \frac{1}{\rho^{\alpha_j}} \mathbf{E}_T \cdot \mathbf{P}^{\alpha_j} - z^{\alpha_j} \Lambda, \quad j = 1, \dots, N \quad (18)$$

$$\lambda_{q_e}^{\alpha_j} + \Lambda = \frac{\rho^{\alpha_j}}{\rho^{\alpha_j}} \frac{\partial \tilde{A}^{\alpha_j}}{\partial z^{\alpha_j}} \quad (19)$$

$$\sum_{\alpha=l, s} \varepsilon^{\alpha} \rho^{\alpha} \left(\eta^{\alpha} + \frac{\partial \tilde{A}^{\alpha}}{\partial T} \right) = 0 \quad (20)$$

$$\sum_{\alpha} \varepsilon^{\alpha} \mathbf{P}^{\alpha} = - \sum_{\alpha} \varepsilon^{\alpha} \rho^{\alpha} \frac{\partial \tilde{A}^{\alpha}}{\partial \mathbf{E}_T} \quad (21)$$

$$\begin{aligned} \varepsilon^s \mathbf{t}_{\text{sym}}^s = & - \sum_{j=1}^N \varepsilon^s \rho^{s_j} (\lambda_{\rho^j}^{s_j} + \tilde{A}^{s_j}) + \varepsilon^s \mathbf{t}_e^s + \varepsilon^l \mathbf{t}_s^l - \varepsilon^s \mathbf{P}^s \cdot \mathbf{E}_T \mathbf{I} \\ & - \sum_{j=1}^N \varepsilon^s \rho^{s_j} \mathbf{v}^{s_j, s} \mathbf{v}^{s_j, s} \end{aligned} \quad (22)$$

$$\mathbf{t}^{s_j} - \frac{\rho^{s_j}}{\rho^{s_N}} \mathbf{t}^{s_N} = -(\mathbf{P}^{s_j} \cdot \mathbf{E}_T - \frac{\rho^{s_j}}{\rho^{s_N}} \mathbf{P}^{s_N} \cdot \mathbf{E}_T) \mathbf{I} - \rho^{s_j} (\lambda_{\rho^j}^{s_j} - \lambda_{\rho^j}^{s_N}) \mathbf{I} \quad (23)$$

$$\varepsilon^l \rho^l \frac{\partial \tilde{A}^l}{\partial \nabla T} + \varepsilon^s \rho^s \frac{\partial \tilde{A}^s}{\partial \nabla T} = \mathbf{0}, \quad (24)$$

where we have defined the effective stress tensor and hydration stress tensor as

$$\mathbf{t}_e^s = \rho^s \nabla \mathbf{F}^s \cdot \frac{\partial \tilde{A}^s}{\partial \mathcal{E}^s} \cdot (\nabla \mathbf{F}^s)^T \quad \mathbf{t}_s^l = \rho^l \nabla \mathbf{F}^s \cdot \frac{\partial \tilde{A}^l}{\partial \mathcal{E}^s} \cdot (\nabla \mathbf{F}^s)^T, \quad (25)$$

respectively. The restrictions obtained from the coefficients of the variables listed in (16) indicate that the modified Helmholtz free energies are not a function of $\mathbf{v}^{\alpha_j, \alpha}$, $\nabla \rho^{\alpha_j}$, $\mathbf{v}^{l, s}$, \mathbf{d}^l , $\boldsymbol{\omega}^{\alpha}$, $\nabla \mathbf{v}^{l_j, l}$, and the restrictions corresponding to the variables listed in (17) require that the Lagrange multipliers, $\lambda_{q_e}^{\alpha_j}$, $\Lambda_E^{\alpha_j}$, and $\lambda_D^{\alpha_j}$ must all be identically zero.

Equations (18) and (19) define the Lagrange multipliers $\lambda_{\rho^{\alpha_j}}^{\alpha_j}$ and $\lambda_{q_e}^{\alpha_j}$, respectively. Equation (20) states that η^{α} and T are dual variables with respect to the *modified* Helmholtz potential, and this is in agreement with [2, 18]. Equation (24) states that the modified Helmholtz potential of the entire system is independent of ∇T .

The definitions of the effective stress tensor indicates that the effective stress tensor measures a change in energy of the solid phase with respect to the strain in the solid phase. The strain in the solid phase is purely a geometrical quantity (intuitively, one takes the solid phase, smears it out to obtain a continuous

medium at the macroscale, and measures its deformation - see the definition of $\boldsymbol{\mathcal{E}}$ following (11)). If the solid phase is connected, the strain represents an average of the microscale strain, and the effective stress tensor is non-negligible if strain occurs. For a disconnected solid phase, the energy of the solid phase is negligible for large movements of particles, and hence the effective stress tensor is negligible. However in the case where the medium swells (high interaction between liquid and solid phase), and where the solid phase is disconnected, the hydration stress tensor measures the stress the liquid phase supports when the solid phase is sheared. This can occur at low moisture content, see, e.g. [15], so that in this case although the effective stress tensor is negligible, the hydration stress tensor is not. Most swelling porous media have a structure such that both the solid and liquid phase can support shear, in which case neither the hydration nor the effective stress tensors can be neglected. See [8] for a more detailed discussion on this topic.

Equation (21) implies that it is the polarization of the entire medium which is dual to the electric field in this representation. This is in contrast with [18] in which it is shown that the polarization of each component is dual to the constituent's electric field. The disparity results from our choice of independent variables - we use \boldsymbol{E}_T and Eringen uses $\boldsymbol{E}^{\alpha_j}$ as independent variables.

We define the pressure thermodynamically by

$$p^\alpha = \sum_{j=1}^N \rho^{\alpha_j} (\lambda_\rho^{\alpha_j} + \tilde{A}^{\alpha_j}) + \boldsymbol{P}^\alpha \cdot \boldsymbol{E}_T + q_e^\alpha \Lambda \quad (26)$$

$$= \sum_{j=1}^N \left(\rho^\alpha \rho^{\alpha_j} \frac{\partial \tilde{A}^\alpha}{\partial \rho^{\alpha_j}} \right) \quad (27)$$

To see how this variable corresponds to what is classically thought of as pressure, we re-write (22), the expression for the symmetric part of the solid-phase stress tensor, as

$$\boldsymbol{t}_{\text{sym}}^s = -(p^s - q_e^s \Lambda) \boldsymbol{I} + \boldsymbol{t}_e^s + \frac{\varepsilon^l}{\varepsilon^s} \boldsymbol{t}_s^l - \sum_{j=1}^N \rho^{s_j} \boldsymbol{v}^{s_j, s} \boldsymbol{v}^{s_j, s} \quad (28)$$

so that by comparison [17], we see that $p^s - q_e^s \Lambda$ represents what is traditionally thought of as pressure.

Charges and the electric field enter into this expression through the term containing the Lagrange multiplier enforcing charge neutrality, $q_e^s \Lambda$, and through the definition of \tilde{A}^α in the remaining terms. The role played by the effective and hydration stress tensors are discussed in [7, 8, 27, 28]. We remark that if the solid phase is considered incompressible then the material time derivative of ρ^{s_j} is zero, ρ^{s_j} is not considered an independent variable, and $\lambda_\rho^{s_j}$ is the Lagrange multiplier which enforces the remaining part of the conservation of mass for constituent s_j . In that case we obtain the same results, except that p^s is a primary unknown which must be solved for directly.

We define the chemical potential as the change of the total Helmholtz potential with respect to the mass of species j (keeping the total volume fixed) [13]. Intuitively it is the scalar quantity representing the chemical energy required to insert that species into the mixture. Formally dividing this thermodynamic definition by the volume of the REV, we have

$$\mu^{\alpha_j} = \frac{\partial(\varepsilon^\alpha \rho^\alpha \tilde{A}^\alpha)}{\partial(\varepsilon^\alpha \rho^{\alpha_j})} = \tilde{A}^\alpha + \rho^\alpha \left. \frac{\partial \tilde{A}^\alpha}{\partial \rho^{\alpha_j}} \right|_{\varepsilon^\alpha}. \quad (29)$$

The *electro-chemical potential*, incorporates the chemical and electrical energy required to insert the particular species into the mixture. In this formulation this is:

$$\tilde{\mu}^{\alpha_j} = \mu^{\alpha_j} + z^{\alpha_j} \left(\Lambda - \frac{\rho^\alpha}{\rho^{\alpha_j}} \left. \frac{\partial \tilde{A}^\alpha}{\partial z^{\alpha_j}} \right|_{\varepsilon^\alpha, \rho^{\alpha_j}, \dots} \right). \quad (30)$$

The additional terms are generically termed the electrical potential, and classically they are written as $\tilde{z}_{\alpha_j} e \psi$ where \tilde{z}_{α_j} is the charge number of α_j , e is the charge on an electron, and ψ is the electrical potential. The Lagrange multiplier, Λ , has units of energy/charge, and is sometimes referred to as the streaming potential [33]. The first part of the electrical potential has been derived before [23, 20], and is the energy associated with inserting a charged ion into a system when the system wants to remain charge neutral. The second term is novel, and represents the energy of changing the charge of a particular species if, for example, an electron were added to a molecule. Interchanging between the different independent variables z^{α_j} and \tilde{z}_{α_j} , requires the molar weight, M^{α_j} [mass α_j per mole α_j], and Faraday's constant, F_c (96,000 C/mole): $\frac{\partial \tilde{A}^\alpha}{\partial z^{\alpha_j}} = \frac{M^{\alpha_j}}{F_c} \frac{\partial \tilde{A}^\alpha}{\partial \tilde{z}_{\alpha_j}}$.

With (29) as the definition of the chemical potential and by using (23) we can determine the relationship between the chemical potential and the partial stress tensors. By eliminating the Lagrange multipliers and using the definition of μ^{s_j} , (23) becomes

$$\begin{aligned} \mathbf{t}^{s_j} - \frac{\rho^{s_j}}{\rho^{s_N}} \mathbf{t}^{s_N} = & \left[-\rho^{s_j} (\mu^{s_j} - \mu^{s_N}) + \rho^{s_j} (\tilde{A}^{s_j} - \tilde{A}^{s_N}) \right. \\ & \left. + \rho^{s_j} (z^{s_j} - z^{s_N}) \Lambda \right] \mathbf{I}. \end{aligned} \quad (31)$$

Summing these equation on j from 1 to N and using

$$\sum_{j=1}^N \rho^{s_j} \mu^{s_j} = \rho^s \tilde{A}^s + p^s \quad (32)$$

$$\sum_{j=1}^N \mathbf{t}^{s_j} = -(p^s - q_e^s \Lambda) \mathbf{I} + \mathbf{t}_e^s + \frac{\varepsilon^l}{\varepsilon^s} \mathbf{t}_s^l + \mathbf{t}_{as}^s, \quad (33)$$

where as indicates the anti-symmetric portion of the stress tensor, $\mathbf{t}_{as}^s = \mathbf{t}^s - \mathbf{t}_{sym}^s$, one obtains an expression for μ^{sN} , which when substituted back into equation (31) yields

$$\mu^{sj} \mathbf{I} = \tilde{A}^{sj} \mathbf{I} - \frac{1}{\rho^{sj}} \mathbf{t}^{sj} + \frac{1}{\rho^s} \left(\mathbf{t}_e^s + \frac{\varepsilon^l}{\varepsilon^s} \mathbf{t}_s^l + \mathbf{t}_{as}^s \right) + z^{sj} \Lambda \quad j = 1, \dots, N. \quad (34)$$

The first two terms on the right-hand-side form the classical chemical potential (see Bowen, [11]), although these terms do not produce a scalar. In [7, 9] it was shown that incorporating the stress tensors yields an appropriate definition of chemical potential when no electric field or charges exist. Note that changing the effective stress or hydration stress in a porous medium results in a change in the chemical potential, which in turn produces a different balance of species within phases. The last term incorporates charge neutrality and suggests that changing the location of charges changes the *chemical* potential as well.

Taking advantage of these relations and simplifying gives us the dissipative portion of the entropy inequality in Appendix A.

4 Near-Equilibrium Constitutive Restrictions

Equilibrium is defined to occur when the following variables, defined generically as x_a , are zero:

$$\mathbf{d}^l, \varepsilon^l, \mathbf{v}^{l,s}, \nabla \mathbf{v}^{l_j,l}, \mathbf{v}^{\alpha_j,\alpha}, \quad \alpha = l, s \quad j = 1, \dots, N-1 \quad (35)$$

$$\varepsilon^l \rho^{l_j} \hat{c}_s^{l_j}, \boldsymbol{\omega}^\alpha, \varepsilon^l \rho^{l_j} \hat{Z}_s^{l_j}, \quad \alpha = l, s \quad j = 1, \dots, N. \quad (36)$$

Using a dimensionality argument we can show that these variables are functionally independent. Hence we have

$$\frac{\partial}{\partial x_a} \left(\sum_{\alpha=l,s} \varepsilon^\alpha \rho^\alpha T \hat{\Lambda}^\alpha \right)_D \Big|_e = 0, \quad \frac{\partial^2}{\partial (x_a x_b)} \left(\sum_{\alpha=l,s} \varepsilon^\alpha \rho^\alpha T \hat{\Lambda}^\alpha \right)_D \Big|_e \geq 0, \quad (37)$$

where subscript e denotes equilibrium. Note that we have not incorporated \hat{r}^{α_j} and \hat{q}^{α_j} into the above set. This is because without incorporating specific chemical reactions, incorrect results are obtained.

So for example, considering $x_a = \mathbf{d}^l$, we have at equilibrium

$$\mathbf{t}_{sym}^l = -(p^l - q_e^l \Lambda) \mathbf{I}. \quad (38)$$

To obtain results which hold near equilibrium, we expand linearly about equilibrium. For example

$$\begin{aligned} & \left(\mathbf{t}_{sym}^l + (p^l - q_e^l \Lambda) \mathbf{I} + \sum_{j=1}^N \rho^{l_j} \mathbf{v}^{l_j,l} \mathbf{v}^{l_j,l} \right)_{\text{neq}} \\ & \approx \left(\mathbf{t}_{sym}^l + (p^l - q_e^l \Lambda) \mathbf{I} \right)_{\text{eq}} + \mathbf{f}_1 : \mathbf{d}^l + f_2 \varepsilon^l + \dots \end{aligned} \quad (39)$$

where \mathbf{f}_1 is a fourth order tensor and f_2 is a scalar. These linearization coefficients are functions of all independent variables which are not in the lists (35) or (36). In this manner one can obtain cross effects, e.g. [18], and nonlinear terms, e.g. [6]. With the exception of $\mathbf{v}^{l,s}$ and $\mathbf{v}^{\alpha j, \alpha}$, we choose to linearize only about the one variable which produces a quadratic term in the entropy inequality, e.g. for the liquid phase stress tensor:

$$\mathbf{t}_{\text{sym}}^l \approx -(p^l - q_e^l \Lambda) \mathbf{I} + \boldsymbol{\nu} : \mathbf{d}^l - \sum_{j=1}^N \rho^{lj} \mathbf{v}^{lj,l} \mathbf{v}^{lj,l} \quad (40)$$

where $\boldsymbol{\nu}$ is a fourth-order tensor. Note that similar to (28), it is the term $p^l - q_e^l \Lambda$ which represents normal force per unit area.

We remark here that in order to obtain equilibrium results the variables listed in (35) and (36) must be functionally independent. However near equilibrium, one can linearize about any independent variable which is zero at equilibrium.

We define the swelling pressure as

$$\pi^\alpha = -\varepsilon^\alpha \rho^\alpha \left. \frac{\partial \tilde{A}}{\partial \varepsilon^\alpha} \right|_{\rho^{\alpha j}, T, \dots} \quad (41)$$

which represents the change in energy of phase α with respect to the relative quantity of phase α in the system. If the liquid and solid phase are non-interacting (non-swelling), then the energy of either phase would not change if the volume fractions were changed (keeping the densities fixed) and this quantity would be zero. A more detailed discussion of p^α and π^α is forthcoming in another manuscript.

Using these definition and linearizing about ε^l , we obtain

$$\mu^l \varepsilon^l = p^l + \pi^l - (p^s + \pi^s) + \frac{1}{2} \varepsilon_o \mathbf{E}_T \cdot (\mathbf{E}^l - \mathbf{E}^s), \quad (42)$$

where μ^l is the linearization coefficient and is not to be confused with the chemical potential. Thus if there are no effects of the electric field and $p^l + \pi^l > p^s + \pi^s$ the volume fraction will change so as to increase the amount of the liquid phase. The last term involves the differences in a portion of the electro-stress tensor $\mathbf{t}_E = \mathbf{D}\mathbf{E} - \frac{1}{2} \varepsilon_o \mathbf{E} \cdot \mathbf{E}\mathbf{I}$ (see the conservation of linear momentum equation in Part I). Thus if the contribution of the electric field of one phase is greater than the other, then the equilibrium volume fraction will be affected, but the electrical potential does *not* effect the equilibrium volume fraction.

Linearizing about $\boldsymbol{\omega}^\alpha = \boldsymbol{\nabla} \mathbf{v}^l - \mathbf{d}^l$ yields the traditional result

$$\varepsilon^\alpha \mathbf{t}_{\text{as}}^\alpha = \mathbf{Q}^\alpha : \boldsymbol{\omega}^\alpha, \quad (43)$$

where \mathbf{Q}^α is a second-order tensor which may be a function of all independent variables not necessarily zero at equilibrium, $\boldsymbol{\omega}^\alpha$ is the anti-symmetric part of the gradient of the velocity of phase α , and $\mathbf{t}_{\text{as}}^\alpha$ is the anti-symmetric part of the

stress tensor. This expression states that the stress tensors are in general not symmetric, which was known from the conservation of angular momentum (see Part I [5]). Cross effects can also be obtained [18].

Linearizing about the conservation of charge exchange term, $\widehat{Z}_s^{l_j}$, yields the following near-equilibrium result

$$\varepsilon^l \rho^{l_j} G^{l_j} \widehat{Z}_s^{l_j} = \frac{\rho^s}{\rho^{s_j}} \frac{\partial \widetilde{A}^s}{\partial z^{s_j}} - \frac{\rho^l}{\rho^{l_j}} \frac{\partial \widetilde{A}^l}{\partial z^{l_j}}, \quad (44)$$

where G^{l_j} is the linearization constant and where we assumed there are no cross effects. Thus a transfer of ions of one species between phases occurs only if there is an imbalance in the part of the electric-potential involving ion disassociation.

Adsorption relations are obtained by linearizing about the rate at which mass is transferred from the solid phase to the liquid phase, $\varepsilon^l \rho^{l_j} \widehat{e}_s^{l_j}$. At equilibrium we obtain

$$\mu^{l_j} - \mu^{s_j} = (z^{s_j} - z^{l_j})\Lambda + \left(\frac{z^{l_j} \rho^l}{\rho^{l_j}} \frac{\partial \widetilde{A}^l}{\partial z^{l_j}} - \frac{z^{s_j} \rho^s}{\rho^{s_j}} \frac{\partial \widetilde{A}^s}{\partial z^{s_j}} \right), \quad (45)$$

or

$$\widetilde{\mu}^{l_j} = \widetilde{\mu}^{s_j} \quad (46)$$

which is why we defined the electro-chemical potential as we did. This is the boundary condition between phases, and in a more general framework (see e.g. [3, 4]) this would produce the boundary condition for an osmotic experiment in which the mixture on one side contains ions.

To obtain a near-equilibrium result governing phase transition, we linearize about $\widehat{e}_\beta^{l_j}$. Neglecting quadratic terms of relative velocities yields

$$\rho^{l_j} \mathbf{K}^{l_j} \widehat{e}_s^{l_j} = \widetilde{\mu}^{s_j} - \widetilde{\mu}^{l_j} + \rho^{l_j} z^{s_j} G^{l_j} \widehat{Z}_s^{l_j} \quad (47)$$

where, by (44), the last term on the right-hand-side is zero at equilibrium. Thus the larger the difference in the electro-chemical potentials, the faster the phase transitions occur.

The relationship between the chemical potential and the partial stress tensor of the liquid phase is obtained exactly as in the previous section for the solid phase, except that the liquid phase result holds only at equilibrium:

$$\mu^{l_j} \mathbf{I} = \widetilde{A}^{l_j} \mathbf{I} - \frac{1}{\rho^{l_j}} \mathbf{t}^{l_j} + z^{l_j} \Lambda \mathbf{I}. \quad (48)$$

5 Bulk-Phase Flow and Diffusion

The equations which govern momentum balance in porous media are known as generalized Darcy's equations, after Darcy, who in 1856 empirically derived

the rather simple relationship that flux is proportional to the gradient in fluid pressure:

$$\varepsilon^l \mathbf{v}^{l,s} = -\mathbf{K} \nabla p^l + \varepsilon^l \rho^l \mathbf{g}, \quad (49)$$

where \mathbf{K} is the conductivity of the material. It is generally thought to be valid for slow-moving viscous fluids through a homogeneous granular media. We would like to determine the generalization of this law for the swelling charged porous media considered here. To begin with, we obtain a near equilibrium expression for $\widehat{\mathbf{T}}_s^l$ by linearizing the coefficient of $\mathbf{v}^{l,s}$ about $\mathbf{v}^{l,s}$ and the diffusive velocities, $\mathbf{v}^{l_j,l}$ in order to capture the effects of ion hydration (see e.g. (39)). This expression may then be substituted into the conservation of momentum equation. Neglecting inertial effects, the Brinkman correction term, $\nabla \cdot \nabla \mathbf{v}^l$, as well as the term involving $\nabla \cdot \boldsymbol{\omega}^l$ (see (43)), and using (38) to eliminate \mathbf{t}^l we obtain:

$$\begin{aligned} \mathbf{K} \cdot \mathbf{v}^{l,s} &= -\varepsilon^l \nabla p^l + \varepsilon^l \rho^l (\mathbf{g}^l + \mathbf{g}_I^l) + \pi^l \nabla \varepsilon^l + \varepsilon^l q_e^l \mathbf{E}_T \\ &+ \varepsilon^l q_e^l \nabla \Lambda - \varepsilon^l \rho^l \frac{\partial \widetilde{A}^l}{\partial \boldsymbol{\mathcal{E}}^s} : (\nabla \boldsymbol{\mathcal{E}}^s)^T - \varepsilon^l \rho^l \frac{\partial \widetilde{A}^l}{\partial \mathbf{E}_T} \cdot (\nabla \mathbf{E}_T)^T \\ &- \varepsilon^l \rho^l \frac{\partial \widetilde{A}^l}{\partial (\nabla T)} \cdot (\nabla^2 T) - \sum_{j=1}^N \mathbf{r}^{l_j} \cdot \mathbf{v}^{l_j,l}, \end{aligned} \quad (50)$$

where $\frac{\partial A^l}{\partial \boldsymbol{\mathcal{E}}^s} : (\nabla \boldsymbol{\mathcal{E}}^s)^T = \frac{\partial A^l}{\partial \boldsymbol{\mathcal{E}}_{ij}^s} \boldsymbol{\mathcal{E}}_{ij,k}^s$ in indicial notation. The linearization coefficients \mathbf{K} and \mathbf{r}^{l_j} are second-order tensors which may be a function of all independent variables not equal to zero at equilibrium, including ε^l . The first 2 terms on the right-hand side recover the standard Darcy's equation (49), except that p^l is not the classical pressure of normal force per unit area, but a thermodynamic definition of pressure, see equation (38). The third term involving \mathbf{g}_I^l , is due to fluctuations in the electric field, see its definition in Appendix A of [5]. The terms not involving the electric field have been derived before [4] and these results are discussed in detail in [8]. They indicate that flow can be driven by a gradient in the volume fraction if the medium swells ($\pi^l \neq 0$) and also by gradients in shear strain, the latter of which may be appropriate for swelling media with low water content. These terms account for the chemical/hydration forces between the solid and liquid phase. The term involving $(\nabla^2 T)$ is likely negligible - first order thermal effects are obtained by considering cross terms. In addition to these terms, we have the Lorentz force ($\varepsilon^l q_e^l \mathbf{E}_T$), the Kelvin force (using equation (21)) $\varepsilon^l \mathbf{P}^l \cdot \nabla \mathbf{E}_T$, and a term enforcing charge neutrality, $\varepsilon^l q_e^l \nabla \Lambda$. The last term involving summation over species is a cross-term put in specifically to capture the hydrating effect of ions. Each charged particle surrounds itself with water molecules, thereby impeding or enhancing bulk phase flow when the diffusive velocity of the charged species are non-negligible. This term is negligible for non-hydrating species.

Alternatively we can re-write Darcy's law in terms of the bulk phase chemical potential, as this is the formulation often used in applications [20, 23]. Define

the bulk phase potential as the Gibb's potential:

$$G^l = \sum_{j=1}^N C^{lj} \mu^{lj} = \tilde{A}^l + \sum_{j=1}^N \rho^{lj} \frac{\partial \tilde{A}^l}{\partial \rho^{lj}} = \tilde{A}^l + \frac{p^l}{\rho^l}. \quad (51)$$

Further we wish to re-write the electrical forcing terms in terms of the Maxwell stress tensor:

$$\mathbf{t}_M^l = \mathbf{D}^l \mathbf{E}_T - \frac{1}{2} \varepsilon_o \mathbf{E}^l \cdot \mathbf{E}_T \mathbf{I}, \quad (52)$$

Assuming that the electric fields are defined such that the exchange term in Gauss law is zero ($\nabla \cdot (\varepsilon^l \mathbf{D}^l) - \varepsilon^l q_e^l = 0$) we have

$$\begin{aligned} \varepsilon^l q_e^l \mathbf{E}_T + \varepsilon^l \mathbf{P}^l \cdot \nabla \mathbf{E}_T &= \nabla \cdot (\varepsilon^l \mathbf{D}^l \mathbf{E}_T - \frac{1}{2} \varepsilon_o \mathbf{E}^l \cdot \mathbf{E}_T \mathbf{I}) \\ &+ \frac{1}{2} \varepsilon_o \mathbf{E}^l \cdot \mathbf{E}_T \nabla \varepsilon^l - \frac{1}{2} \varepsilon_o \varepsilon^l (\mathbf{E}^l \cdot \nabla \mathbf{E}_T - \nabla \mathbf{E}^l \cdot \mathbf{E}_T). \end{aligned} \quad (53)$$

Further, assuming $\varepsilon^l \rho^l \mathbf{g}_I^l - \frac{1}{2} \varepsilon_o \varepsilon^l (\mathbf{E}^l \cdot \nabla \mathbf{E}_T - \nabla \mathbf{E}^l \cdot \mathbf{E}_T = \sum_{j=1}^N \frac{1}{2} \varepsilon_o \varepsilon^l [\langle \nabla \mathbf{E}^j \cdot \mathbf{E} \rangle^l - \langle \nabla \mathbf{E} \cdot \mathbf{E}^j \rangle^l]$ (see Part I, Appendices B and C), is negligible, we have

$$\begin{aligned} \mathbf{K} \cdot \mathbf{v}^{l,s} &= -\varepsilon^l \rho^l \nabla G^l + \sum_{j=1}^N \varepsilon^l (\rho^l)^2 \frac{\partial \tilde{A}^l}{\partial \rho^{lj}} \nabla C^{lj} + \varepsilon^l q_e^l \nabla \Lambda + \sum_{j=1}^N \varepsilon^l \rho^l \frac{\partial \tilde{A}^l}{\partial z^{lj}} \nabla z^{lj} \\ &- \varepsilon^l \nabla \mathbf{E}_T \cdot \mathbf{P}^l + \varepsilon^l \rho^l \mathbf{g}^l + \nabla \cdot (\varepsilon^l \mathbf{t}_M^l) + \varepsilon^l \rho^l \frac{\partial \tilde{A}^l}{\partial T} \nabla T + \frac{1}{2} \varepsilon_o \mathbf{E}_T \cdot \mathbf{E}^l \nabla \varepsilon^l \\ &- \sum_{j=1}^N \mathbf{r}^{lj} \cdot \mathbf{v}^{lj,l}, \end{aligned} \quad (54)$$

which is comparable to what is derived in [20, 23]. The first term is denoted as the *mechanochemical force* since it does not incorporate the electrical potential, the second term is due to osmotic effects, the third and fourth terms due to the electrical potential. The next two terms on the second line accounts for the Kelvin force and gravity, respectively, and the following term states that the Maxwell stress tensor effects flow. Thermal effects appear explicitly in this form, and since $\frac{\partial \tilde{A}}{\partial T} < 0$ (see (20)), we see that flow goes from hot to cold regions. The last term on the second line magnifies the effects due to gradients in volume fractions if electric fields are non-negligible. The last term is due to hydration and was discussed above.

Diffusion in a single-phase mixture is governed by *Fick's law*, which states diffusive velocity is proportional to the gradient of the chemical potential. Here we derive a novel form of Fick's law. Begin with the coefficient of $\mathbf{v}^{lj,l}$ in the residual entropy inequality which, when set to zero, gives at equilibrium:

$$\varepsilon^\alpha \rho^{\alpha j} (\hat{\mathbf{i}}^{\alpha j} + \hat{\mathbf{T}}_\beta^{\alpha j}) - \varepsilon^\alpha \rho^{\alpha j} (\hat{\mathbf{i}}^{\alpha N} + \hat{\mathbf{T}}_\beta^{\alpha N}) = -\nabla [\varepsilon^\alpha \rho^{\alpha j} (\tilde{A}^{\alpha j} - \tilde{A}^{\alpha N})]$$

$$\begin{aligned}
& -\varepsilon^\alpha \nabla \mathbf{E}_T \cdot (\mathbf{P}^{\alpha_j} - \frac{\rho^{\alpha_j}}{\rho^{\alpha_N}} \mathbf{P}^{\alpha_N}) + \frac{1}{2} \varepsilon_o \mathbf{E}_T \cdot (\mathbf{E}^{\alpha_j} - \frac{\rho^{\alpha_j}}{\rho^{\alpha_N}} \mathbf{E}^{\alpha_N}) \nabla \varepsilon^\alpha \\
& + \rho^\alpha \left(\frac{\partial \tilde{A}^\alpha}{\partial \rho^{\alpha_j}} - \frac{\partial \tilde{A}^\alpha}{\partial \rho^{\alpha_N}} \right) \nabla (\varepsilon^\alpha \rho^{\alpha_j}) + \varepsilon^\alpha \rho^\alpha \left(\frac{\partial \tilde{A}^\alpha}{\partial z^{\alpha_j}} \nabla z^{\alpha_j} - \frac{\rho^{\alpha_j}}{\rho^{\alpha_N}} \frac{\partial \tilde{A}^\alpha}{\partial z^{\alpha_N}} \nabla z^{\alpha_N} \right) \\
& - \Lambda \nabla (\varepsilon^\alpha \rho^{\alpha_j} (z^{\alpha_j} - z^{\alpha_N})) - \varepsilon^\alpha (q_e^{\alpha_j} - \frac{\rho^{\alpha_j}}{\rho^{\alpha_N}} q_e^{\alpha_N}) \mathbf{E}_T \\
& - \varepsilon^\alpha \nabla \left(\frac{\rho^{\alpha_j}}{\rho^{\alpha_N}} \right) \cdot \mathbf{t}^{\alpha_N} \Big] \quad j = 1, \dots, N-1.
\end{aligned} \tag{55}$$

Summing (55) over j from 1 to N and making use of the equilibrium relationship

$$\begin{aligned}
\sum_{j=1}^N \varepsilon^l \rho^{l_j} \hat{\mathbf{T}}_s^{l_j} &= \varepsilon^l \rho^l \hat{\mathbf{T}}_s^l = -\varepsilon^l \rho^l \nabla \tilde{A}^l + \sum_{j=1}^N \rho^l \frac{\partial \tilde{A}^l}{\partial \rho^{l_j}} \nabla (\varepsilon^l \rho^{l_j}) + \sum_{j=1}^N \varepsilon^l \rho^l \frac{\partial \tilde{A}^l}{\partial z^{l_j}} \nabla z^{l_j} \\
& + \varepsilon^l \rho^l \frac{\partial \tilde{A}^l}{\partial T} \nabla T - \varepsilon^l \nabla \mathbf{E}_T \cdot \mathbf{P}^l + \frac{1}{2} \varepsilon_o \mathbf{E}_T \cdot \mathbf{E}^l \nabla \varepsilon^l \\
& - \Lambda \nabla (\varepsilon^l q_e^l)
\end{aligned} \tag{56}$$

we obtain (57) for the case $j = N$. Substituting this result back into (55) and again making use of (29) and (48) we obtain the equilibrium result:

$$\begin{aligned}
\varepsilon^l \rho^{l_j} (\hat{\mathbf{i}}^{l_j} + \hat{\mathbf{T}}_s^{l_j}) &= -\varepsilon^l \rho^{l_j} \nabla \mu^{l_j} - \nabla \cdot (\varepsilon^l \mathbf{t}^{l_j}) + \varepsilon^l q_e^{l_j} \nabla \Lambda \\
& + \varepsilon^l \rho^{l_j} \frac{\partial \tilde{A}^l}{\partial T} \nabla T - \varepsilon^l \nabla \mathbf{E}_T \cdot \mathbf{P}^{l_j} + \varepsilon^l \rho^{l_j} (z^l - z^{l_j}) \mathbf{E}_T + \frac{1}{2} \varepsilon_o \mathbf{E}_T \cdot \mathbf{E}^{l_j} \nabla \varepsilon^l
\end{aligned} \tag{57}$$

Next we linearize the coefficient of $\mathbf{v}^{l_j, l}$ about equilibrium by expanding the coefficient in the original entropy inequality given in Appendix B in terms of both $\mathbf{v}^{l_j, l}$ and $\mathbf{v}^{l, s}$ so that Onsager's principal is still satisfied. This allows us to obtain non-relative results since $j = 1, \dots, N$. Here we make use of the fact that \tilde{A}^l and the primary independent variables, listed in (8), are the same at equilibrium and near-equilibrium. That this holds for \tilde{A}^l is justified by \tilde{A}^l not being a function of any of the variables which define equilibrium. Using this result to eliminate $\varepsilon^l \rho^{l_j} (\hat{\mathbf{i}}^{l_j} + \hat{\mathbf{T}}_s^{l_j})$ in the conservation of momentum equation, neglecting the inertial term, and approximating μ^{l_j} using equation (48), we obtain

$$\begin{aligned}
\mathbf{R}^{l_j} \mathbf{v}^{l_j, l} &= -\varepsilon^l \rho^{l_j} \nabla \mu^{l_j} + \varepsilon^l \rho^{l_j} (\mathbf{g}^{l_j} - \mathbf{g}_I^{l_j}) + \varepsilon^l \rho^l \frac{\partial \tilde{A}^l}{\partial z^{l_j}} \nabla z^{l_j} + \varepsilon^l q_e^{l_j} \nabla \Lambda \\
& - \varepsilon^l \rho^{l_j} z^l \mathbf{E}_T + \varepsilon^l \rho^{l_j} \frac{\partial \tilde{A}^l}{\partial T} \nabla T - \mathbf{k}^{l_j} \cdot \mathbf{v}^{l, s}
\end{aligned} \tag{58}$$

where \mathbf{R}^{lj} and \mathbf{k}^{lj} are linearization constants and must be such that \mathbf{K} , \mathbf{r}^{lj} , \mathbf{R}^{lj} and \mathbf{k}^{lj} satisfy the Onsager relationship. Note that this is similar in form to the bulk flow equation (54). The Lorentz term, $\varepsilon^l \rho^{lj} z^l \mathbf{E}_T$, is actually a relative Lorentz term, and the form is a consequence of the bulk phase velocity, \mathbf{v}^l , being a mass-averaged velocity.

To analyze this further, assume that body force, \mathbf{g}^{lj} is gravity, \mathbf{g} , temperature gradients are negligible, the body force due to electric field fluctuations is negligible $\mathbf{g}_I^{lj} = 0$, and we enforce charge neutrality with the Lagrange multiplier, Λ , and that the charge number on species j is constant ($\nabla z^{lj} = \mathbf{0}$). In this case (58) simplifies to

$$\begin{aligned} \mathbf{R}^{lj} \mathbf{v}^{lj,l} = & -\varepsilon^l \rho^{lj} \nabla \mu^{lj} + \varepsilon^l q_e^{lj} \nabla \Lambda + \varepsilon^l \rho^{lj} \mathbf{g} \\ & - \varepsilon^l C^{lj} q_e^l \mathbf{E}_T - \mathbf{k}^{lj} \cdot \mathbf{v}^{l,s} \end{aligned} \quad (59)$$

The first two terms (on the right-hand-side) state that the driving forces are the chemical potential and the streaming potential. The Lorentz term involves the bulk-phase force weighted by the mass fraction, just as the gravitational force is weighted by the mass density. This term is new and should be evaluated carefully, although similar bulk terms have been derived before, [2]. The last term in (59) is the result of linearizing the dissipative terms about both $\mathbf{v}^{l,s}$ and $\mathbf{v}^{lj,l}$ and accounts for hydrating effects.

6 Discussion

We exploited the entropy inequality to obtain restrictions on the form of constitutive relations for swelling porous media composed of a possibly polarizable solid and liquid phase, with charges and an electric field. This has applications in swelling clay soils, biopolymers, biological membranes, pulsed electrophoresis, chromatography, drug delivery, and other swelling systems. We did so under the philosophy that it is the total electric field which contributes to the force and work terms in the conservation of momentum and energy, and that it is only the total electric field which is measurable. This produced an additional forcing term involving the gradient of the volume fraction, and an additional body force which is a result of fluctuations in the electric field, appearing in the macroscale conservation of momentum equation. The new body force term appears wherever gravity appears, and the extra term involving the gradient of the volume fraction, $\frac{1}{2} \varepsilon_o \mathbf{E}_T \cdot \mathbf{E}^l \nabla \varepsilon^l$, affects only the bulk phase flow when this equation is written in terms of the Maxwell stress tensor of the liquid phase, see (54). These terms are a consequence of assuming that the primitive form of the momentum and energy equation is the form written in terms of the Lorentz force and Kelvin force, instead of the Maxwell stress tensor (see Part I).

The Lagrange multiplier which enforces charge neutrality is shown to correspond with the electrical potential and is seen to affect the macroscopic pressure (see e.g. (28) and (40)), so that classical pressure is not the thermodynamically defined pressure, p^α , but is $p^\alpha - q_e^\alpha \Lambda$. Thus care must be taken in interpreting the pressure term given in the generalized Darcy law, (50).

It was assumed that ion-disassociation can occur, and this is represented by terms which contain the partial of the Helmholtz free energy density with respect to the charge per unit mass. This term can also be related to the charge per molecule, see the discussion following (30). This term does not affect pressure, but does manifest itself in bulk phase flow and diffusion.

The boundary condition between phases is a natural by-product of this formulation, and it is shown that the electric field does not influence the boundary condition, but that it is the balance of the electro-chemical potential which determines equilibrium, see (46). Polarization enters into it only through the definition of \tilde{A}^α , see (6).

It was also shown that the rate at which the medium swells is determined by the difference in the thermodynamic and swelling pressures, $(p^l + \pi^l) - (p^s + \pi^s)$ and the difference of a portion of the electro-stress tensor, see equation (42).

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Appendix A. Dissipative Entropy Inequality

The dissipative portion of the entropy inequality is

$$\begin{aligned}
& \left(\sum_{\alpha} \varepsilon^{\alpha} \rho^{\alpha} T \widehat{\Lambda}^{\alpha} \right)_D = \\
& \mathbf{d}^l : \left[\varepsilon^l \mathbf{t}_{\text{sym}}^l + \sum_{j=1}^N \varepsilon^l \rho^{lj} \mathbf{v}^{lj,l} \mathbf{v}^{lj,l} + \varepsilon^l p^l - \varepsilon^l q_e^l \Lambda \right] \\
& + \dot{\varepsilon}^l \left[-\varepsilon^l \rho^l \frac{\partial \widetilde{A}^l}{\partial \varepsilon^l} - \varepsilon^s \rho^s \frac{\partial \widetilde{A}^s}{\partial \varepsilon^l} + p^l - p^s + \frac{1}{2} \varepsilon_o \mathbf{E}_T \cdot (\mathbf{E}^l - \mathbf{E}^s) \right] \\
& + \mathbf{v}^{l,s} \cdot \left[-\varepsilon^l \rho^l \nabla \widetilde{A}^l + \sum_{j=1}^N \rho^l \frac{\partial \widetilde{A}^l}{\partial \rho^{lj}} \nabla (\varepsilon^l \rho^{lj}) + \sum_{j=1}^N \varepsilon^l \rho^l \frac{\partial \widetilde{A}^l}{\partial z^{lj}} \nabla z^{lj} \right. \\
& \quad \left. + \varepsilon^l \rho^l \frac{\partial \widetilde{A}^l}{\partial T} \nabla T - \varepsilon^l \nabla \mathbf{E}_T \cdot \mathbf{P}^l + \frac{1}{2} \varepsilon_o \mathbf{E}_T \cdot \mathbf{E}^l \nabla \varepsilon^l - \Lambda \nabla (\varepsilon^l q_e^l) - \varepsilon^l \rho^l \widehat{\mathbf{T}}_s^l \right] \\
& + \sum_{j=1}^{N-1} \nabla \mathbf{v}^{lj,l} : \varepsilon^l \left[\mathbf{t}^{lj} - \frac{\rho^{lj}}{\rho^{lN}} \mathbf{t}^{lN} + \rho^l \rho^{lj} \left(\frac{\partial \widetilde{A}^l}{\partial \rho^{lj}} - \frac{\partial \widetilde{A}^l}{\partial \rho^{lN}} \right) - \rho^{lj} (\widetilde{A}^{lj} - \widetilde{A}^{lN}) \mathbf{I} \right. \\
& \quad \left. - (q_e^{lj} - \frac{\rho^{lj}}{\rho^{lN}} q_e^{lN}) \Lambda \mathbf{I} \right] \\
& + \sum_{\alpha=l,s} \sum_{j=1}^{N-1} \mathbf{v}^{\alpha j, \alpha} \cdot \left[-\varepsilon^{\alpha} \rho^{\alpha j} (\widehat{\mathbf{i}}^{\alpha j} + \widehat{\mathbf{T}}_{\beta}^{\alpha j}) + \varepsilon^{\alpha} \rho^{\alpha j} (\widehat{\mathbf{i}}^{\alpha N} + \widehat{\mathbf{T}}_{\beta}^{\alpha N}) \right. \\
& \quad - \nabla (\varepsilon^{\alpha} \rho^{\alpha j} (A^{\alpha j} - A^{\alpha N})) - \varepsilon^{\alpha} \nabla \mathbf{E}_T \cdot (\mathbf{P}^{\alpha j} - \frac{\rho^{\alpha j}}{\rho^{\alpha N}} \mathbf{P}^{\alpha N}) \\
& \quad + \frac{1}{2} \varepsilon_o \mathbf{E}_T \cdot (\mathbf{E}^{\alpha j} - \frac{\rho^{\alpha j}}{\rho^{\alpha N}} \mathbf{E}^{\alpha N}) \nabla \varepsilon^{\alpha} + \rho^{\alpha} \left(\frac{\partial \widetilde{A}^{\alpha}}{\partial \rho^{\alpha j}} - \frac{\partial \widetilde{A}^{\alpha}}{\partial \rho^{\alpha N}} \right) \nabla (\varepsilon^{\alpha} \rho^{\alpha j}) \\
& \quad + \varepsilon^{\alpha} \rho^{\alpha} \left(\frac{\partial \widetilde{A}^{\alpha}}{\partial z^{\alpha j}} \nabla z^{\alpha j} - \frac{\rho^{\alpha j}}{\rho^{\alpha N}} \frac{\partial \widetilde{A}^{\alpha}}{\partial z^{\alpha N}} \nabla z^{\alpha N} \right) - \Lambda \left(\nabla (\varepsilon^{\alpha} \rho^{\alpha j} z^{\alpha j}) - \nabla (\varepsilon^{\alpha} \rho^{\alpha j} z^{\alpha N}) \right) \\
& \quad \left. - \varepsilon^{\alpha} (q_e^{\alpha j} - \frac{\rho^{\alpha j}}{\rho^{\alpha N}} q_e^{\alpha N}) \mathbf{E}_T - \varepsilon^{\alpha} \nabla \left(\frac{\rho^{\alpha j}}{\rho^{\alpha N}} \right) \cdot \mathbf{t}^{\alpha N} \right] \\
& + \sum_{\alpha=l,s} \frac{\varepsilon^{\alpha}}{T} \nabla T \cdot \left[\mathbf{q}^{\alpha} + \sum_{j=1}^N \left(\rho^{\alpha j} \mathbf{v}^{\alpha j, \alpha} (\widetilde{A}^{\alpha j} + \frac{1}{2} (\mathbf{v}^{\alpha j, \alpha})^2) - \mathbf{t}^{\alpha j} \cdot \mathbf{v}^{\alpha j, \alpha} \right) \right. \\
& \quad \left. - \rho^{\alpha} T \left(\eta^{\alpha} + \frac{\partial \widetilde{A}^{\alpha}}{\partial T} \right) \mathbf{v}^{\alpha, s} \right] \\
& + \sum_{\alpha=l,s} \sum_{j=1}^N \varepsilon^l \rho^{lj} \widehat{e}_s^{lj} \left[-\widetilde{A}^l + \widetilde{A}^s - \rho^l \frac{\partial \widetilde{A}^l}{\partial \rho^{lj}} + \rho^s \frac{\partial \widetilde{A}^s}{\partial \rho^{sj}} + \frac{\rho^s}{\rho^{sj}} \frac{\partial \widetilde{A}^s}{\partial z^{sj}} (z^{lj} - z^{sj}) \right]
\end{aligned}$$

$$\begin{aligned}
& +(z^{lj} - z^{sj})\Lambda + \frac{1}{2}\mathbf{v}^{sj,s} \cdot \mathbf{v}^{sj,s} - \frac{1}{2}\mathbf{v}^{lj,l} \cdot \mathbf{v}^{lj,l} - \frac{1}{2}\mathbf{v}^{l,s} \cdot \mathbf{v}^{l,s}] \\
& + \sum_{\alpha=l,s} \sum_{j=1}^N \varepsilon^\alpha \rho^{\alpha_j} \widehat{r}^{\alpha_j} \left[-\rho^\alpha \frac{\partial \widetilde{A}^\alpha}{\partial \rho^{\alpha_j}} + z^{\alpha_j} \Lambda - \frac{1}{2}(\mathbf{v}^{\alpha_j,\alpha})^2 \right] \\
& + \sum_{\alpha=l,s} \boldsymbol{\omega}^\alpha : [\varepsilon^\alpha \mathbf{t}_{as}^\alpha] + \sum_{\alpha=l,s} \sum_{j=1}^N \nabla \cdot (\varepsilon^\alpha \mathcal{J}^{\alpha_j}) \left[\rho^\alpha \frac{\partial \widetilde{A}^\alpha}{\partial q_e^{\alpha_j}} - \Lambda \right] \\
& + \sum_{\alpha=l,s} \varepsilon^\alpha \mathcal{J}^\alpha \cdot \mathbf{E}_T - \sum_{\alpha=l,s} \sum_{j=1}^N \varepsilon^\alpha \widehat{q}^{\alpha_j} \left[\rho^\alpha \frac{\partial \widetilde{A}^\alpha}{\partial q_e^{\alpha_j}} - \Lambda \right] \\
& + \sum_{j=1}^N \varepsilon^l \rho^{lj} \widehat{Z}_s^{lj} \left[\frac{\rho^s}{\rho^{sj}} \frac{\partial \widetilde{A}^s}{\partial z^{sj}} - \frac{\rho^l}{\rho^{lj}} \frac{\partial \widetilde{A}^l}{\partial z^{lj}} \right] \geq 0, \tag{60}
\end{aligned}$$

where subscripted *sym* and *as* mean the symmetric and anti-symmetric part of the tensor, respectively.

Appendix B. Entropy Inequality

The entropy inequality in its entirety is:

$$\begin{aligned}
& \sum_{\alpha=l,s} \varepsilon^\alpha \rho^\alpha T \hat{\Lambda}^\alpha = \\
& \sum_{\alpha=l,s} \sum_{j=1}^N \varepsilon^\alpha \frac{D^s \rho^{\alpha j}}{Dt} \left[-\rho^\alpha \frac{\partial \tilde{A}^\alpha}{\partial \rho^{\alpha j}} + \lambda_\rho^{\alpha j} + \tilde{A}^{\alpha j} + \frac{1}{\rho^{\alpha j}} \mathbf{E}_T \cdot \mathbf{P}^{\alpha j} + z^{\alpha j} \Lambda \right] \\
& + \dot{\mathbf{E}}_T \cdot \left[-\varepsilon^l \rho^l \frac{\partial \tilde{A}^l}{\partial \mathbf{E}_T} - \varepsilon^s \rho^s \frac{\partial \tilde{A}^s}{\partial \mathbf{E}_T} - \varepsilon^l \mathbf{P}^l - \varepsilon^s \mathbf{P}^s \right] \\
& + \dot{T} \cdot \left[-\varepsilon^l \rho^l \eta^l - \varepsilon^l \rho^l \frac{\partial \tilde{A}^l}{\partial T} - \varepsilon^s \rho^s \eta^s - \varepsilon^s \rho^s \frac{\partial \tilde{A}^s}{\partial T} \right] \\
& + \mathbf{d}^l : \left[\varepsilon^l \mathbf{t}_{\text{sym}}^l + \varepsilon^l \mathbf{P}^l \cdot \mathbf{E}_T \mathbf{I} + \sum_{j=1}^N \varepsilon^l \rho^{lj} (\lambda_\rho^{lj} \mathbf{I} + \tilde{A}^{lj} \mathbf{I} + \mathbf{v}^{lj,l} \mathbf{v}^{lj,l}) \right] \\
& + \mathbf{d}^s : \left[\varepsilon^s \mathbf{t}_{\text{sym}}^s + \varepsilon^s \mathbf{P}^s \cdot \mathbf{E}_T \mathbf{I} + \sum_{j=1}^N \varepsilon^s \rho^{sj} (\lambda_\rho^{sj} \mathbf{I} + \tilde{A}^{sj} \mathbf{I} + \mathbf{v}^{sj,s} \mathbf{v}^{sj,s}) \right. \\
& \quad \left. - \varepsilon^l \rho^l \nabla \mathbf{F}^s \cdot \frac{\partial \tilde{A}^l}{\partial \boldsymbol{\varepsilon}^s} \cdot (\nabla \mathbf{F}^s)^T - \varepsilon^s \rho^s \nabla \mathbf{F}^s \cdot \frac{\partial \tilde{A}^s}{\partial \boldsymbol{\varepsilon}^s} \cdot (\nabla \mathbf{F}^s)^T \right] \\
& + \sum_{\alpha=l,s} \boldsymbol{\omega}^\alpha : \left[\varepsilon^\alpha \mathbf{t}_{\text{as}}^\alpha \right] + \sum_{\alpha=l,s} \sum_{j=1}^{N-1} \frac{D^s \mathbf{v}^{\alpha j, \alpha}}{Dt} \cdot \left[-\varepsilon^\alpha \rho^\alpha \frac{\partial \tilde{A}^\alpha}{\partial \mathbf{v}^{\alpha j, \alpha}} \right] \\
& + \nabla \dot{T} \cdot \left[-\varepsilon^l \rho^l \frac{\partial \tilde{A}^l}{\partial \nabla T} - \varepsilon^s \rho^s \frac{\partial \tilde{A}^s}{\partial \nabla T} \right] \\
& + \sum_{\alpha=l,s} \sum_{j=1}^N \nabla \frac{D^s \rho^{\alpha j}}{Dt} \cdot \left[-\varepsilon^\alpha \rho^\alpha \frac{\partial \tilde{A}^\alpha}{\partial (\nabla \rho^{\alpha j})} \right] \\
& + \dot{\varepsilon}^l \cdot \left[\sum_{j=1}^N (\rho^{lj} \lambda_\rho^{lj} - \rho^{sj} \lambda_\rho^{sj}) + \rho^l A^l - \rho^s A^s + \frac{1}{2} \varepsilon_o \mathbf{E}_T \cdot (\mathbf{E}^l - \mathbf{E}^s) \right. \\
& \quad \left. + \mathbf{E}_T \cdot (\mathbf{P}^l - \mathbf{P}^s) + \Lambda (q_e^l - q_e^s) - \varepsilon^l \rho^l \frac{\partial \tilde{A}^l}{\partial \varepsilon^l} - \varepsilon^s \rho^s \frac{\partial \tilde{A}^s}{\partial \varepsilon^l} \right] \\
& + \dot{\mathbf{v}}^{l,s} \cdot \left[-\varepsilon^l \rho^l \frac{\partial \tilde{A}^l}{\partial \mathbf{v}^{l,s}} \right] + \dot{\mathbf{d}}^l : \left[-\varepsilon^l \rho^l \frac{\partial \tilde{A}^l}{\partial \mathbf{d}^l} \right] + \dot{\mathbf{w}}^l : \left[-\varepsilon^l \rho^l \frac{\partial \tilde{A}^l}{\partial \mathbf{w}^l} \right] \\
& + \nabla \dot{\mathbf{v}}^{lj,l} : \left[-\varepsilon^l \rho^l \frac{\partial \tilde{A}^l}{\partial (\nabla \mathbf{v}^{lj,l})} \right] \\
& + \mathbf{v}^{l,s} \cdot \left[-\varepsilon^l \rho^l \frac{\partial \tilde{A}^l}{\partial \varepsilon^l} \nabla \varepsilon^l - \sum_{j=1}^N \varepsilon^l \rho^l \frac{\partial \tilde{A}^l}{\partial \rho^{lj}} \nabla \rho^{lj} - \varepsilon^l \rho^l \frac{\partial \tilde{A}^l}{\partial \boldsymbol{\varepsilon}^s} : (\nabla \boldsymbol{\varepsilon}^s)^T - \varepsilon^l \rho^l \frac{\partial \tilde{A}^l}{\partial \mathbf{E}_T} \cdot (\nabla \mathbf{E}_T)^T \right]
\end{aligned}$$

$$\begin{aligned}
& - \sum_{j=1}^N \varepsilon^l \rho^l \frac{\partial \tilde{A}^l}{\partial z^{lj}} \nabla z^{lj} - \varepsilon^l \nabla \mathbf{E}_T \cdot \mathbf{P}^l - \varepsilon^l \rho^l \hat{\mathbf{T}}_s^l + \frac{1}{2} \varepsilon_o \mathbf{E}_T \cdot \mathbf{E}^l \nabla \varepsilon^l \\
& + \sum_{j=1}^N (\tilde{A}^{lj} + \frac{1}{\rho^{lj}} \mathbf{E}_T \cdot \mathbf{P}^{lj}) \nabla (\varepsilon^l \rho^{lj}) + \sum_{j=1}^N \lambda_\rho^{lj} \nabla (\varepsilon^l \rho^{lj}) + \sum_{j=1}^N \varepsilon^l \rho^{lj} \lambda_{q_e}^{lj} \nabla z^{lj} \\
& - \varepsilon^l \rho^l \frac{\partial \tilde{A}^l}{\partial \mathbf{v}^{l,s}} \cdot (\nabla \mathbf{v}^{l,s})^T - \sum_{j=1}^{N-1} \varepsilon^l \rho^l \frac{\partial \tilde{A}^l}{\partial \mathbf{v}^{l,j,l}} \cdot (\nabla \mathbf{v}^{l,j,l})^T - \varepsilon^l \rho^l \frac{\partial \tilde{A}^l}{\partial \nabla T} \cdot \nabla^2 T \\
& - \varepsilon^l \rho^l \frac{\partial \tilde{A}^l}{\partial \nabla \mathbf{v}^{l,j,l}} : \nabla^2 \mathbf{v}^{l,j,l} - \sum_{j=1}^N \varepsilon^l \rho^l \frac{\partial \tilde{A}^l}{\partial (\nabla \rho^{lj})} \cdot \nabla^2 \rho^{lj} \\
& - \varepsilon^l \rho^l \frac{\partial \tilde{A}^l}{\partial \mathbf{d}^l} : (\nabla \mathbf{d}^l)^T - \varepsilon^l \rho^l \frac{\partial \tilde{A}^l}{\partial \mathbf{w}^l} : (\nabla \mathbf{w}^l)^T \Big] \\
& + \sum_{\alpha=l,s} \sum_{j=1}^N (\nabla \mathbf{v}^{\alpha j, \alpha})^T : \left[\varepsilon^\alpha \mathbf{t}^{\alpha j} + \varepsilon^\alpha \mathbf{P}^{\alpha j} \cdot \mathbf{E}_T \mathbf{I} + \varepsilon^\alpha \rho^{\alpha j} \lambda_\rho^{\alpha j} \mathbf{I} \right] \\
& + \sum_{\alpha=l,s} \frac{\varepsilon^\alpha}{T} \nabla T \cdot \left[\mathbf{q}^\alpha + \sum_{j=1}^N \left(\rho^{\alpha j} \mathbf{v}^{\alpha j, \alpha} (\tilde{A}^{\alpha j} + \frac{1}{2} (\mathbf{v}^{\alpha j, \alpha})^2) - \mathbf{t}^{\alpha j} \cdot \mathbf{v}^{\alpha j, \alpha} \right) \right. \\
& \quad \left. - T \rho^\alpha \left(\eta^\alpha + \frac{\partial \tilde{A}^\alpha}{\partial T} \right) \mathbf{v}^{\alpha, s} \right] \\
& + \sum_{\alpha=l,s} \sum_{j=1}^N \mathbf{v}^{\alpha j, \alpha} \cdot \left[- \varepsilon^\alpha \rho^{\alpha j} \hat{\mathbf{i}}^{\alpha j} - \sum_{\beta \neq \alpha} \varepsilon^\alpha \rho^{\alpha j} \hat{\mathbf{T}}_\beta^{\alpha j} - \varepsilon^\alpha \rho^{\alpha j} \nabla \tilde{A}^{\alpha j} \right. \\
& \quad \left. + \frac{1}{\rho^{\alpha j}} \mathbf{E}_T \cdot \mathbf{P}^{\alpha j} \nabla (\varepsilon^\alpha \rho^{\alpha j}) - \varepsilon^\alpha \nabla \mathbf{E}_T \cdot \mathbf{P}^{\alpha j} + \frac{1}{2} \varepsilon_o \mathbf{E}_T \cdot \mathbf{E}^{\alpha j} \nabla \varepsilon^\alpha \right. \\
& \quad \left. + \lambda_\rho^{\alpha j} \nabla (\varepsilon^\alpha \rho^{\alpha j}) + \varepsilon^\alpha \rho^{\alpha j} \lambda_{q_e}^{\alpha j} \nabla z^{\alpha j} - \varepsilon^\alpha q_e^{\alpha j} \mathbf{E}_T \right] \\
& + \sum_{\alpha=l,s} \varepsilon^\alpha \mathcal{J}^\alpha \cdot \mathbf{E}_T \\
& + \sum_{\alpha=l,s} \sum_{j=1}^N \sum_{\beta \neq \alpha} \varepsilon^\alpha \rho^{\alpha j} \hat{\mathbf{e}}_\beta^{\alpha j} \left[- \tilde{A}^{\alpha j} - \frac{1}{\rho^{\alpha j}} \mathbf{E}_T \cdot \mathbf{P}^{\alpha j} - \frac{1}{2} (\mathbf{v}^{\alpha j, \alpha})^2 - \lambda_\rho^{\alpha j} \right. \\
& \quad \left. - \tilde{A}^\alpha - \frac{1}{2} (\mathbf{v}^{\alpha, s})^2 \right] \\
& + \sum_{\alpha=l,s} \sum_{j=1}^N \varepsilon^\alpha \rho^{\alpha j} \hat{\mathbf{r}}^{\alpha j} \left[- \tilde{A}^{\alpha j} - \frac{1}{\rho^{\alpha j}} \mathbf{E}_T \cdot \mathbf{P}^{\alpha j} - \lambda_\rho^{\alpha j} - \frac{1}{2} (\mathbf{v}^{\alpha j, \alpha})^2 \right] \\
& + \sum_{\alpha=l,s} \nabla \cdot \mathbf{D}^{\alpha j} \left[\varepsilon^\alpha \lambda_D^{\alpha j} \right]
\end{aligned}$$

$$\begin{aligned}
& + \sum_{\alpha=l,s} \sum_{j=1}^N \frac{D^s z^{\alpha_j}}{Dt} \left[-\varepsilon^\alpha \rho^\alpha \frac{\partial \tilde{A}^\alpha}{\partial z^{\alpha_j}} + \varepsilon^\alpha \rho^{\alpha_j} \lambda_{q_e}^{\alpha_j} + \varepsilon^\alpha \rho^{\alpha_j} \Lambda \right] \\
& + \sum_{\alpha=l,s} \sum_{j=1}^N \nabla \times \mathbf{E}^{\alpha_j} \cdot \left[\mathbf{\Lambda}_E^{\alpha_j} \varepsilon^\alpha \right] \\
& + \sum_{\alpha=l,s} \sum_{j=1}^N \lambda_D^{\alpha_j} \left[\mathbf{D}^{\alpha_j} \cdot \nabla \varepsilon^\alpha - \varepsilon^\alpha q_e^{\alpha_j} - \varepsilon^\alpha \widehat{d}^{\alpha_j} - \sum_{\beta \neq \alpha} \varepsilon^\alpha \widehat{d}_\beta^{\alpha_j} \right] \\
& + \sum_{\alpha=l,s} \sum_{j=1}^N \mathbf{\Lambda}_E^{\alpha_j} \cdot \left[\nabla \varepsilon^\alpha \times \mathbf{E}^{\alpha_j} - \varepsilon^\alpha \widehat{\boldsymbol{\sigma}}^{\alpha_j} - \sum_{\beta \neq \alpha} \varepsilon^\alpha \widehat{\boldsymbol{\sigma}}_\beta^{\alpha_j} \right] \\
& + \sum_{\alpha=l,s} \sum_{j=1}^N \lambda_{q_e}^{\alpha_j} \left[\nabla \cdot (\varepsilon^\alpha \mathcal{J}^{\alpha_j}) - \varepsilon^\alpha \widehat{q}^{\alpha_j} - \sum_{\beta \neq \alpha} \varepsilon^\alpha \rho^{\alpha_j} \widehat{Z}_\beta^{\alpha_j} \right] \geq 0,
\end{aligned}$$

where subscripted *sym* and *as* mean the symmetric and anti-symmetric part of the tensor, respectively.