

A thermodynamically consistent theory of multicomponent porous media: finite-deformation mechanics, compositional flow, electrostatics, reactions, and phase transformations

John T. Foster

The Hildebrand Department of Petroleum & Geosystems Engineering

Department of Aerospace Engineering & Engineering Mechanics

The Oden Institute for Computational Engineering & Science

The University of Texas at Austin

`john.foster@utexas.edu`

<https://orcid.org/0000-0002-7173-4728>

This manuscript is a non-peer-reviewed preprint submitted to EarthArXiv.

October 9, 2026

A thermodynamically consistent theory of multicomponent porous media: finite-deformation mechanics, compositional flow, electrostatics, reactions, and phase transformations

John T. Foster^{*1,2,3}

¹*The Hildebrand Department of Petroleum & Geosystems Engineering, The University of Texas at Austin*

²*Department of Aerospace Engineering & Engineering Mechanics, The University of Texas at Austin*

³*The Oden Institute for Computational Engineering & Science, The University of Texas at Austin*

October 9, 2026

Abstract

Reactive reservoir models must combine compositional flow, deformation, electrostatics, chemical reactions, and phase transformations without losing the thermodynamic origin of each term. This paper develops such a theory for multicomponent, multiphase porous media at finite deformation. Component mass conservation is first written on phase-attached material regions and then volume averaged, which separates molecular diffusion and mechanical dispersion from bulk phase motion. Mobile fluids and load-bearing multicomponent solids use the same phase/component variables. Solid composition can therefore change stress-free deformation, elasticity, plastic flow, and nonlinear Biot coupling. A fixed-pressure Legendre transform gives phase Biot coefficients at the current reacted state; an optional additive component specialization resolves those coefficients into component contributions.

The derivation combines a constrained Hamilton–d’Alembert statement for the phase-coordinate balances with Onsager stationarity for dissipative saturation redistribution, reaction, and component-relative transport. Varying component material measures and phase Jacobians together produces the momentum carried by inserted mass and a generalized Darcy-like relative-flux law. The same calculation gives the composition restrictions, transfer-potential equations, and phase-transfer equilibrium conditions. Material-carried charge is tied directly to component mass. Traditional reaction affinities are sums of electrochemical potentials. Away from uniform temperature, charged transport instead keeps the temperature-weighted neutral-potential gradient separate from the electric field so that the force is independent of the arbitrary electric-potential level. The entropy inequality identifies admissible stress, pressure, reaction, drag, diffusion, dispersion, heat-transfer, and plastic-flow laws. A capillary-history state extends the interfacial energy to drainage–imbibition hysteresis, with its evolution restricted by the same dissipation inequality. An optional dynamic-capillary resistance relates the pressure lag to the skeleton-following saturation rate and supplies its d’Alembert work in the phase momentum balances. Standard compositional flow, black-oil flow, nonlinear poromechanics, and single-solid, single-fluid Biot theory follow as stated limits of the full solid-reference formulation.

^{*}Electronic address: john.foster@utexas.edu

1 Introduction

Reservoir flow, reactive transport, and geomechanics are usually formulated from different primary variables and with different levels of thermodynamic resolution. Compositional simulators evolve phase/component inventories and close phase fluxes with Darcy laws, phase behavior, and capillary relations. Poromechanics instead emphasizes deformation, pore pressure, and effective stress, while electrochemical and geochemical models introduce charge, diffusion, and reaction through additional constitutive laws. These specializations are effective in their intended regimes, but their direct coupling can obscure whether a pressure, source, flux, or interaction force is derived from a balance law, a constraint, or a dissipative closure.

Several established theories supply the ingredients needed for a more unified description. Reacting-mixture variational theories already provide phase-attached motions, material conversion, constituent momentum production, and Darcy-type porous-flow reductions [2, 22, 3, 21]. Macroscopic porous-medium thermodynamics derives multiphase balances, capillary restrictions, and generalized transport laws from averaged energy and entropy statements [36, 30]. Internal-variable extensions represent drainage–imbibition hysteresis as dissipative evolution within the interfacial state [57]. Poromechanics identifies effective-stress and equivalent-pressure structures [16, 39]. Seguin and Walkington give a nonreactive multicomponent, multiphase poroelastic theory in a solid observer [52], and Foster and Xu derive a fixed-pressure nonlinear Biot coefficient for a finite-deformation binary mixture [25]. For reacting and diffusing mixtures, force–flux restrictions follow from continuum thermodynamics and Onsager stationarity [10, 18, 56]; nonisothermal chemical-potential gradients also require explicit attention to potential gauges [29]. Finally, electroelastic potential theory relates electric enthalpy, displacement, and Maxwell stress [42, 19]. Bennethum and Cushman derive the macroscale electroquasistatic field equations for multicomponent, multiphase porous media [5] and the corresponding constitutive restrictions for phase stresses, diffusion, and Darcy flow [6].

This paper integrates these structures in one open-system phase/component derivation. The resulting theory couples seven extensions of the established balance, variational, thermodynamic, electrostatic, and reactive-solid constructions.

The derivation has three steps with distinct roles. A constrained Hamilton–d’Alembert statement determines the phase-coordinate equations, storage multipliers, momentum balances, and electrostatic field equation. Its virtual work carries prescribed loading and the d’Alembert work of constitutive nonconservative forces. A Coleman–Noll exploitation of two subsystem energy balances and the entropy inequality determines the admissible stresses, pressures, entropies, component potentials, and residual force–rate products. Onsager stationarity then supplies near-equilibrium closures for saturation redistribution, reaction, and component-relative transport. In the dynamic capillary branch, the saturation force is held fixed in the coordinate variation and varied through its conjugate rate in the Onsager statement. This separation distinguishes balance and constraint equations from the material-specific closures that determine the dissipative rates.

Within that construction, the paper makes seven specific contributions.

1. The open-system momentum balance retains the momentum carried by mass converted into each phase. Its fluid reduction gives a generalized Darcy law containing the actual phase-pressure gradients, body force, Maxwell stress, inertia, and conversion-insertion momentum. Net phase conversion changes the algebraic resistance and mobility used to eliminate the phase velocity; the exact nonsingularity and stronger positive-resistance conditions are distinguished from dissipation of the underlying drag.
2. A fixed-equivalent-pressure Legendre transform extends the nonlinear Biot construction from a binary mixture to multiple reacting solid phases at finite deformation. The phase Biot

coefficient is evaluated at the current reacted state and changes through solid mass, composition, distension, intrinsic specific volume, stress-free deformation, and internal variables.

3. The thermal and electrical construction gives gauge-invariant electrochemical transport and reaction forces when the mobile-fluid and solid subsystems have different temperatures. The temperature-weighted component-potential gradient remains separate from the electric field, while the usual electrochemical-potential gradient is recovered in the isothermal limit.
4. The constrained interfacial energy gives the stored capillary pressure at the current saturation and capillary-history state, with history evolution selecting drainage, imbibition, and scanning paths; an optional positive-semidefinite resistance adds a dynamic pressure lag proportional to the skeleton-following saturation rate. The unresolved interface carries separate fluid-subsystem entropy and internal-energy storage on the skeleton trajectory, so bulk phase convection transports only phase caloric quantities. Because the phases are derived as one coupled system, the phase electrical enthalpy differences enter the capillary pressure relations as a correction that uncoupled capillary closures omit. The electric potential also generates electric displacement, Maxwell stress, and dielectric pressure, and these stored, electrical, and dissipative contributions together set the actual phase pressures in the momentum and Darcy equations and give the electrically corrected equivalent pore pressure.
5. Variation of component mass fractions gives a generalized composition-stationarity system. At equilibrium it recovers equality of the appropriate electrochemical potentials; away from equilibrium it determines phase-reference values of the specific generalized transfer-work potentials. Consequently, the conversion force for phase change, dissolution, precipitation, and pore filling differs from the traditional stoichiometric affinity by an explicit phase-transfer-work term.
6. A single phase/component balance structure governs the mobile phases and the multiple load-bearing solid phases that share the skeleton motion but retain phase-specific true deformation, distension, stress-free maps, composition, and internal variables. Pore-filling conversion therefore appears as skeleton-attached solid mass that changes phase volume and can alter stress-free deformation, elasticity, and plastic flow, extending reactive-solid kinematics to an open multiphase porous medium with simultaneous transport and pressure coupling.
7. The plastic dissipation fixes the stress that drives plastic flow: plastic work is performed by the deviatoric intrinsic phase stress mapped through the elastic true-deformation and distension factors, and the nonlinear Biot–Terzaghi effective-stress relation connects this driving stress to the fixed-pressure skeleton stress entering the momentum balance. The distension decomposition supplies a second conjugate stress–rate pair for volumetric plastic accommodation. Together, the true-plastic and distension pairs provide the kinematic and thermodynamic structure for a coupled generalized plasticity specialization. A shared rate constraint and stress-dependent dissipation can then make normality in generalized-force space project as a non-associated pressure-dependent flow rule in true-stress space, following the thermodynamic construction of Collins and Houlsby [15]. The uncoupled mobility laws used here are a sufficient separately dissipative specialization; coupled deformation–distension laws remain admissible whenever their combined conjugate power in the residual dissipation is nonnegative.

These features are intended to preserve a direct route to familiar engineering models. The theory is pulled back to the solid reference configuration and then reduced explicitly to classical compositional

flow, a black-oil model, a Nernst–Planck–Darcy system, and finite- and small-deformation single-solid/single-fluid Biot equations. Each reduction states which electrical, thermal, conversion, kinematic, or constitutive terms are removed. The resulting correspondence checks the general formulation. Application to a particular material or reservoir additionally requires equations of state, relative permeabilities, capillary-history evolution laws, kinetic data, and numerical algorithms.

The scope is deliberately local and continuum-scale. Constitutive functions are assumed sufficiently smooth between phase and hysteresis switching events, with positive phase densities, volume fractions, and temperatures. Separate switching conditions are needed when a phase or component appears or disappears. Continuous capillary-history variables encode saturation reversal and phase trapping, while material-specific evolution laws select drainage, imbibition, and scanning paths. A dynamic pressure lag is admitted as an optional dissipative closure for rapid saturation transients, including fracture–matrix exchange in tight and shale reservoirs. Independent interfacial-area evolution remains outside the present state. The electroquasistatic state describes an isotropic dielectric response without permanent polarization, dielectric relaxation, or electromagnetic-wave dynamics. Mass added to or removed from a phase carries that phase’s specific internal energy and entropy. The general two-temperature reaction force uses neutral transfer coefficients, which keep charged transfer between the thermal subsystems independent of the electric-potential gauge. The reaction rate and associated reaction-energy transfer may be related by a joint linear near-equilibrium law with cross-coupling, provided their combined entropy production is nonnegative for each mechanism. These are near-equilibrium laws. Boundary data, gauges, and compatibility conditions are stated, but analysis of well-posedness and numerical validation is deferred.

The phase/component mass and charge balances introduce their notation as it is needed. The Hamilton–d’Alembert construction is then developed, followed by the constitutive restrictions and the Onsager closures they identify. Section 5 introduces the solid kinematics, performs the Coleman–Noll restriction, and derives the dissipative closures, Biot–Terzaghi effective-stress relations, and crystallization specialization. The solid-reference equations are then collected for reservoir implementation, and the final reductions establish correspondence with the classical models listed above. Appendix A collects the detailed observer, gauge, and admissible-data conditions.

2 Material form of conservation of mass

The derivation begins with component mass because every later force, multiplier, and closure is tied to how mass is stored, converted, and transported. The mixture phases occupy a common current configuration $\mathcal{B}$ (fig. 1). A phase label ξ identifies material that moves with one motion χ_ξ , while a superscript α distinguishes chemical species or constituents within that phase. Liquids, gases, and solids are therefore described by the same phase/component notation: a phase is the collection of components sharing the trajectory χ_ξ . Given a differential mass dm_ξ^α of component α in phase ξ , define the component partial density per current mixture volume by

$$\rho_\xi^\alpha(\mathbf{x}, t) = \frac{dm_\xi^\alpha}{dv}, \quad (1)$$

where $dv = dx_1 dx_2 dx_3$ is a current-configuration volume element of the mixture. Each phase is tracked from its own reference coordinates $\mathbf{X}_\xi$ and reference volume element

$$dV_\xi = (dX_1)_\xi (dX_2)_\xi (dX_3)_\xi. \quad (2)$$

The phase reference coordinates are related to the common current coordinates by a one-to-one, invertible, and continuously differentiable map on the region where that phase is present,

$$\mathbf{x} = \chi_\xi(\mathbf{X}_\xi, t), \quad (3)$$

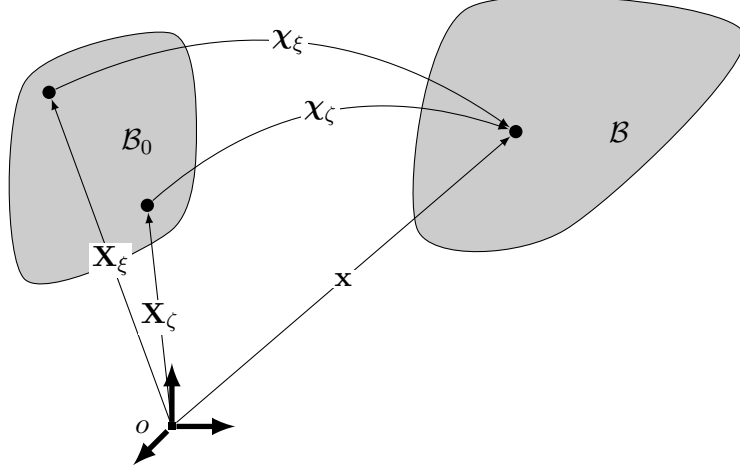


Figure 1: Schematic description of mixture kinematics showing the deformation maps, χ_ξ , linking phase reference configurations, $\mathbf{X}_\xi$, to the common current configuration, $\mathbf{x}$.

The associated phase deformation gradient $\mathbf{F}_\xi$ maps differential vectors from the phase reference coordinates to the current coordinates, and its determinant J_ξ is the phase Jacobian.

$$\begin{aligned}\mathbf{F}_\xi &= \frac{\partial \chi_\xi}{\partial \mathbf{X}_\xi} \\ &= \nabla_{\mathbf{X}_\xi} \mathbf{u}_\xi + \mathbf{I}.\end{aligned}\tag{4}$$

$$J_\xi = \det(\mathbf{F}_\xi).\tag{5}$$

Here $\mathbf{u}_\xi = \mathbf{u}_\xi(\mathbf{X}_\xi, t)$ is the phase displacement field, with $\mathbf{u}_\xi = \mathbf{x} - \mathbf{X}_\xi$, and $\nabla_{\mathbf{X}_\xi}$ is the gradient operator taken with respect to the phase reference coordinates $\mathbf{X}_\xi$.

Let $\rho_{\xi 0}^\alpha(\mathbf{X}_\xi)$ denote the initial component partial density, evaluated at $\mathbf{x}(\mathbf{X}_\xi, t = 0) = \mathbf{X}_\xi$. Let $\mathcal{C}_\xi^\alpha(\mathbf{X}_\xi, t)$ denote the increment of mass of component α added to phase ξ per unit phase reference volume by internal conversion. Internal conversion includes chemical reactions, sorption/desorption, and pure phase transformations. The first material statement isolates this conversion-only subproblem; relative component transport is added in §2.1. The component mass balance in integral form is

$$\int_{B_{\xi 0}} (\rho_{\xi 0}^\alpha + \mathcal{C}_\xi^\alpha) dV_\xi = \int_B \rho_\xi^\alpha dv\tag{6}$$

$$= \int_{B_{\xi 0}} \rho_\xi^\alpha J_\xi dV_\xi.\tag{7}$$

Here, the last equality pulls the current integral back to the phase reference configuration $B_{\xi 0}$. The Jacobian J_ξ accounts for the change in volume between the phase reference configuration and the common current configuration.

Since (7) must hold for arbitrary $B_{\xi 0}$,

$$\rho_{\xi 0}^\alpha + \mathcal{C}_\xi^\alpha = \rho_\xi^\alpha J_\xi.\tag{8}$$

The material time derivative of a quantity $\square_\xi$ observed along the velocity $\mathbf{v}_\zeta$ of phase ζ is

$$\frac{D_\zeta \square_\xi}{Dt} = \frac{\partial \square_\xi}{\partial t} + \mathbf{v}_\zeta \cdot \nabla_{\mathbf{x}} \square_\xi, \quad (9)$$

Here, $\nabla_{\mathbf{x}}$ is the spatial gradient operator. The dot shorthand $\dot{\square}_\xi = D_\xi \square_\xi / Dt$ denotes the material time derivative following phase ξ . Taking the material time derivative of (8) following phase ξ and using the identity $\dot{J}_\xi = J_\xi \nabla_{\mathbf{x}} \cdot \mathbf{v}_\xi$ gives

$$\frac{D_\xi \rho_\xi^\alpha}{Dt} + \rho_\xi^\alpha \nabla_{\mathbf{x}} \cdot \mathbf{v}_\xi = \frac{\dot{\mathcal{C}}_\xi^\alpha}{J_\xi}. \quad (10)$$

The rate of component mass addition per current mixture volume is defined by

$$\dot{c}_\xi^\alpha(\mathbf{x}, t) \equiv \frac{\dot{\mathcal{C}}_\xi^\alpha}{J_\xi}. \quad (11)$$

Substituting (11) into (10) and expanding the material time derivative gives the spatial component mass balance for phase ξ ,

$$\frac{\partial \rho_\xi^\alpha}{\partial t} + \nabla_{\mathbf{x}} \cdot (\rho_\xi^\alpha \mathbf{v}_\xi) = \dot{c}_\xi^\alpha. \quad (12)$$

Introduce the phase partial density $\rho_\xi = \sum_\alpha \rho_\xi^\alpha$ and the mass fraction of component α in phase ξ ,

$$\eta_\xi^\alpha = \frac{\rho_\xi^\alpha}{\rho_\xi}, \quad (13)$$

Summing (13) over α gives the mass-fraction constraint within phase ξ ,

$$\sum_\alpha \eta_\xi^\alpha = 1. \quad (14)$$

The phase volume fraction is defined as

$$\phi_\xi = \frac{dv_\xi}{dv}, \quad (15)$$

and summing over ξ gives the volume-fraction constraint,

$$\sum_\xi \phi_\xi = 1. \quad (16)$$

The phase intrinsic density is $\bar{\rho}_\xi = dm_\xi / dv_\xi$, so that

$$\rho_\xi = \phi_\xi \bar{\rho}_\xi, \quad (17a)$$

$$\rho_\xi^\alpha = \phi_\xi \bar{\rho}_\xi \eta_\xi^\alpha. \quad (17b)$$

Substituting (17b) into (12) and summing over phases gives the global component mass balance,

$$\frac{\partial}{\partial t} \left(\sum_\xi \phi_\xi \bar{\rho}_\xi \eta_\xi^\alpha \right) + \nabla_{\mathbf{x}} \cdot \left(\sum_\xi \phi_\xi \bar{\rho}_\xi \eta_\xi^\alpha \mathbf{v}_\xi \right) = \sum_\xi \dot{c}_\xi^\alpha. \quad (18)$$

Let $r_{(m)}$ be the current progress rate of internal mechanism (m) . Its mass-based stoichiometric coefficient for component α in phase ξ is $\nu_{\xi(m)}^\alpha$. The product $\nu_{\xi(m)}^\alpha r_{(m)}$ is therefore the component mass-production rate per unit current mixture volume. Equivalently, a molar progress rate may be used if $\nu_{\xi(m)}^\alpha$ is the signed molar stoichiometric coefficient multiplied by component molar mass. Before unresolved relative transport is introduced, this rate is generated only by conversion, so that

$$\dot{c}_\xi^\alpha = \sum_m \nu_{\xi(m)}^\alpha r_{(m)}. \quad (19)$$

The mechanism index (m) includes chemical reactions, sorption/desorption, and pure phase transformations. Sorption/desorption and pure phase transformations of component α from phase ξ to phase ζ have the one-to-one stoichiometry $\nu_{\xi(m)}^\alpha = -1$, $\nu_{\zeta(m)}^\alpha = +1$, with all other entries zero. A chemical reaction may change both component identity and phase label. Substituting (19) into (18) and summing over α gives the overall mass balance

$$\frac{\partial}{\partial t} \left(\sum_\xi \sum_\alpha \phi_\xi \bar{\rho}_\xi \eta_\xi^\alpha \right) + \nabla_{\mathbf{x}} \cdot \left(\sum_\xi \sum_\alpha \phi_\xi \bar{\rho}_\xi \eta_\xi^\alpha \mathbf{v}_\xi \right) = \sum_m \sum_\xi \sum_\alpha \nu_{\xi(m)}^\alpha r_{(m)}, \quad (20)$$

or equivalently,

$$\frac{\partial \rho}{\partial t} + \nabla_{\mathbf{x}} \cdot (\rho \mathbf{v}) = 0. \quad (21)$$

Here $\rho = \sum_\xi \rho_\xi$ is the mixture density and $\mathbf{v}$ is the barycentric mixture velocity

$$\mathbf{v} = \frac{1}{\rho} \sum_\xi \rho_\xi \mathbf{v}_\xi. \quad (22)$$

Each internal mechanism satisfies $\sum_\xi \sum_\alpha \nu_{\xi(m)}^\alpha = 0$, so the right-hand side of (20) vanishes. Equation (21) is the overall mixture statement of mass conservation.

2.1 Averaged component transport and the extended material balance

The phase construction above applies at both the local and resolved scales. For the local description used in this averaging step, each component is treated as a one-component phase and traced by its own motion. The resolved phase ξ groups the selected one-component phases, and its mass-averaged component velocity defines their common upscaled phase trajectory. Averaging the component motion inside a representative current volume exposes transport not resolved by that phase trajectory, following the standard volume-averaging decomposition for porous-medium species transport [51, 31]. A hat denotes a local, unaveraged quantity inside the averaging volume, whereas angle brackets denote its volume average. Thus

$$\rho_\xi^\alpha = \langle \hat{\rho}_\xi^\alpha \rangle, \quad \hat{\rho}_\xi^\alpha = \rho_\xi^\alpha + \tilde{\rho}_\xi^\alpha, \quad \langle \tilde{\rho}_\xi^\alpha \rangle = 0. \quad (23)$$

The local, unaveraged velocity of component α is decomposed into the resolved phase velocity, an unresolved fluctuation of the phase motion, and motion of the component relative to the local, unaveraged phase motion,

$$\hat{\mathbf{v}}_\xi^\alpha = \mathbf{v}_\xi + \tilde{\mathbf{v}}_\xi + \hat{\mathbf{u}}_\xi^\alpha, \quad \langle \tilde{\mathbf{v}}_\xi \rangle = \mathbf{0}. \quad (24)$$

Here $\tilde{\mathbf{v}}_\xi$ produces mechanical dispersion and $\hat{\mathbf{u}}_\xi^\alpha$ produces molecular diffusion. The resolved phase velocity is chosen to be the mass-averaged component velocity,

$$\rho_\xi \mathbf{v}_\xi = \sum_\alpha \langle \hat{\rho}_\xi^\alpha \hat{\mathbf{v}}_\xi^\alpha \rangle. \quad (25)$$

This choice fixes the phase trajectory used in (9). The local, unaveraged material derivative following component α is the extension

$$\frac{\widehat{D}_\xi^\alpha \widehat{\square}_\xi}{Dt} = \frac{\partial \widehat{\square}_\xi}{\partial t} + \left(\mathbf{v}_\xi + \widetilde{\mathbf{v}}_\xi + \widehat{\mathbf{u}}_\xi^\alpha \right) \cdot \nabla_{\mathbf{x}} \widehat{\square}_\xi. \quad (26)$$

At the local scale, the hatted material identity and Jacobian are the componentwise forms of (8) and (5). Applying this derivative to the hatted material identity and using the associated kinematic identity $\widehat{D}_\xi^\alpha \widehat{J}_\xi^\alpha / Dt = \widehat{J}_\xi^\alpha \nabla_{\mathbf{x}} \cdot \widehat{\mathbf{v}}_\xi^\alpha$, and writing the result in divergence form gives

$$\frac{\partial \widehat{\rho}_\xi^\alpha}{\partial t} + \nabla_{\mathbf{x}} \cdot \left(\widehat{\rho}_\xi^\alpha \widehat{\mathbf{v}}_\xi^\alpha \right) = \sum_m \nu_{\xi(m)}^\alpha r_{(m)}. \quad (27)$$

The progress rates on the right are resolved current-volume rates taken to be uniform over the averaging volume. They are therefore unchanged by averaging, which introduces fluctuation contributions through the storage and transport terms. Substitution of (23) and (24) into (27) produces two relative fluxes,

$$\mathbf{j}_{\xi, \text{disp}}^\alpha = \left\langle \widehat{\rho}_\xi^\alpha \widetilde{\mathbf{v}}_\xi \right\rangle, \quad (28a)$$

$$\mathbf{j}_{\xi, \text{diff}}^\alpha = \left\langle \widehat{\rho}_\xi^\alpha \widehat{\mathbf{u}}_\xi^\alpha \right\rangle. \quad (28b)$$

Equations (28a) and (28b) define what the averaged fluxes measure, but the macroscopic theory does not resolve the density and velocity fluctuations inside the averages. Varying those subscale fields would add unknowns and closure equations. The variational problem in §4 therefore treats $\mathbf{j}_{\xi, \text{disp}}^\alpha$ and $\mathbf{j}_{\xi, \text{diff}}^\alpha$ as macroscopic process rates. Their virtual changes enter the Onsager part of the formulation, and the entropy inequality restricts their constitutive force–flux laws [18, 56].

The dispersion flux $\mathbf{j}_{\xi, \text{disp}}^\alpha$ is the covariance between unresolved density and phase-velocity fluctuations, while the diffusion flux $\mathbf{j}_{\xi, \text{diff}}^\alpha$ is the averaged mass carried by component motion relative to the phase. The averaged component balance is consequently

$$\frac{\partial \rho_\xi^\alpha}{\partial t} + \nabla_{\mathbf{x}} \cdot \left(\rho_\xi^\alpha \mathbf{v}_\xi + \mathbf{j}_{\xi, \text{disp}}^\alpha + \mathbf{j}_{\xi, \text{diff}}^\alpha \right) = \sum_m \nu_{\xi(m)}^\alpha r_{(m)}. \quad (29)$$

Equation (29) governs composition when relative transport is present. The corresponding phase-reference material increment $\mathcal{C}_\xi^\alpha$ is the component mass added to a phase-attached region per unit phase reference volume by both conversion mechanisms and relative transport. Multiplication of (29) by J_ξ , together with $\dot{J}_\xi = J_\xi \nabla_{\mathbf{x}} \cdot \mathbf{v}_\xi$, gives

$$\frac{D_\xi}{Dt} \left(J_\xi \rho_\xi^\alpha \right) = J_\xi \sum_m \nu_{\xi(m)}^\alpha r_{(m)} - J_\xi \nabla_{\mathbf{x}} \cdot \left(\mathbf{j}_{\xi, \text{disp}}^\alpha + \mathbf{j}_{\xi, \text{diff}}^\alpha \right). \quad (30)$$

Comparing (30) with the material-balance structure in (8) and its rate form (10) identifies $\dot{\mathcal{C}}_\xi^\alpha$ as

$$\dot{\mathcal{C}}_\xi^\alpha = J_\xi \sum_m \nu_{\xi(m)}^\alpha r_{(m)} - J_\xi \nabla_{\mathbf{x}} \cdot \left(\mathbf{j}_{\xi, \text{disp}}^\alpha + \mathbf{j}_{\xi, \text{diff}}^\alpha \right). \quad (31)$$

With zero initial accumulations, integration on the phase reference trajectory gives the same material-balance structure as (8),

$$\rho_{\xi 0}^\alpha + \mathcal{C}_\xi^\alpha = J_\xi \rho_\xi^\alpha = J_\xi \phi_\xi \bar{\rho}_\xi \eta_\xi^\alpha. \quad (32)$$

Here $\mathcal{C}_\xi^\alpha$ has the expanded meaning supplied by (31): its rate contains both internal conversion and unresolved relative transport. The reaction production and relative-flux parts therefore remain visible in the rate of the material increment.

Substituting the component density and velocity decompositions (23)–(24) into the total component mass flux, using $\rho_\xi = \sum_\alpha \rho_\xi^\alpha$ and $\langle \tilde{\mathbf{v}}_\xi \rangle = \mathbf{0}$, gives

$$\begin{aligned} \sum_\alpha \langle \hat{\rho}_\xi^\alpha \hat{\mathbf{v}}_\xi^\alpha \rangle &= \rho_\xi \mathbf{v}_\xi + \sum_\alpha \left(\langle \hat{\rho}_\xi^\alpha \tilde{\mathbf{v}}_\xi \rangle + \langle \hat{\rho}_\xi^\alpha \hat{\mathbf{u}}_\xi^\alpha \rangle \right) \\ &= \rho_\xi \mathbf{v}_\xi + \sum_\alpha \left(\langle \hat{\rho}_\xi^\alpha \tilde{\mathbf{v}}_\xi \rangle + \langle \hat{\rho}_\xi^\alpha \hat{\mathbf{u}}_\xi^\alpha \rangle \right) \\ &= \rho_\xi \mathbf{v}_\xi + \sum_\alpha \left(\mathbf{j}_{\xi,\text{disp}}^\alpha + \mathbf{j}_{\xi,\text{diff}}^\alpha \right). \end{aligned} \quad (33)$$

The last equality uses the flux definitions (28a) and (28b). By the mass-averaged definition (25), the left-hand side of (33) is $\rho_\xi \mathbf{v}_\xi$. Subtracting this resolved phase flux from both sides therefore leaves

$$\sum_\alpha \left(\mathbf{j}_{\xi,\text{disp}}^\alpha + \mathbf{j}_{\xi,\text{diff}}^\alpha \right) = \mathbf{0}. \quad (34)$$

Relative transport therefore redistributes component mass within a phase while preserving the phase total mass. The combined relative flux has only $N - 1$ independent component directions in each phase. Equation (34) fixes only the sum of dispersion and diffusion. The block-diagonal constitutive split used below adopts the stronger specialization that the two flux families are separately zero-sum,

$$\sum_\alpha \mathbf{j}_{\xi,k}^\alpha = \mathbf{0}, \quad k \in \{\text{disp}, \text{diff}\}. \quad (35)$$

The material increment $\mathcal{C}_\xi^\alpha$ is tied to the transfer potential introduced in §4, while its relative-flux contribution is closed later by Onsager relations involving differences of the specific generalized transfer-work potentials and a separate electric-field contribution. The Coleman–Noll procedure then identifies these differences with chemical-potential differences; at uniform temperature, the chemical-potential and electric contributions combine into the usual electrochemical-potential gradient. Summing (29) over phases gives the global component balance,

$$\frac{\partial}{\partial t} \left(\sum_\xi \phi_\xi \bar{\rho}_\xi \eta_\xi^\alpha \right) + \nabla_{\mathbf{x}} \cdot \sum_\xi \left(\phi_\xi \bar{\rho}_\xi \eta_\xi^\alpha \mathbf{v}_\xi + \mathbf{j}_{\xi,\text{disp}}^\alpha + \mathbf{j}_{\xi,\text{diff}}^\alpha \right) = \sum_\xi \sum_m \nu_{\xi(m)}^\alpha r_{(m)}. \quad (36)$$

Summing (36) over components recovers the overall mass balance (21): the relative fluxes cancel phase by phase by (34), and each internal mechanism conserves total mass. Applying the same summation to (31) gives, again by stoichiometric mass balance and (34),

$$\sum_\xi \sum_\alpha \frac{\dot{\mathcal{C}}_\xi^\alpha}{J_\xi} = 0. \quad (37)$$

This zero-sum identity becomes the material-insertion constraint in the Hamilton–d’Alembert principle. The averaged balances determine where the two fluxes enter component transport; the entropy-admissible dissipation potential in §4 supplies their constitutive laws.

3 Conservation of charge

Electric charge is carried by the same phase/component material measures as mass. Weighting each component balance by the charge carried per unit mass and summing gives the charge balance. The field equation for the electric potential is introduced with the electrical variation; the electrochemical component potentials are identified later by the Coleman–Noll procedure.

Let z_ξ^α denote the charge carried per unit mass of component α in phase ξ . The charge density per unit current mixture volume associated with that component is

$$\varrho_\xi^\alpha = z_\xi^\alpha \rho_\xi^\alpha = z_\xi^\alpha \phi_\xi \bar{\rho}_\xi \eta_\xi^\alpha. \quad (38)$$

The coefficient z_ξ^α may vanish for neutral components, may be a constant valence-to-mass ratio for a mobile ion, or may be an effective charge per mass for a solid component representing fixed surface or exchange-site charge. Fixed surface or exchange-site charge and mobile ionic charge are represented by the same phase/component variables [41, 47]. A charged component may belong to any phase; components treated as electrically neutral have $z_\xi^\alpha = 0$. The total free charge density is

$$\varrho = \sum_\xi \sum_\alpha z_\xi^\alpha \phi_\xi \bar{\rho}_\xi \eta_\xi^\alpha. \quad (39)$$

Thus every free-charge contribution is carried by a component mass measure. The charge density ϱ is the field-source coefficient in the electrical virtual work and in Gauss' law, and it multiplies the rate of the electric potential in the bulk field-source power. In particular, representing fixed charge as a solid component ties charge storage, deformation, reaction, and ion exchange to the same material measures used for mass.

The material charge measure follows by multiplying the augmented component material measure (32) by z_ξ^α ,

$$z_\xi^\alpha \rho_{\xi 0}^\alpha + z_\xi^\alpha \mathcal{C}_\xi^\alpha = J_\xi \varrho_\xi^\alpha. \quad (40)$$

For constant z_ξ^α , its material rate gives

$$\frac{\partial \varrho_\xi^\alpha}{\partial t} + \nabla_{\mathbf{x}} \cdot (\varrho_\xi^\alpha \mathbf{v}_\xi) = \frac{z_\xi^\alpha \dot{\mathcal{C}}_\xi^\alpha}{J_\xi}. \quad (41)$$

Here and below, z_ξ^α is constant. A state-dependent effective charge requires additional material-rate and transport terms.

Combining (41) with (31) gives the charge balance for each charged component,

$$\frac{\partial \varrho_\xi^\alpha}{\partial t} + \nabla_{\mathbf{x}} \cdot \left[z_\xi^\alpha \left(\rho_\xi^\alpha \mathbf{v}_\xi + \mathbf{j}_{\xi, \text{disp}}^\alpha + \mathbf{j}_{\xi, \text{diff}}^\alpha \right) \right] = z_\xi^\alpha \sum_m \nu_{\xi(m)}^\alpha r_{(m)}. \quad (42)$$

The current density carried by phase motion and relative component transport is

$$\mathbf{i} = \sum_\xi \sum_\alpha z_\xi^\alpha \left(\rho_\xi^\alpha \mathbf{v}_\xi + \mathbf{j}_{\xi, \text{disp}}^\alpha + \mathbf{j}_{\xi, \text{diff}}^\alpha \right). \quad (43)$$

Summing (42) over phases and components gives

$$\frac{\partial}{\partial t} \left(\sum_\xi \sum_\alpha \varrho_\xi^\alpha \right) + \nabla_{\mathbf{x}} \cdot \mathbf{i} = \sum_m \left(\sum_\xi \sum_\alpha z_\xi^\alpha \nu_{\xi(m)}^\alpha \right) r_{(m)}. \quad (44)$$

Local internal mechanisms must conserve electric charge,

$$\sum_{\xi} \sum_{\alpha} z_{\xi}^{\alpha} \nu_{\xi(m)}^{\alpha} = 0, \quad \text{for each mechanism } (m), \quad (45)$$

so the total charge balance is

$$\frac{\partial \rho}{\partial t} + \nabla_{\mathbf{x}} \cdot \mathbf{i} = 0. \quad (46)$$

Equation (45) is the charge analogue of the mass-conservation restriction $\sum_{\xi} \sum_{\alpha} \nu_{\xi(m)}^{\alpha} = 0$. As one example, an ion-exchange mechanism between an aqueous phase and charged solid sites may remove an aqueous component and a solid-site component while creating the exchanged aqueous and solid-site components. This mechanism changes fluid composition and solid-site occupancy while satisfying both mass conservation and (45). More generally, the phase/component formulation admits exchange among any represented phases and components whose stoichiometry satisfies these two conservation restrictions. Thus charge attached to deforming solid sites is transported by the component current $\mathbf{i}$.

Ion-exchange and surface-complexation models can be represented by retaining charged site components in the surface-bearing phase, imposing (45) on the exchange stoichiometry, and choosing admissible kinetic or equilibrium closures for the corresponding mechanism rates. The electrostatic field equation is Gauss' law, derived in §4.

4 Variational principle derivation

The phase-coordinate balances are derived by Hamilton–d'Alembert stationarity, and the dissipative process rates are closed separately by Onsager stationarity. The Hamilton–d'Alembert calculation follows the extended Hamilton principles used by Bedford and Drumheller for porous and reacting immiscible mixtures [2, 22, 3] and determines the mixture coordinates and constraints. Its virtual work also carries the d'Alembert work of a constitutive dissipative force when dynamic capillarity is active. The Onsager calculation pairs dissipative saturation, reaction, and relative-transport rates with their thermodynamic forces. Exploitation of the entropy inequality then requires nonnegative dissipation [18, 56]. This is the continuum counterpart of using virtual work for coordinate changes and virtual power for process rates [26, 33]. The saturation force is held fixed during the coordinate variation and paired with $\dot{S}_f$ during the Onsager variation, so the two statements supply complementary coordinate and constitutive equations.

The formulation applies to any specified collection of solid $\mathcal{S}$ and fluid $\mathcal{F}$ phases. Here fluid means a nonsolid pore phase, such as an aqueous, oleic, or gas phase. The symbol $s \in \mathcal{S}$ denotes a solid phase, $f \in \mathcal{F}$ denotes a fluid phase, and $\xi \in \mathcal{S} \cup \mathcal{F}$ ranges over all phases. Components within each phase are indexed by α .

4.1 Hamilton–d'Alembert principle for the coordinate balances

Let t_1 and t_2 be the endpoint times and let δ denote an admissible virtual variation that vanishes at those endpoints. The Hamilton–d'Alembert statement contains the kinetic and stored-energy variation, mechanical and electrical source work, the volume and composition constraints, and the material insertion constraint:

$$\delta \int_{t_1}^{t_2} (T - U) \, dt + \int_{t_1}^{t_2} \left(\delta W + \sum_{k=1}^4 \delta C_k \right) \, dt = 0. \quad (47)$$

In the virtual-work term below, $\mathbf{g}$ is the body force per unit phase mass and $\mathbf{b}_\xi$ is the force density exerted on phase ξ through interaction with the other phases. The individual interaction forces may include dissipative drag, but they transfer momentum only within the mixture. They therefore satisfy the global balance

$$\sum_{\xi} \mathbf{b}_\xi = \mathbf{0}. \quad (48)$$

The energies, virtual work, and four constraints are defined together by

$$T = \sum_{\xi} \int_{\mathcal{B}} \frac{1}{2} \rho_{\xi} \mathbf{v}_{\xi} \cdot \mathbf{v}_{\xi} \, dv, \quad (49)$$

$$U = \sum_{\xi} \int_{\mathcal{B}} \rho_{\xi} \psi_{\xi}(\mathbf{F}_{\xi}, \bar{\rho}_{\xi}, \{\eta_{\xi}^{\alpha}\}, \theta_{\xi}) \, dv + \int_{\mathcal{B}} \phi \gamma(\{S_f\}_{f \in \mathcal{F}}, \mathbf{h}, \theta_{\mathcal{F}}) \, dv + \sum_{\xi} \int_{\mathcal{B}} \phi_{\xi} \omega_{\xi}^+(\mathbf{E}, \bar{\rho}_{\xi}, \{\eta_{\xi}^{\alpha}\}, \theta_{\xi}) \, dv, \quad (50)$$

$$\begin{aligned} \delta W = \int_{\mathcal{B}} & \left[\sum_{\xi} (\rho_{\xi} \mathbf{g} + \mathbf{b}_{\xi}) \cdot \delta \mathbf{x}_{\xi} + \sum_{\xi} \sum_{\alpha} (\psi_{\xi} + L_{\xi}^{\alpha}) \frac{\delta \mathcal{C}_{\xi}^{\alpha}}{J_{\xi}} - \phi \sum_{f \in \mathcal{F}} \mathcal{L}_f^{\text{sat}} \delta S_f - \varrho \delta \varphi \right] dv \\ & + \sum_{\xi} \int_{\partial \mathcal{B}} \mathbf{t}_{\xi} \cdot \delta \mathbf{x}_{\xi} \, da + \int_{\partial \mathcal{B}} \bar{q} \delta \varphi \, da, \end{aligned} \quad (51)$$

$$C_1 = \int_{\mathcal{B}} \lambda \left(\sum_{\xi} \phi_{\xi} - 1 \right) \, dv, \quad (52)$$

$$C_2 = \sum_{\xi} \sum_{\alpha} \int_{\mathcal{B}_{\xi 0}} \pi_{\xi}^{\alpha} \left(J_{\xi} - \frac{\phi_{\xi 0} \eta_{\xi 0}^{\alpha} \bar{\rho}_{\xi 0} + \mathcal{C}_{\xi}^{\alpha}}{\phi_{\xi} \eta_{\xi}^{\alpha} \bar{\rho}_{\xi}} \right) \, dV_{\xi}, \quad (53)$$

$$C_3 = \sum_{\xi} \int_{\mathcal{B}} \Pi_{\xi} \left(\sum_{\alpha} \eta_{\xi}^{\alpha} - 1 \right) \, dv, \quad (54)$$

$$C_4 = \int_{\mathcal{B}} \tau \left(\sum_{\xi} \sum_{\alpha} \frac{\dot{\mathcal{C}}_{\xi}^{\alpha}}{J_{\xi}} \right) \, dv. \quad (55)$$

Here $\psi_{\xi} + L_{\xi}^{\alpha}$ is the mass-specific energetic supply associated with component insertion. Both terms have units of energy per unit mass; L_{ξ}^{α} is the specific generalized transfer-work potential, normalized by the mass of component α inserted into phase ξ . Under the local-equilibrium insertion convention, added material carries the recipient-phase Helmholtz storage ψ_{ξ} , while L_{ξ}^{α} supplies the associated transfer work. This energy partition fixes the coefficient before stationarity is taken. The stored-energy variation contributes $-\psi_{\xi} \delta \mathcal{C}_{\xi}^{\alpha} / J_{\xi}$, whereas δW contributes $(\psi_{\xi} + L_{\xi}^{\alpha}) \delta \mathcal{C}_{\xi}^{\alpha} / J_{\xi}$; their sum gives the transfer-work term in the component-increment Euler–Lagrange equation. The thermodynamic restrictions below relate $\psi_{\xi} + L_{\xi}^{\alpha}$ to the component potential. The relation includes the electrical contribution, a phase-common transfer-potential rate, and inertia. The resulting sign and conjugate pairing agrees with the Bedford–Drumheller form [22, eqs. (2.2) and (2.8)].

The coefficient $\mathcal{L}_f^{\text{sat}}$ is the generalized force per unit pore volume conjugate to saturation redistribution. It has pressure units and is held fixed during the coordinate variation. The saturation variation in (51) follows the same current-spatial convention as $\delta \phi_f$; the integration over $\mathcal{B}$ makes a separate fixed-point qualifier unnecessary. No additional multiplier is needed for saturation normalization. The definitions $S_f = \phi_f / \phi$ and $\phi = \sum_f \phi_f$ in (64) make $\sum_f S_f = 1$ an identity, and their induced variations satisfy $\sum_f \delta S_f = 0$. Thus only differences of the coefficients $\mathcal{L}_f^{\text{sat}}$ perform work. A multiplier would only add the same scalar to every coefficient, and that common contribution vanishes for every admissible saturation variation.

The electrical boundary is partitioned into Γ_φ , where φ is prescribed and $\delta\varphi = 0$, and $\Gamma_{\bar{q}}$, where $\bar{q}$ is the prescribed outward free surface-charge density. The electrical terms in δW define a free-charge source-work ensemble: ϱ and $\bar{q}$ prescribe source work conjugate to $\delta\varphi$ in the volume and on the boundary, respectively. The component-carried part of ϱ is the component sum in (39). As for the body-force coefficients in δW , the material variation holds these source coefficients and prescribed loading data fixed.

For each phase map, let $\partial\mathcal{B} = \Gamma_{\mathbf{x}_\xi} \cup \Gamma_{\mathbf{t}_\xi}$, with disjoint interiors, $\mathbf{x}_\xi$ prescribed and $\delta\mathbf{x}_\xi = \mathbf{0}$ on $\Gamma_{\mathbf{x}_\xi}$, and prescribed outward traction $\mathbf{t}_\xi$ on $\Gamma_{\mathbf{t}_\xi}$. Accordingly, the boundary terms in (51) yield the natural traction and electrical conditions derived below.

The phase electric enthalpy supplies the Maxwell contribution to the reversible phase stress derived below. The Hamilton–d’Alembert principle probes those reversible coordinate changes at a specified instantaneous thermal state, so $\delta\theta_{\mathcal{F}} = \delta\theta_{\mathcal{S}} = 0$. The temperatures remain constitutive arguments of the stored energy because the coordinate equations depend on the current thermal state. Their physical rates are supplied by the fluid and solid energy balances and enter the entropy inequality, whose Coleman–Noll exploitation determines the associated constitutive restrictions [14]. This division between variational motion, energy balance, and thermodynamic restriction follows the thermomechanical mixture construction of Bedford and Drumheller [22, Secs. 2–4].

The phase-assigned temperature is $\theta_\xi = \theta_{\mathcal{F}}$ for $f \in \mathcal{F}$ and $\theta_\xi = \theta_{\mathcal{S}}$ for $s \in \mathcal{S}$. Constraint C_1 enforces the volume-fraction constraint, C_2 enforces the augmented component material measure, and C_3 enforces mass-fraction normalization.

Constraint C_4 enforces zero net material insertion over all phases and components. Writing the rate of component mass addition per current mixture volume as $\dot{c}_\xi^\alpha = \dot{C}_\xi^\alpha/J_\xi$, this constraint imposes $\sum_\xi \sum_\alpha \dot{c}_\xi^\alpha = 0$. Internal conversion satisfies the constraint through stoichiometric mass conservation, while relative component transport satisfies it phase by phase through (34).

The transfer multiplier τ is the Bedford–Drumheller kinematic potential conjugate to the globally conservative accumulated material insertion. It has units of action per unit mass, so $\nabla_{\mathbf{x}}\tau$ has velocity units and $D_\xi\tau/Dt$ has units of energy per unit mass. Thus τ supplies the conversion transfer-momentum coefficient in the reversible variation.

The coordinate variations are $\mathbf{x}_\xi$, η_ξ^α , ϕ_ξ , $\bar{\rho}_\xi$, and $\mathcal{C}_\xi^\alpha$. The mechanism rates and the two relative fluxes are varied later as independent process rates through the constrained Onsager entropy-rate functional in Section 4.3. In the optional dynamic-capillary branch, the independent zero-sum saturation rates are Onsager rates driven by the generalized force in (51). The entropy inequality later supplies the constitutive admissibility condition.

4.1.1 Extending Bedford and Drumheller transport identity

Bedford and Drumheller [22, eq. (1.28)] give an identity for the variation of a constituent-attached spatial field Υ_ξ weighted by the current phase density ρ_ξ . The same transport argument extends componentwise to the compositional setting used here.

The component material increment $\mathcal{C}_\xi^\alpha$ is attached to the phase- ξ reference coordinates. It is the added component mass appearing in (32). In the reversible Hamilton–d’Alembert variation, its componentwise virtual increment is therefore carried with the phase-attached material measure.

For any phase field Υ_ξ , the Bedford–Drumheller identity extends componentwise as

$$\begin{aligned}\delta \int_B \rho_\xi^\alpha \Upsilon_\xi \, dv &= \delta \int_{B_{\xi 0}} \left(\rho_{\xi 0}^\alpha + \mathcal{C}_\xi^\alpha \right) \Upsilon_\xi \, dV_\xi \\ &= \int_{B_{\xi 0}} \left[\delta \mathcal{C}_\xi^\alpha \Upsilon_\xi + J_\xi \rho_\xi^\alpha \delta \Upsilon_\xi \right] dV_\xi \\ &= \int_B \left[\rho_\xi^\alpha \delta \Upsilon_\xi + \frac{\delta \mathcal{C}_\xi^\alpha}{J_\xi} \Upsilon_\xi \right] dv.\end{aligned}\tag{56}$$

Summing both sides of (56) over α gives

$$\delta \int_B \rho_\xi \Upsilon_\xi \, dv = \int_B \left[\rho_\xi \delta \Upsilon_\xi + \sum_\alpha \frac{\delta \mathcal{C}_\xi^\alpha}{J_\xi} \Upsilon_\xi \right] dv,\tag{57}$$

where $\rho_\xi = \sum_\alpha \rho_\xi^\alpha$.

4.1.2 Variation of the kinetic energy

The variation of kinetic energy using (57) is then

$$\delta T = \sum_\xi \int_B \rho_\xi \mathbf{v}_\xi \cdot \delta \mathbf{v}_\xi + \frac{1}{2} \mathbf{v}_\xi \cdot \mathbf{v}_\xi \sum_\alpha \frac{\delta \mathcal{C}_\xi^\alpha}{J_\xi} dv.\tag{58}$$

Since $\delta \mathbf{v}_\xi = \delta \dot{\mathbf{x}}_\xi$ and $\delta \mathbf{x}_\xi|_{t_1} = \delta \mathbf{x}_\xi|_{t_2} = \mathbf{0}$, integration by parts in time gives

$$\int_{t_1}^{t_2} \delta T \, dt = \int_{t_1}^{t_2} \sum_\xi \int_B \left[-\rho_\xi \mathbf{a}_\xi - \sum_\alpha \ddot{\mathcal{C}}_\xi^\alpha \mathbf{v}_\xi \right] \cdot \delta \mathbf{x}_\xi + \frac{1}{2} \mathbf{v}_\xi \cdot \mathbf{v}_\xi \sum_\alpha \frac{\delta \mathcal{C}_\xi^\alpha}{J_\xi} dv \, dt.\tag{59}$$

4.1.3 Variation of the phase free energies

For every phase, solid or fluid, let ψ_ξ denote the nonelectrical specific Helmholtz free energy and let N be the number of tracked components in that phase. At the fixed thermal state specified above, its contribution to the stored thermodynamic potential is written

$$U \supset U_\xi = \sum_\xi \int_B \rho_\xi \psi_\xi(\mathbf{F}_\xi, \bar{\rho}_\xi, \{\eta_\xi^\alpha\}, \theta_\xi) \, dv.\tag{60}$$

Here $\{\eta_\xi^\alpha\}$ denotes the indexed collection of all component mass fractions for phase ξ . The constitutive dependence on $\mathbf{F}_\xi$ may be trivial for fluid phases, but keeping it in the notation allows one calculation for all phases. The local free-energy variation is

$$\delta \psi_\xi = \left. \frac{\partial \psi_\xi}{\partial \mathbf{F}_\xi} \right|_{\bar{\rho}_\xi, \{\eta_\xi^\alpha\}, \theta_\xi} : \delta \mathbf{F}_\xi + \left. \frac{\partial \psi_\xi}{\partial \bar{\rho}_\xi} \right|_{\mathbf{F}_\xi, \{\eta_\xi^\alpha\}, \theta_\xi} \delta \bar{\rho}_\xi + \sum_\alpha \left. \frac{\partial \psi_\xi}{\partial \eta_\xi^\alpha} \right|_{\mathbf{F}_\xi, \bar{\rho}_\xi, \eta_\xi^{\beta \neq \alpha}, \theta_\xi} \delta \eta_\xi^\alpha.\tag{61}$$

Using (57), integrating the $\delta \mathbf{F}_\xi$ term by parts, and collecting independent variations gives

$$\begin{aligned}\delta U_\xi &= \sum_\xi \int_B \left[-\nabla_{\mathbf{x}} \cdot \boldsymbol{\sigma}'_\xi \cdot \delta \mathbf{x}_\xi + \rho_\xi \left. \frac{\partial \psi_\xi}{\partial \bar{\rho}_\xi} \right|_{\mathbf{F}_\xi, \{\eta_\xi^\alpha\}, \theta_\xi} \delta \bar{\rho}_\xi \right. \\ &\quad \left. + \sum_\alpha \rho_\xi \left. \frac{\partial \psi_\xi}{\partial \eta_\xi^\alpha} \right|_{\mathbf{F}_\xi, \bar{\rho}_\xi, \eta_\xi^{\beta \neq \alpha}, \theta_\xi} \delta \eta_\xi^\alpha + \sum_\alpha \psi_\xi \frac{\delta \mathcal{C}_\xi^\alpha}{J_\xi} \right] dv + \sum_\xi \int_{\partial B} (\boldsymbol{\sigma}'_\xi \mathbf{n}) \cdot \delta \mathbf{x}_\xi \, da.\end{aligned}\tag{62}$$

The corresponding Cauchy effective stress is denoted with a single prime because it is the fixed-intrinsic-density stress, analogous to a Terzaghi effective stress. The fixed-pressure effective stress is denoted later with a double prime.

$$\boldsymbol{\sigma}'_{\xi} \equiv \rho_{\xi} \left. \frac{\partial \psi_{\xi}}{\partial \mathbf{F}_{\xi}} \right|_{\bar{\rho}_{\xi}, \{\eta_{\xi}^{\alpha}\}, \theta_{\xi}} \mathbf{F}_{\xi}^T. \quad (63)$$

For fluid phases, ψ_f may be independent of $\mathbf{F}_f$, giving $\boldsymbol{\sigma}'_f = \mathbf{0}$.

4.1.4 Variation of the interfacial energies

Let $\mathcal{I}$ denote the set of oriented fluid interfaces. Each $(w, n) \in \mathcal{I}$ identifies a wetting phase w and a non-wetting phase n . The total fluid volume fraction and the fluid saturations are

$$\phi = \sum_{f \in \mathcal{F}} \phi_f, \quad S_f = \frac{\phi_f}{\phi}, \quad \sum_{f \in \mathcal{F}} S_f = 1. \quad (64)$$

The saturations are used here only as ratios of the primitive volume-fraction fields; the variations are still taken with respect to the primitive ϕ_f . The notation $\{S_f\}_{f \in \mathcal{F}}$ denotes the fluid saturation state subject to the constraint in (64). Thus the energy may be written in terms of any independent set of fluid saturations, with the remaining saturation determined by the constraint. The derivation below keeps this sum constraint explicit, so all fluid phases are treated symmetrically. The vector $\mathbf{h} \in \mathbb{R}^{N_h}$ collects continuous local capillary-history variables carried by the solid skeleton. These variables record the reversal and trapping state needed to distinguish drainage, imbibition, and scanning paths; their constitutive evolution is restricted by the entropy inequality below. The effective interfacial Helmholtz free-energy density per unit current pore volume is a single constitutive potential of the constrained saturation and capillary-history state

$$\gamma = \gamma(\{S_f\}_{f \in \mathcal{F}}, \mathbf{h}, \theta_{\mathcal{F}}). \quad (65)$$

Its contribution to the stored thermodynamic potential per current mixture volume is $\phi\gamma$, so

$$U \supset U_{\gamma} = \int_{\mathcal{B}} \phi \gamma(\{S_f\}_{f \in \mathcal{F}}, \mathbf{h}, \theta_{\mathcal{F}}) \, dv. \quad (66)$$

The reversible coordinate variation holds $\mathbf{h}$ and $\theta_{\mathcal{F}}$ fixed and therefore acts through the primitive fluid volume fractions and their saturation ratios.

The Bedford–Drumheller spatial identity (cf. [22] equation (1.25)) gives, for each fluid phase field ϕ_f ,

$$\delta \phi_{\xi}|_{\mathbf{x}} = \delta \phi_{\xi} - \nabla_{\mathbf{x}} \phi_{\xi} \cdot \delta \mathbf{x}_{\xi}. \quad (67)$$

Using

$$\delta \phi = \sum_{f \in \mathcal{F}} \delta \phi_f, \quad \delta S_f = \frac{\delta \phi_f - S_f \delta \phi}{\phi}, \quad (68)$$

the fixed-point contribution and the transport correction from (67) are collected in one calculation:

$$\begin{aligned} \delta U_{\gamma} &= \int_{\mathcal{B}} \left[\gamma \delta \phi + \sum_{f \in \mathcal{F}} \left. \frac{\partial \gamma}{\partial S_f} \right|_{S_{g \neq f}, \mathbf{h}, \theta_{\mathcal{F}}} (\delta \phi_f - S_f \delta \phi) \right] dv \\ &\quad - \int_{\mathcal{B}} \sum_{f \in \mathcal{F}} \gamma_f \nabla_{\mathbf{x}} \phi_f \cdot \delta \mathbf{x}_f \, dv \\ &= \int_{\mathcal{B}} \sum_{f \in \mathcal{F}} \gamma_f \delta \phi_f \, dv - \int_{\mathcal{B}} \sum_{f \in \mathcal{F}} \gamma_f \nabla_{\mathbf{x}} \phi_f \cdot \delta \mathbf{x}_f \, dv. \end{aligned} \quad (69)$$

The subscript g denotes the set of all fluid phases excluding f . The held-fixed derivatives¹ are evaluated at the physical saturation state. The physical variations in (68) preserve $\sum_f \delta S_f = 0$. The phase interfacial potential appearing in (69) is

$$\gamma_f = \gamma + \left. \frac{\partial \gamma}{\partial S_f} \right|_{S_{g \neq f}, \mathbf{h}, \theta_{\mathcal{F}}} - \sum_{g \in \mathcal{F}} S_g \left. \frac{\partial \gamma}{\partial S_g} \right|_{S_{k \neq g}, \mathbf{h}, \theta_{\mathcal{F}}}, \quad (70)$$

where the common derivative shift described in the footnote cancels from the displayed combination. For each oriented wetting/non-wetting pair, the interfacial difference defines the capillary pressure

$$p_{c,nw} \equiv \gamma_n - \gamma_w, \quad (w, n) \in \mathcal{I}. \quad (71)$$

The form (69) keeps the gradient terms generated by the scalar transport of the phase-attached volume fractions. These terms combine with the volume-fraction and component-storage multiplier gradients in the phase momentum balances after the volume-fraction Euler–Lagrange equations are used. The later thermodynamic balance evaluates the volume-fraction rates in a control volume following the common solid skeleton, whereas the present coordinate variations remain phase-specific. Both operations differentiate the same primitive volume-fraction fields, so the conjugate interfacial coefficient remains γ_f .

At fixed $\mathbf{h}$, the stored capillary contribution remains algebraic at the current saturations and fluid temperature. Evolution of $\mathbf{h}$ makes that contribution depend on the drainage–imbibition path. Setting $N_h = 0$ recovers the single-valued equilibrium closure, where N_h is the number of continuous capillary-history variables.

Dynamic capillarity is introduced through the generalized saturation force in (51) while leaving the stored potential γ unchanged. The generalized saturation force $\mathcal{L}_f^{\text{sat}}$ is closed by Onsager stationarity subject to the admissible dissipation conditions derived below. Independent interfacial-area evolution would require an additional stored state and kinetic equation and is not included here.

4.1.5 Variation of the phase electric enthalpy

The electrical contribution to the Hamilton action is assigned phase by phase through U_ξ^+ . The phase electric-enthalpy density $\omega_\xi^+ = \omega_\xi^+(\mathbf{E}, \bar{\rho}_\xi, \{\eta_\xi^\alpha\}, \theta_\xi)$ is normalized per current phase volume; $\phi_\xi \omega_\xi^+$ is therefore its contribution per current mixture volume. Its arguments are the electric field, intrinsic phase density, composition, and temperature. For each phase,

$$U \supset U_\xi^+ = \int_B \phi_\xi \omega_\xi^+(\mathbf{E}, \bar{\rho}_\xi, \{\eta_\xi^\alpha\}, \theta_\xi) \, dv = \int_{B_{\xi 0}} J_\xi \phi_\xi \omega_\xi^+(\mathbf{E}, \bar{\rho}_\xi, \{\eta_\xi^\alpha\}, \theta_\xi) \, dV_\xi. \quad (72)$$

Let φ denote the electrostatic potential. In the electroquasistatic specialization, the electric field and the phase and mixture electric displacements are

$$\mathbf{E} = -\nabla_{\mathbf{x}} \varphi, \quad \mathbf{d}_\xi = - \left. \frac{\partial \omega_\xi^+}{\partial \mathbf{E}} \right|_{\bar{\rho}_\xi, \{\eta_\xi^\alpha\}, \theta_\xi}, \quad \mathbf{d} = \sum_\xi \phi_\xi \mathbf{d}_\xi. \quad (73)$$

¹Here, γ is defined only for saturations whose sum is one. The indicated partial derivatives are evaluated from any twice continuously differentiable continuation to nearby saturation values. At a physical saturation state, different continuations change every such derivative by the same scalar, so the combinations used below are independent of that continuation.

Thus $\mathbf{E}$ is the electrical constitutive argument, while $\mathbf{d}_\xi$ is derived from ω_ξ^+ . The electric potential φ is the corresponding reversible coordinate in the variational principle, consistent with electroelastic potential formulations [19]. The objective single-vector electrical specialization and its material-symmetry limitation are stated in §A.

With $\otimes$ denoting the tensor outer product, the volume-fraction variation is the phase-attached variation from (67), left here as $\delta\phi_\xi$ so its direct coefficient remains visible. The current-configuration variation is

$$\begin{aligned}\delta U_\xi^+ &= \int_{\mathcal{B}} \left[\omega_\xi^+ \delta\phi_\xi + \phi_\xi \left. \frac{\partial \omega_\xi^+}{\partial \bar{\rho}_\xi} \right|_{\mathbf{E}, \{\eta_\xi^\alpha\}, \theta_\xi} \delta \bar{\rho}_\xi \right] dv \\ &\quad + \int_{\mathcal{B}} \left[\phi_\xi \sum_\alpha \left. \frac{\partial \omega_\xi^+}{\partial \eta_\xi^\alpha} \right|_{\mathbf{E}, \bar{\rho}_\xi, \eta_\xi^{\beta \neq \alpha}, \theta_\xi} \delta \eta_\xi^\alpha + \phi_\xi \mathbf{d}_\xi \cdot \nabla_{\mathbf{x}} \delta \varphi \right] dv \\ &\quad + \int_{\mathcal{B}} \boldsymbol{\sigma}_\xi^+ : \nabla_{\mathbf{x}} \delta \mathbf{x}_\xi \, dv.\end{aligned}\tag{74}$$

The mechanical coefficient in (74) defines the reversible electrical stress assigned to the phase pullback. Variation of the current volume element and convection of the spatial electric field produce the phase-attributed Maxwell stress, consistently with electric-enthalpy virtual-work derivations [42]. We denote this Maxwell stress by $\boldsymbol{\sigma}_\xi^+$,

$$\boldsymbol{\sigma}_\xi^+ = \phi_\xi \left(\omega_\xi^+ \mathbf{I} + \mathbf{E} \otimes \mathbf{d}_\xi \right).\tag{75}$$

Thus the total reversible stress used in the phase momentum equation is

$$\boldsymbol{\sigma}_\xi'^+ \equiv \boldsymbol{\sigma}_\xi' + \boldsymbol{\sigma}_\xi^+.\tag{76}$$

4.1.6 Variation of constraint C_1 : volume-fraction

The constraint C_1 is imposed in the current configuration, so the natural variation is taken at fixed spatial point $\mathbf{x}$. Since each ϕ_ξ is a constituent-attached spatial field, (67) expresses the variation in terms of the spatial variation $\delta\phi_\xi$ and the motion variation $\delta\mathbf{x}_\xi$:

$$\delta C_1 = \int_{\mathcal{B}} \delta \lambda \left(\sum_\xi \phi_\xi - 1 \right) dv + \sum_\xi \int_{\mathcal{B}} \lambda (\delta\phi_\xi - \nabla_{\mathbf{x}} \phi_\xi \cdot \delta \mathbf{x}_\xi) dv.\tag{77}$$

The first term returns the volume-fraction constraint $\sum_\xi \phi_\xi = 1$. The remaining terms contribute λ to each $\delta\phi_\xi$ equation and $-\lambda \nabla_{\mathbf{x}} \phi_\xi$ to each momentum variation $\delta\mathbf{x}_\xi$.

4.1.7 Variation of constraint C_2 : component material mass balance

The component material mass balance constraint is

$$C_2 = \sum_\xi \sum_\alpha \int_{\mathcal{B}_{\xi 0}} \pi_\xi^\alpha \left(J_\xi - \frac{\phi_{\xi 0} \bar{\rho}_{\xi 0} \eta_{\xi 0}^\alpha + \mathcal{C}_\xi^\alpha}{\phi_\xi \bar{\rho}_\xi \eta_\xi^\alpha} \right) dV_\xi.\tag{78}$$

The multiplier π_ξ^α enforces the component material-mass balance for component α in phase ξ . Its variation gives

$$\begin{aligned}
\delta C_2 &= \sum_\xi \sum_\alpha \int_{B_{\xi 0}} \delta \pi_\xi^\alpha \left(J_\xi - \frac{\phi_{\xi 0} \bar{\rho}_{\xi 0} \eta_{\xi 0}^\alpha + \mathcal{C}_\xi^\alpha}{\phi_\xi \bar{\rho}_\xi \eta_\xi^\alpha} \right) dV_\xi \\
&\quad + \sum_\xi \sum_\alpha \int_{B_{\xi 0}} \pi_\xi^\alpha \delta J_\xi dV_\xi \\
&\quad + \sum_\xi \sum_\alpha \int_{B_{\xi 0}} \pi_\xi^\alpha \frac{\phi_{\xi 0} \bar{\rho}_{\xi 0} \eta_{\xi 0}^\alpha + \mathcal{C}_\xi^\alpha}{\phi_\xi^2 \bar{\rho}_\xi \eta_\xi^\alpha} \delta \phi_\xi dV_\xi \\
&\quad + \sum_\xi \sum_\alpha \int_{B_{\xi 0}} \pi_\xi^\alpha \frac{\phi_{\xi 0} \bar{\rho}_{\xi 0} \eta_{\xi 0}^\alpha + \mathcal{C}_\xi^\alpha}{\phi_\xi \bar{\rho}_\xi^2 \eta_\xi^\alpha} \delta \bar{\rho}_\xi dV_\xi \\
&\quad + \sum_\xi \sum_\alpha \int_{B_{\xi 0}} \pi_\xi^\alpha \frac{\phi_{\xi 0} \bar{\rho}_{\xi 0} \eta_{\xi 0}^\alpha + \mathcal{C}_\xi^\alpha}{\phi_\xi \bar{\rho}_\xi (\eta_\xi^\alpha)^2} \delta \eta_\xi^\alpha dV_\xi \\
&\quad - \sum_\xi \sum_\alpha \int_{B_{\xi 0}} \frac{\pi_\xi^\alpha}{\phi_\xi \bar{\rho}_\xi \eta_\xi^\alpha} \delta \mathcal{C}_\xi^\alpha dV_\xi. \\
&= \sum_\xi \sum_\alpha \int_{B_{\xi 0}} \delta \pi_\xi^\alpha \left(J_\xi - \frac{\phi_{\xi 0} \bar{\rho}_{\xi 0} \eta_{\xi 0}^\alpha + \mathcal{C}_\xi^\alpha}{\phi_\xi \bar{\rho}_\xi \eta_\xi^\alpha} \right) dV_\xi \\
&\quad - \sum_\xi \sum_\alpha \int_B \nabla_{\mathbf{x}} \pi_\xi^\alpha \cdot \delta \mathbf{x}_\xi dv \\
&\quad + \sum_\xi \sum_\alpha \int_B \left[\frac{\pi_\xi^\alpha}{\phi_\xi} \delta \phi_\xi + \frac{\pi_\xi^\alpha}{\bar{\rho}_\xi} \delta \bar{\rho}_\xi + \frac{\pi_\xi^\alpha}{\eta_\xi^\alpha} \delta \eta_\xi^\alpha - \frac{\pi_\xi^\alpha}{\phi_\xi \bar{\rho}_\xi \eta_\xi^\alpha} \frac{\delta \mathcal{C}_\xi^\alpha}{J_\xi} \right] dv + \sum_\xi \sum_\alpha \int_{\partial B} \pi_\xi^\alpha \mathbf{n} \cdot \delta \mathbf{x}_\xi da. \quad (79)
\end{aligned}$$

Here the second equality uses $dv = J_\xi dV_\xi$ and $\phi_{\xi 0} \bar{\rho}_{\xi 0} \eta_{\xi 0}^\alpha + \mathcal{C}_\xi^\alpha = J_\xi \phi_\xi \bar{\rho}_\xi \eta_\xi^\alpha$.

4.1.8 Variation of constraint C_3 : mass partition within phase

$$\begin{aligned}
\delta C_3 &= \sum_\xi \int_B \delta \Pi_\xi \left(\sum_\alpha \eta_\xi^\alpha - 1 \right) dv + \sum_\xi \sum_\alpha \int_B \Pi_\xi \left(\delta \eta_\xi^\alpha - \nabla_{\mathbf{x}} \eta_\xi^\alpha \cdot \delta \mathbf{x}_\xi \right) dv, \\
&= \sum_\xi \int_B \delta \Pi_\xi \left(\sum_\alpha \eta_\xi^\alpha - 1 \right) dv + \sum_\xi \sum_\alpha \int_B \Pi_\xi \delta \eta_\xi^\alpha dv. \quad (80)
\end{aligned}$$

The last term in the first line vanishes by recognizing $\sum_\alpha \nabla_{\mathbf{x}} \eta_\xi^\alpha = 0$ by (14).

4.1.9 Variation of constraint C_4 : material insertion

The Bedford–Drumheller transfer constraint contains the component material increment $\mathcal{C}_\xi^\alpha$ carried by phase ξ . Its rate variation must be integrated-by-parts with the same phase material derivative before any stationarity condition is used. A single transfer potential τ enforces the total insertion-rate

constraint. Varying τ , the material measure, and the phase map gives

$$\begin{aligned} \int_{t_1}^{t_2} \delta C_4 \, dt &= \int_{t_1}^{t_2} \int_{\mathcal{B}} \delta \tau \left[\sum_{\xi} \sum_{\alpha} \frac{\dot{\mathcal{C}}_{\xi}^{\alpha}}{J_{\xi}} \right] dv \, dt \\ &\quad + \int_{t_1}^{t_2} \int_{\mathcal{B}} \sum_{\xi} \sum_{\alpha} \left[-\frac{D_{\xi} \tau}{Dt} \frac{\delta \mathcal{C}_{\xi}^{\alpha}}{J_{\xi}} + \frac{\dot{\mathcal{C}}_{\xi}^{\alpha}}{J_{\xi}} \nabla_{\mathbf{x}} \tau \cdot \delta \mathbf{x}_{\xi} \right] dv \, dt + \int_{\mathcal{B}} \sum_{\xi} \sum_{\alpha} \tau \frac{\delta \mathcal{C}_{\xi}^{\alpha}}{J_{\xi}} dv \bigg|_{t_1}^{t_2}. \end{aligned} \quad (81)$$

The component-material variations vanish at t_1 and t_2 , so the final endpoint term in (81) is zero for every admissible variation. Varying τ in (81) enforces the zero-sum insertion rate. Varying the material measure gives the coefficient $D_{\xi} \tau / Dt$, and varying the phase map contributes the momentum coefficient $\nabla_{\mathbf{x}} \tau$.

4.1.10 Collected Hamilton–d’Alembert variation

The Hamilton–d’Alembert terms are now collected before any stationarity equation is substituted back into another variation. This collection contains the coordinate, constraint, and prescribed d’Alembert-force coefficients, including those from δC_4 :

$$\begin{aligned} 0 &= \int_{t_1}^{t_2} \left\{ \sum_{\xi} \int_{\mathcal{B}} \left[-\rho_{\xi} \mathbf{a}_{\xi} + \nabla_{\mathbf{x}} \cdot \boldsymbol{\sigma}_{\xi}^{\prime+} + \rho_{\xi} \mathbf{g} + \mathbf{b}_{\xi} - \lambda \nabla_{\mathbf{x}} \phi_{\xi} - \sum_{\alpha} \nabla_{\mathbf{x}} \pi_{\xi}^{\alpha} + \sum_{\alpha} \dot{\mathcal{C}}_{\xi}^{\alpha} (\nabla_{\mathbf{x}} \tau - \mathbf{v}_{\xi}) \right] \cdot \delta \mathbf{x}_{\xi} \, dv \right. \\ &\quad + \sum_{f \in \mathcal{F}} \int_{\mathcal{B}} \left[\left(\gamma_f + \mathcal{L}_f^{\text{sat}} - \sum_{g \in \mathcal{F}} S_g \mathcal{L}_g^{\text{sat}} \right) \nabla_{\mathbf{x}} \phi_f \right] \cdot \delta \mathbf{x}_f \, dv \\ &\quad + \sum_{\xi} \int_{\mathcal{B}} \left[\lambda + \sum_{\alpha} \frac{\pi_{\xi}^{\alpha}}{\phi_{\xi}} - \omega_{\xi}^+ \right] \delta \phi_{\xi} \, dv \\ &\quad + \sum_{f \in \mathcal{F}} \int_{\mathcal{B}} \left[-\gamma_f - \mathcal{L}_f^{\text{sat}} + \sum_{g \in \mathcal{F}} S_g \mathcal{L}_g^{\text{sat}} \right] \delta \phi_f \, dv \\ &\quad + \sum_{\xi} \int_{\mathcal{B}} \left[-\rho_{\xi} \frac{\partial \psi_{\xi}}{\partial \bar{\rho}_{\xi}} \bigg|_{\mathbf{F}_{\xi}, \{\eta_{\xi}^{\alpha}\}} - \phi_{\xi} \frac{\partial \omega_{\xi}^+}{\partial \bar{\rho}_{\xi}} \bigg|_{\mathbf{E}, \{\eta_{\xi}^{\alpha}\}, \theta_{\xi}} + \sum_{\alpha} \frac{\pi_{\xi}^{\alpha}}{\bar{\rho}_{\xi}} \right] \delta \bar{\rho}_{\xi} \, dv \\ &\quad + \sum_{\xi} \sum_{\alpha} \int_{\mathcal{B}} \left[\frac{\pi_{\xi}^{\alpha}}{\eta_{\xi}^{\alpha}} + \Pi_{\xi} - \rho_{\xi} \frac{\partial \psi_{\xi}}{\partial \eta_{\xi}^{\alpha}} \bigg|_{\mathbf{F}_{\xi}, \bar{\rho}_{\xi}, \eta_{\xi}^{\beta \neq \alpha}} - \phi_{\xi} \frac{\partial \omega_{\xi}^+}{\partial \eta_{\xi}^{\alpha}} \bigg|_{\mathbf{E}, \bar{\rho}_{\xi}, \eta_{\xi}^{\beta \neq \alpha}, \theta_{\xi}} \right] \delta \eta_{\xi}^{\alpha} \, dv \\ &\quad + \sum_{\xi} \sum_{\alpha} \int_{\mathcal{B}} \left[\frac{1}{2} \mathbf{v}_{\xi} \cdot \mathbf{v}_{\xi} + L_{\xi}^{\alpha} - \frac{D_{\xi} \tau}{Dt} - \frac{\pi_{\xi}^{\alpha}}{\phi_{\xi} \bar{\rho}_{\xi} \eta_{\xi}^{\alpha}} \right] \frac{\delta \mathcal{C}_{\xi}^{\alpha}}{J_{\xi}} \, dv \\ &\quad + \int_{\mathcal{B}} [\nabla_{\mathbf{x}} \cdot \mathbf{d} - \varrho] \delta \varphi \, dv \Big\} dt \\ &\quad + \text{multiplier variations} + \text{boundary terms}. \end{aligned} \quad (82)$$

The stationarity conditions obtained from the individual coefficients and multiplier variations in (82) are developed in §4.2.

4.2 Euler–Lagrange equations

Setting the coefficients in (82) to zero first gives algebraic relations for the storage and constraint multipliers. Substitution of these relations into the remaining stationarity equations exposes the

phase momentum balances and the electrostatic field equation.

4.2.1 Storage and multiplier relations

The intrinsic-density variation $\delta\bar{\rho}_\xi$ gives

$$\sum_{\alpha} \frac{\pi_{\xi}^{\alpha}}{\phi_{\xi}} = \bar{\rho}_{\xi}^2 \left. \frac{\partial \psi_{\xi}}{\partial \bar{\rho}_{\xi}} \right|_{\mathbf{F}_{\xi}, \{\eta_{\xi}^{\alpha}\}} + \bar{\rho}_{\xi} \left. \frac{\partial \omega_{\xi}^{+}}{\partial \bar{\rho}_{\xi}} \right|_{\mathbf{E}, \{\eta_{\xi}^{\alpha}\}, \theta_{\xi}}. \quad (83)$$

We recognize the first term on the right-hand side as the thermodynamic phase pressure contribution. The second term is present when the phase electric enthalpy depends on intrinsic density. We define the phase pressure as

$$\bar{p}_{\xi} \equiv \bar{\rho}_{\xi}^2 \left. \frac{\partial \psi_{\xi}}{\partial \bar{\rho}_{\xi}} \right|_{\mathbf{F}_{\xi}, \{\eta_{\xi}^{\alpha}\}} + \bar{\rho}_{\xi} \left. \frac{\partial \omega_{\xi}^{+}}{\partial \bar{\rho}_{\xi}} \right|_{\mathbf{E}, \{\eta_{\xi}^{\alpha}\}, \theta_{\xi}}. \quad (84)$$

Equation (84) therefore identifies the total phase pressure as the usual thermodynamic pressure plus the dielectric pressure correction induced by the intrinsic-density dependence of the phase electric enthalpy.

For solid phases $s \in \mathcal{S}$ without an explicit capillary contribution, the phase-volume-fraction variation $\delta\phi_{\xi}$ gives

$$\phi_{\xi} \lambda = - \sum_{\alpha} \pi_{\xi}^{\alpha} + \phi_{\xi} \omega_{\xi}^{+}. \quad (85)$$

This relation is used to simplify the phase momentum equations below and, for fluid phases, to eliminate the volume-constraint multiplier in favor of phase pressure and interfacial terms. For a fluid phase the variation also carries the primitive capillary potential, so its coefficient in (82) contains the interfacial potential γ_f , the electric enthalpy ω_f^{+} , and the generalized saturation force. The corresponding Euler–Lagrange equation is

$$\lambda + \sum_{\alpha} \frac{\pi_f^{\alpha}}{\phi_f} - \gamma_f - \omega_f^{+} - \mathcal{L}_f^{\text{sat}} + \sum_{g \in \mathcal{F}} S_g \mathcal{L}_g^{\text{sat}} = 0. \quad (86)$$

Using (83) and (84) gives

$$\lambda + \bar{p}_f - \gamma_f - \omega_f^{+} - \mathcal{L}_f^{\text{sat}} + \sum_{g \in \mathcal{F}} S_g \mathcal{L}_g^{\text{sat}} = 0, \quad (87a)$$

or

$$\bar{p}_f - \omega_f^{+} - \gamma_f = \mathcal{L}_f^{\text{sat}} - \sum_{g \in \mathcal{F}} S_g \mathcal{L}_g^{\text{sat}} - \lambda. \quad (87b)$$

Consequently the coordinate stationarity identifies the generalized-force differences with the phase-pressure force differences,

$$(\bar{p}_f - \omega_f^{+} - \gamma_f) - (\bar{p}_g - \omega_g^{+} - \gamma_g) = \mathcal{L}_f^{\text{sat}} - \mathcal{L}_g^{\text{sat}}. \quad (88)$$

When the saturation-force differences vanish and the phases are electrically neutral, this relation gives the standard capillary-equilibrium condition

$$\bar{p}_n - \bar{p}_w = p_{c,nw}, \quad (w, n) \in \mathcal{I}. \quad (89)$$

For two fluid phases with $\mathcal{F} = \{w, n\}$ and one oriented pair (w, n) , the zero-rate form of (88) combines the intrinsic capillary contribution $p_{c,nw}$ with the pressure-like electrical contribution $\omega_n^+ - \omega_w^+$. This electrocapillary relation is consistent with electrowetting interface balances, in which the free energy contains surface, electrostatic, and ionic contributions and stationarity of the interface position gives a pressure-difference balance against capillary and Maxwell or electro-osmotic terms [50, 58]. The same phase-attributed electrical enthalpy enters the phase momentum balances, reversible stresses, and thermodynamic restrictions. The dynamic branch augments the pressure difference in (88) by the lag in (196), which is proportional to $D_S S_n / Dt$. If the interfacial energy is parameterized by the wetting saturation S_w , then $p_{c,nw} = -d\gamma(S_w, 1 - S_w, \mathbf{h}, \theta_{\mathcal{F}}) / dS_w$ at fixed $\mathbf{h}$ and $\theta_{\mathcal{F}}$.

The same relations identify the equivalent pore pressure associated with the volume constraint. Define

$$\bar{p}_E \equiv -\lambda. \quad (90)$$

Multiplying (87) by the fluid saturations and summing over fluid phases eliminates the generalized force: because the saturations sum to unity, $\sum_f S_f = 1$, the term $\sum_f S_f \mathcal{L}_f^{\text{sat}}$ cancels against $(\sum_f S_f)(\sum_g S_g \mathcal{L}_g^{\text{sat}}) = \sum_g S_g \mathcal{L}_g^{\text{sat}}$, and the multiplier term becomes $-\lambda \sum_f S_f = -\lambda = \bar{p}_E$. The result is

$$\sum_{f \in \mathcal{F}} S_f \bar{p}_f = \bar{p}_E + \sum_{f \in \mathcal{F}} S_f \gamma_f + \sum_{f \in \mathcal{F}} S_f \omega_f^+. \quad (91)$$

The primitive potentials satisfy

$$\sum_{f \in \mathcal{F}} S_f \gamma_f = \gamma. \quad (92)$$

Therefore

$$\boxed{\bar{p}_E = \sum_{f \in \mathcal{F}} S_f (\bar{p}_f - \omega_f^+) - \gamma}. \quad (93)$$

When $\omega_f^+ = 0$, equation (93) reduces to the equivalent pore pressure used in thermodynamically stable coupled multiphase poromechanics [16, 39]. The term $-\sum_{f \in \mathcal{F}} S_f \omega_f^+$ is the present electrical extension of the equivalent pore pressure, obtained from the phase-pressure relation above. The common pore-volume restriction (170b) restates this identity in the actual phase pressures, and it remains valid when the dynamic lag is active because the lag cancels from the saturation-weighted combination.

The remaining independent variations determine the composition and component-transfer relations. For a phase with N tracked components, the composition variations $\delta\eta_\xi^\alpha$ give

$$0 = \frac{\pi_\xi^\alpha}{\eta_\xi^\alpha} + \Pi_\xi - \rho_\xi \left. \frac{\partial \psi_\xi}{\partial \eta_\xi^\alpha} \right|_{\mathbf{F}_\xi, \bar{\rho}_\xi, \eta_\xi^{\beta \neq \alpha}} - \phi_\xi \left. \frac{\partial \omega_\xi^+}{\partial \eta_\xi^\alpha} \right|_{\mathbf{E}, \bar{\rho}_\xi, \eta_\xi^{\beta \neq \alpha}, \theta_\xi}, \quad \alpha = 1, \dots, N, \quad (94)$$

while the multiplier variation $\delta\Pi_\xi$ returns the phase mass-fraction constraint

$$\sum_{\alpha=1}^N \eta_\xi^\alpha = 1. \quad (95)$$

Thus Π_ξ is the phase-level multiplier that enforces the redundant composition coordinate. Equation (94) may be read componentwise as

$$\rho_\xi \left. \frac{\partial \psi_\xi}{\partial \eta_\xi^\alpha} \right|_{\mathbf{F}_\xi, \bar{\rho}_\xi, \eta_\xi^{\beta \neq \alpha}} + \phi_\xi \left. \frac{\partial \omega_\xi^+}{\partial \eta_\xi^\alpha} \right|_{\mathbf{E}, \bar{\rho}_\xi, \eta_\xi^{\beta \neq \alpha}, \theta_\xi} - \frac{\pi_\xi^\alpha}{\eta_\xi^\alpha} = \Pi_\xi, \quad (96)$$

The first term in (96) is the mixing contribution to composition stationarity. The second term is the composition derivative of the phase electric enthalpy. Coleman–Noll later combines these storage derivatives into the component potential. If ω_ξ^+ includes composition-dependent dielectric or electrical-double-layer free energy, this derivative contains the corresponding electrostatic or double-layer contribution [47, 41]. Choosing component N as the reference and comparing against $\alpha = 1, \dots, N-1$ gives a system of $N-1$ equations,

$$\begin{aligned} \rho_\xi \left(\frac{\partial \psi_\xi}{\partial \eta_\xi^\alpha} \Big|_{\mathbf{F}_\xi, \bar{\rho}_\xi, \eta_\xi^{\beta \neq \alpha}} - \frac{\partial \psi_\xi}{\partial \eta_\xi^N} \Big|_{\mathbf{F}_\xi, \bar{\rho}_\xi, \eta_\xi^{\beta \neq N}} \right) + \phi_\xi \left(\frac{\partial \omega_\xi^+}{\partial \eta_\xi^\alpha} \Big|_{\mathbf{E}, \bar{\rho}_\xi, \eta_\xi^{\beta \neq \alpha}, \theta_\xi} - \frac{\partial \omega_\xi^+}{\partial \eta_\xi^N} \Big|_{\mathbf{E}, \bar{\rho}_\xi, \eta_\xi^{\beta \neq N}, \theta_\xi} \right) \\ = \frac{\pi_\xi^\alpha}{\eta_\xi^\alpha} - \frac{\pi_\xi^N}{\eta_\xi^N}, \quad \alpha = 1, \dots, N-1. \end{aligned} \quad (97)$$

Finally, the component-material-measure variations $\delta \mathcal{C}_\xi^\alpha$ give

$$\frac{D_\xi \tau}{Dt} = \frac{1}{2} \mathbf{v}_\xi \cdot \mathbf{v}_\xi + L_\xi^\alpha - \frac{\pi_\xi^\alpha}{\phi_\xi \bar{\rho}_\xi \eta_\xi^\alpha}. \quad (98)$$

Equation (98) is the component-density extension of the microinertia-free Bedford–Drumheller phase-level transfer-potential relation [22, eq. (2.8)] [21, eq. (48)]. Because τ is one scalar field shared by all phases and components, one phase trajectory supplies its evolution equation. The remaining componentwise relations then fix the specific generalized transfer-work potentials: the reference-component relation determines the reference potential L_ξ^N , and subtracting it from the other component relations determines the within-phase differences $L_\xi^\alpha - L_\xi^N$. The closure that makes the retained- τ system fully determined, and its thermodynamic restrictions, are obtained later from the component-supply terms in the Coleman–Noll procedure.

4.2.2 Solid-phase momentum balance

For a solid phase $s \in \mathcal{S}$, the phase-motion variation $\delta \mathbf{x}_s$, after substitution of (85) and the equivalent-pore-pressure definition (90), gives

$$\rho_s \mathbf{a}_s = \nabla_{\mathbf{x}} \cdot \boldsymbol{\sigma}'_s{}^+ + \rho_s \mathbf{g} + \mathbf{b}_s - \phi_s \nabla_{\mathbf{x}} \bar{p}_E - \nabla_{\mathbf{x}} \left(\phi_s \omega_s^+ \right) + \sum_{\alpha} \dot{c}_s^\alpha (\nabla_{\mathbf{x}} \tau - \mathbf{v}_s), \quad (99)$$

The boundary coefficients from (62), (74), (79), and the prescribed traction work in (51) give the solid-phase natural traction. Eliminating the component-supply sum through (85) and replacing λ by the equivalent pore pressure (90) expresses the traction in terms of $\bar{p}_E$:

$$\left[\boldsymbol{\sigma}'_s{}^+ - \phi_s \left(\bar{p}_E + \omega_s^+ \right) \mathbf{I} \right] \mathbf{n} = \mathbf{t}_s \quad \text{on } \Gamma_{\mathbf{t}_s}. \quad (100)$$

The complementary prescribed-motion condition is $\delta \mathbf{x}_s = \mathbf{0}$ on $\Gamma_{\mathbf{x}_s}$.

The fluid-phase balance contains additional capillary forces and is reduced separately below.

4.2.3 Fluid-phase momentum balance

For any fluid phase $f \in \mathcal{F}$, the collected variation (82) gives the general intermediate form

$$\begin{aligned} \rho_f \mathbf{a}_f = \nabla_{\mathbf{x}} \cdot \boldsymbol{\sigma}'_f{}^+ + \rho_f \mathbf{g} + \mathbf{b}_f - \lambda \nabla_{\mathbf{x}} \phi_f - \sum_{\alpha} \nabla_{\mathbf{x}} \pi_f^\alpha \\ + \gamma_f \nabla_{\mathbf{x}} \phi_f + \left(\mathcal{L}_f^{\text{sat}} - \sum_{g \in \mathcal{F}} S_g \mathcal{L}_g^{\text{sat}} \right) \nabla_{\mathbf{x}} \phi_f + \sum_{\alpha} \dot{c}_f^\alpha (\nabla_{\mathbf{x}} \tau - \mathbf{v}_f), \quad f \in \mathcal{F}. \end{aligned} \quad (101)$$

Using $\sum_{\alpha} \pi_f^{\alpha} = \phi_f \bar{p}_f$ and the fluid volume-fraction Euler–Lagrange relation (87a), the multiplier, interfacial-gradient, electric-enthalpy, and saturation-force terms collapse as

$$-\lambda \nabla_{\mathbf{x}} \phi_f - \nabla_{\mathbf{x}} (\phi_f \bar{p}_f) + \gamma_f \nabla_{\mathbf{x}} \phi_f + \left(\mathcal{L}_f^{\text{sat}} - \sum_{g \in \mathcal{F}} S_g \mathcal{L}_g^{\text{sat}} \right) \nabla_{\mathbf{x}} \phi_f = -\phi_f \nabla_{\mathbf{x}} \bar{p}_f - \omega_f^+ \nabla_{\mathbf{x}} \phi_f. \quad (102)$$

The generalized saturation force enters the collected variation (82) both directly, as the gradient term in (101), and through the volume-fraction multiplier λ in (87a). These two contributions cancel in the combination (102), so the collapse into the actual phase-pressure gradient carries no explicit saturation force. The saturation change forces instead enter the phase-pressure difference relation (88) and, after summation, the overall solid–fluid momentum balance. Substituting the total reversible stress definition (76), the Maxwell stress (75), and combining $-\omega_f^+ \nabla_{\mathbf{x}} \phi_f$ with the isotropic Maxwell contribution absorbs the isotropic electric-enthalpy force into the phase-pressure gradient. The general fluid-phase momentum balance therefore uses the actual phase-pressure gradient,

$$\boxed{\rho_f \mathbf{a}_f = \nabla_{\mathbf{x}} \cdot (\boldsymbol{\sigma}'_f + \phi_f \mathbf{E} \otimes \mathbf{d}_f) - \phi_f \nabla_{\mathbf{x}} (\bar{p}_f - \omega_f^+) + \rho_f \mathbf{g} + \mathbf{b}_f + \sum_{\alpha} \dot{c}_f^{\alpha} (\nabla_{\mathbf{x}} \tau - \mathbf{v}_f), \quad f \in \mathcal{F}.} \quad (103)$$

The boundary coefficients from (62), (74), (79), and the prescribed traction work in (51) give the fluid-phase natural traction. The component material constraint contributes $\sum_{\alpha} \pi_f^{\alpha} \mathbf{n}$ to the boundary coefficient. Using $\sum_{\alpha} \pi_f^{\alpha} = \phi_f \bar{p}_f$ and (75) gives

$$\left[\boldsymbol{\sigma}'_f + \phi_f \mathbf{E} \otimes \mathbf{d}_f - \phi_f (\bar{p}_f - \omega_f^+) \mathbf{I} \right] \mathbf{n} = \mathbf{t}_f \quad \text{on } \Gamma_{\mathbf{t}_f}. \quad (104)$$

The complementary prescribed-motion condition is $\delta \mathbf{x}_f = \mathbf{0}$ on $\Gamma_{\mathbf{x}_f}$. The electrical force in the general balance is carried by the anisotropic Maxwell term $\nabla_{\mathbf{x}} \cdot (\phi_f \mathbf{E} \otimes \mathbf{d}_f)$, while the isotropic electric-enthalpy contribution is absorbed into the pressure reconstruction. The dynamic capillary lag, closed later by Onsager stationarity, does not appear as a body force in this individual balance; it enters through the phase-pressure difference (88) and, through the saturation-weighted combination, in the summed solid–fluid momentum balance. Related Maxwell forces appear in leaky-dielectric and electrowetting theories [43, 58].

When the generalized saturation-force differences vanish, the zero-lag reversible limit, the pressure relation (87b) gives $\bar{p}_f - \omega_f^+ = \bar{p}_E + \gamma_f$, and (103) reduces to the equivalent-pore-pressure form

$$\rho_f \mathbf{a}_f = \nabla_{\mathbf{x}} \cdot (\boldsymbol{\sigma}'_f + \phi_f \mathbf{E} \otimes \mathbf{d}_f) - \phi_f \nabla_{\mathbf{x}} (\bar{p}_E + \gamma_f) + \rho_f \mathbf{g} + \mathbf{b}_f + \sum_{\alpha} \dot{c}_f^{\alpha} (\nabla_{\mathbf{x}} \tau - \mathbf{v}_f), \quad f \in \mathcal{F}. \quad (105)$$

Under the neutral, conversion-free specialization $\omega_f^+ = 0$ and $\dot{c}_f^{\alpha} = 0$, (103) reduces to the standard pressure-gradient form,

$$\rho_f \mathbf{a}_f = \nabla_{\mathbf{x}} \cdot \boldsymbol{\sigma}'_f - \phi_f \nabla_{\mathbf{x}} \bar{p}_f + \rho_f \mathbf{g} + \mathbf{b}_f, \quad f \in \mathcal{F}. \quad (106)$$

4.2.4 Electrostatic field equation

The electrostatic-potential variation $\delta \varphi$ gives Gauss' law,

$$\nabla_{\mathbf{x}} \cdot \mathbf{d} = \rho. \quad (107)$$

The corresponding natural electrical boundary condition is

$$\mathbf{d} \cdot \mathbf{n} = \bar{q} \quad \text{on } \Gamma_{\bar{q}}. \quad (108)$$

The complementary essential condition prescribes φ on Γ_φ , so $\delta\varphi = 0$ there.

Combined with the local charge balance from §3, the electroquasistatic field equation implies the following equivalent compatibility forms.

$$\nabla_{\mathbf{x}} \cdot \left(\frac{\partial \mathbf{d}}{\partial t} + \mathbf{i} \right) = 0. \quad (109a)$$

Equation (109a) uses the Eulerian partial derivative obtained by differentiating Gauss' law at fixed $\mathbf{x}$. It is a compatibility relation, not an additional Euler–Lagrange equation. Its signs follow from $\nabla_{\mathbf{x}} \cdot \mathbf{d} = \varrho$ and (46); every term inside the spatial divergence has units of current per area. The neutral specialization additionally sets $\omega_\xi^+ = 0$ and $z_\xi^\alpha = 0$, where z_ξ^α is the charge per unit component mass.

4.3 Onsager principle for dissipative saturation, reaction, and transport

The Hamilton–d'Alembert variation determines the coordinate equations at fixed endpoint variations and holds any constitutive d'Alembert-force coefficient fixed. Saturation redistribution, reactions, and relative component transport are closed separately by an Onsager principle: at a fixed current thermodynamic state, the process rates for the immediate response are chosen by stationarity of an entropy-rate functional containing a dissipation potential and the linear thermodynamic rate [18, 56]. This statement is local in time and selects near-equilibrium rates. The entropy-rate form displayed here remains valid when $\theta_{\mathcal{F}} \neq \theta_{\mathcal{S}}$. Its coefficients are retained in the specific generalized transfer-work form delivered by the reversible variation; their chemical-potential interpretation is derived later by the Coleman–Noll procedure. The state variables that enter the coefficients are held fixed during this minimization. For each active phase, select one active reference component N . The independent process rates are the $|\mathcal{F}| - 1$ saturation rates and the external progress rates $r_{(m)}$, $\mathbf{j}_{\xi, \text{disp}}^\alpha$, and $\mathbf{j}_{\xi, \text{diff}}^\alpha$ for $\alpha \neq N$. The reference-component fluxes are reconstructed separately for dispersion and diffusion by

$$\mathbf{j}_{\xi, k}^N = - \sum_{\alpha \neq N} \mathbf{j}_{\xi, k}^\alpha, \quad k \in \{\text{disp}, \text{diff}\}. \quad (110)$$

Thus every admissible flux variation satisfies the same zero-sum condition. The heavy dot $\dot{\square} = D_{\mathcal{S}}\square/Dt$ denotes the material time derivative following the solid skeleton. It is used for saturation rates because the saturation field is defined on the current configuration of the porous medium, whose material frame is the solid skeleton; the solid-skeleton-following rate preserves the saturation-sum constraint $\sum_f S_f = 1$ under differentiation and avoids the relative-velocity advection that a phase-following rate would introduce into the intrinsic saturation dynamics. Choose one active reference fluid phase $f_\star$ and write $\dot{S}_{f_\star} = - \sum_{f \neq f_\star} \dot{S}_f$. The remaining saturation rates are independent. The held-fixed current configuration and constitutive state include $\mathbf{F}_\xi$, $\bar{\rho}_\xi$, η_ξ^α , ϕ_ξ , $\theta_{\mathcal{F}}$, $\theta_{\mathcal{S}}$, φ , J_ξ , and any internal variables entering the potentials or mobilities.

The phase free energy ψ_ξ , specific generalized transfer-work potentials L_ξ^α , generalized saturation forces $\mathcal{L}_f^{\text{sat}}$, and electric potential φ enter as fixed state coefficients during rate stationarity. The absolute conversion coefficient is $\psi_\xi + L_\xi^\alpha + z_\xi^\alpha \varphi$. Relative transport depends only on the within-phase neutral difference $L_\xi^\alpha - L_\xi^N$ and the separate electric-field contribution. Coleman–Noll will show that the neutral difference equals the corresponding chemical-potential difference and will

then introduce the electrochemical potential. Keeping the neutral and electric parts separate also preserves invariance under the additive gauge of φ at nonuniform temperature.

The dependent accumulation rate $\dot{C}_\xi^\alpha/J_\xi$ is eliminated before stationarity using (31) and (110). For $\xi \in \mathcal{G}$, the resulting neutral thermodynamic rate is combined with the direct work of the electric field on the relative charge flux. The zero-sum reconstruction gives $\sum_\alpha z_\xi^\alpha \mathbf{j}_{\xi,k}^\alpha = \sum_{\alpha \neq N} (z_\xi^\alpha - z_\xi^N) \mathbf{j}_{\xi,k}^\alpha$, and the component balance and $\mathbf{E} = -\nabla_{\mathbf{x}} \varphi$ give the gauge-invariant identity

$$\begin{aligned} \sum_\alpha \frac{\psi_\xi + L_\xi^\alpha}{\theta_{\mathcal{G}}} \frac{\dot{C}_\xi^\alpha}{J_\xi} - \frac{1}{\theta_{\mathcal{G}}} \sum_\alpha z_\xi^\alpha (\mathbf{j}_{\xi,\text{disp}}^\alpha + \mathbf{j}_{\xi,\text{diff}}^\alpha) \cdot \mathbf{E} &= \sum_m \left(\frac{1}{\theta_{\mathcal{G}}} \sum_\alpha (\psi_\xi + L_\xi^\alpha) \nu_{\xi(m)}^\alpha \right) r_{(m)} \\ &\quad - \sum_{\alpha \neq N} \frac{L_\xi^\alpha - L_\xi^N}{\theta_{\mathcal{G}}} \nabla_{\mathbf{x}} \cdot (\mathbf{j}_{\xi,\text{disp}}^\alpha + \mathbf{j}_{\xi,\text{diff}}^\alpha) \\ &\quad + \sum_{\alpha \neq N} \frac{z_\xi^\alpha - z_\xi^N}{\theta_{\mathcal{G}}} \nabla_{\mathbf{x}} \varphi \cdot (\mathbf{j}_{\xi,\text{disp}}^\alpha + \mathbf{j}_{\xi,\text{diff}}^\alpha). \end{aligned} \quad (111)$$

The coefficient of each reaction rate in (111) is the neutral transfer coefficient $(\psi_\xi + L_\xi^\alpha)/\theta_{\mathcal{G}}$, which contains only the phase free energy and the specific generalized transfer-work potential. Within a phase, transport is driven by the potential differences $L_\xi^\alpha - L_\xi^N$, while the electric field enters separately through the direct electrical work. For a mechanism that conserves charge separately within each thermal subsystem, its stoichiometric sum of neutral coefficients may instead be written with the electrochemical potentials introduced later, because the added electric terms cancel identically under that mechanism's charge conservation. A mechanism that transfers net charge between the fluid and solid subsystems must satisfy the reaction-energy admissibility condition, evaluated mechanism by mechanism with the same neutral reaction coefficient, and its reaction rate and reaction-energy transfer may be Onsager-coupled. Both sides of (111) are gauge invariant: the electrical transport term depends on the electric field $\mathbf{E}$, so adding a constant to φ leaves every term unchanged.

After the dependent accumulation rate has been eliminated, the Onsager entropy-rate functional contains the saturation, reaction, and relative-transport dissipation potentials minus their entropy production. The reaction and transport terms use the temperature-weighted thermodynamic rate in (111):

$$\begin{aligned} \mathcal{R} &= \Phi_{\mathcal{R}} - \int_{\mathcal{B}} \frac{\phi}{\theta_{\mathcal{F}}} \sum_{f \in \mathcal{F}} \mathcal{L}_f^{\text{sat}} \dot{S}_f \, dv \\ &\quad + \int_{\mathcal{B}} \sum_m \left[\sum_{\mathcal{G} \in \{\mathcal{F}, \mathcal{S}\}} \frac{1}{\theta_{\mathcal{G}}} \sum_{\xi \in \mathcal{G}} \sum_\alpha (\psi_\xi + L_\xi^\alpha) \nu_{\xi(m)}^\alpha \right] r_{(m)} \, dv \\ &\quad - \int_{\mathcal{B}} \sum_{\mathcal{G} \in \{\mathcal{F}, \mathcal{S}\}} \sum_{\xi \in \mathcal{G}} \sum_{\alpha \neq N} \frac{L_\xi^\alpha - L_\xi^N}{\theta_{\mathcal{G}}} \nabla_{\mathbf{x}} \cdot (\mathbf{j}_{\xi,\text{disp}}^\alpha + \mathbf{j}_{\xi,\text{diff}}^\alpha) \, dv, \\ &\quad + \int_{\mathcal{B}} \sum_{\mathcal{G} \in \{\mathcal{F}, \mathcal{S}\}} \sum_{\xi \in \mathcal{G}} \sum_{\alpha \neq N} \frac{z_\xi^\alpha - z_\xi^N}{\theta_{\mathcal{G}}} \nabla_{\mathbf{x}} \varphi \cdot (\mathbf{j}_{\xi,\text{disp}}^\alpha + \mathbf{j}_{\xi,\text{diff}}^\alpha) \, dv, \\ &\quad + \sum_{\mathcal{G} \in \{\mathcal{F}, \mathcal{S}\}} \sum_{\xi \in \mathcal{G}} \sum_{\alpha \neq N} \int_{\Gamma_{\overline{\mathcal{M}}_\xi^\alpha}} \overline{\mathcal{M}}_\xi^\alpha (\mathbf{j}_{\xi,\text{disp}}^\alpha + \mathbf{j}_{\xi,\text{diff}}^\alpha) \cdot \mathbf{n} \, da, \\ \delta \mathcal{R} &= 0. \end{aligned} \quad (112)$$

The added surface term is the work of a prescribed external component reservoir on $\Gamma_{\overline{\mathcal{M}}_\xi^\alpha}$. Here $\overline{\mathcal{M}}_\xi^\alpha$ is the prescribed temperature-weighted neutral potential difference; the electrical boundary datum

is provided independently by the electric-field problem. The reservoir term acts on the relative component flux only; the phase-advective flux is held fixed during the Onsager rate variation.

The near-equilibrium quadratic dissipation potential is

$$\begin{aligned}
\Phi_{\mathcal{R}} = & \frac{1}{2} \int_{\mathcal{B}} \frac{\phi}{\theta_{\mathcal{F}}} \sum_{f \neq f_{\star}} \sum_{g \neq f_{\star}} \mathcal{T}_{fg} \dot{S}_f \dot{S}_g \, dv \\
& + \frac{1}{2} \int_{\mathcal{B}} \sum_m \frac{r_{(m)}^2}{K_{(m)}} \, dv \\
& + \frac{1}{2} \int_{\mathcal{B}} \sum_{\mathcal{G} \in \{\mathcal{F}, \mathcal{S}\}} \frac{1}{\theta_{\mathcal{G}}} \sum_{\xi \in \mathcal{G}} \sum_{\alpha \neq N} \sum_{\beta \neq N} \mathbf{j}_{\xi, \text{disp}}^{\alpha} \cdot (\mathbf{D}_{\xi, \text{disp}}^{-1})^{\alpha\beta} \mathbf{j}_{\xi, \text{disp}}^{\beta} \, dv \\
& + \frac{1}{2} \int_{\mathcal{B}} \sum_{\mathcal{G} \in \{\mathcal{F}, \mathcal{S}\}} \frac{1}{\theta_{\mathcal{G}}} \sum_{\xi \in \mathcal{G}} \sum_{\alpha \neq N} \sum_{\beta \neq N} \mathbf{j}_{\xi, \text{diff}}^{\alpha} \cdot (\mathbf{D}_{\xi, \text{diff}}^{-1})^{\alpha\beta} \mathbf{j}_{\xi, \text{diff}}^{\beta} \, dv.
\end{aligned} \tag{113}$$

Here $K_{(m)}$ is the mobility conjugate to the temperature-weighted reaction force, and $\mathbf{D}_{\xi, k}^{\alpha\beta}$, with $\alpha, \beta \neq N$, are the reduced mobility tensors in the independent relative-flux coordinates; their inverses are taken in the same $N - 1$ -dimensional component space. The reference flux is then reconstructed by (110). The resistance coefficients $\mathcal{T}_{fg}$ govern dynamic capillary redistribution; they have units of pressure times time and are symmetric ($\mathcal{T}_{fg} = \mathcal{T}_{gf}$). Their admissibility is verified against the entropy inequality in Section 5. The adopted quadratic potential is block diagonal in saturation, reaction, dispersion, and diffusion rates. For a charged mechanism that transfers net charge between the thermal subsystems, the neutral reaction force remains unchanged; the reaction and interphase-energy rates may instead be included in one gauge-invariant Onsager block satisfying the mechanismwise dissipation condition derived later. A block-diagonal choice is also admissible when the reaction-energy term is closed separately. The transport boundary data enter the stationarity through the normal relative-flux variation. On $\Gamma_{m, \xi}^{\alpha}$, the normal total component flux is prescribed, so the relative-flux variation is tangential, $(\delta \mathbf{j}_{\xi, \text{disp}}^{\alpha} + \delta \mathbf{j}_{\xi, \text{diff}}^{\alpha}) \cdot \mathbf{n} = 0$. On the complementary $\Gamma_{\mathcal{M}_{\xi}}^{\alpha}$, the temperature-weighted component-potential difference is prescribed and the normal relative-flux variation is free; its boundary contribution is retained in the collected condition below. For each independent component, these complementary portions prescribe either the normal total component flux in (A.9b) or the temperature-weighted component-potential difference $(L_{\xi}^{\alpha} - L_{\xi}^N)/\theta_{\mathcal{G}}$, with the electric boundary datum supplied by the electrostatic boundary-value problem. Reference-component relative fluxes are reconstructed from (110), so prescribed relative-flux data must satisfy the same zero-sum restriction.

4.3.1 Collected Onsager variation

Collecting the variation of $\mathcal{R}$ over the saturation, reaction, and relative-transport coordinates gives the rate-dependent stationarity condition

$$\begin{aligned}
0 = \delta \mathcal{R} = & \int_{\mathcal{B}} \frac{\phi}{\theta_{\mathcal{F}}} \sum_{f \neq f_{\star}} \left[\sum_{g \neq f_{\star}} \mathcal{T}_{fg} \dot{S}_g - (\mathcal{L}_f^{\text{sat}} - \mathcal{L}_{f_{\star}}^{\text{sat}}) \right] \delta \dot{S}_f \, dv \\
& + \int_{\mathcal{B}} \sum_m \left[\frac{r_{(m)}}{K_{(m)}} + \sum_{\mathcal{G} \in \{\mathcal{F}, \mathcal{S}\}} \frac{1}{\theta_{\mathcal{G}}} \sum_{\xi \in \mathcal{G}} \sum_{\alpha} (\psi_{\xi} + L_{\xi}^{\alpha}) \nu_{\xi(m)}^{\alpha} \right] \delta r_{(m)} \, dv
\end{aligned}$$

$$\begin{aligned}
& + \int_B \sum_{\mathcal{G} \in \{\mathcal{F}, \mathcal{S}\}} \frac{1}{\theta_{\mathcal{G}}} \sum_{\xi \in \mathcal{G}} \sum_{\alpha \neq N} \\
& \quad \left[\sum_{\beta \neq N} (\mathbf{D}_{\xi, \text{disp}}^{-1})^{\alpha\beta} \mathbf{j}_{\xi, \text{disp}}^{\beta} + \theta_{\mathcal{G}} \nabla_{\mathbf{x}} \left(\frac{L_{\xi}^{\alpha} - L_{\xi}^N}{\theta_{\mathcal{G}}} \right) + (z_{\xi}^{\alpha} - z_{\xi}^N) \nabla_{\mathbf{x}} \varphi \right] \cdot \delta \mathbf{j}_{\xi, \text{disp}}^{\alpha} dv \\
& + \int_B \sum_{\mathcal{G} \in \{\mathcal{F}, \mathcal{S}\}} \frac{1}{\theta_{\mathcal{G}}} \sum_{\xi \in \mathcal{G}} \sum_{\alpha \neq N} \\
& \quad \left[\sum_{\beta \neq N} (\mathbf{D}_{\xi, \text{diff}}^{-1})^{\alpha\beta} \mathbf{j}_{\xi, \text{diff}}^{\beta} + \theta_{\mathcal{G}} \nabla_{\mathbf{x}} \left(\frac{L_{\xi}^{\alpha} - L_{\xi}^N}{\theta_{\mathcal{G}}} \right) + (z_{\xi}^{\alpha} - z_{\xi}^N) \nabla_{\mathbf{x}} \varphi \right] \cdot \delta \mathbf{j}_{\xi, \text{diff}}^{\alpha} dv \\
& + \sum_{\mathcal{G} \in \{\mathcal{F}, \mathcal{S}\}} \sum_{\xi \in \mathcal{G}} \sum_{\alpha \neq N} \int_{\Gamma_{\overline{\mathcal{M}}_{\xi}^{\alpha}}} \left[\overline{\mathcal{M}}_{\xi}^{\alpha} - \frac{L_{\xi}^{\alpha} - L_{\xi}^N}{\theta_{\mathcal{G}}} \right] (\delta \mathbf{j}_{\xi, \text{disp}}^{\alpha} + \delta \mathbf{j}_{\xi, \text{diff}}^{\alpha}) \cdot \mathbf{n} da. \tag{114}
\end{aligned}$$

Stationarity with arbitrary normal relative-flux variation on $\Gamma_{\overline{\mathcal{M}}_{\xi}^{\alpha}}$ therefore recovers the prescribed temperature-weighted component-potential difference, $\overline{\mathcal{M}}_{\xi}^{\alpha} = (L_{\xi}^{\alpha} - L_{\xi}^N)/\theta_{\mathcal{G}}$. The component-rate balance is the conservation law (31), which eliminated the dependent accumulation rate before (112); the stationarity condition therefore contains only the independent mechanism-rate and flux variations. Setting each independent variation to zero and inverting the resistances gives the near-equilibrium rate laws. The transport power is unchanged by a common shift of all L_{ξ}^{α} in a phase or by an additive electric gauge. Coleman–Noll will identify the associated chemical potentials and reaction affinity and will show how the transfer-work contribution enters it. Away from local thermal equilibrium, the temperature-weighted sum, with each thermal subsystem weighted by its own temperature, drives the reaction rate:

$$r_{(m)} = -K_{(m)} \left[\left(\sum_{\mathcal{G} \in \{\mathcal{F}, \mathcal{S}\}} \frac{1}{\theta_{\mathcal{G}}} \sum_{\xi \in \mathcal{G}} \sum_{\beta} (\psi_{\xi} + L_{\xi}^{\beta}) \nu_{\xi(m)}^{\beta} \right) \right], \tag{115}$$

$$\mathbf{j}_{\xi, \text{disp}}^{\alpha} = - \sum_{\beta \neq N} \mathbf{D}_{\xi, \text{disp}}^{\alpha\beta} \left[\theta_{\mathcal{G}} \nabla_{\mathbf{x}} \left(\frac{L_{\xi}^{\beta} - L_{\xi}^N}{\theta_{\mathcal{G}}} \right) + (z_{\xi}^{\beta} - z_{\xi}^N) \nabla_{\mathbf{x}} \varphi \right], \quad \xi \in \mathcal{G}, \quad \alpha \neq N, \tag{116}$$

$$\mathbf{j}_{\xi, \text{diff}}^{\alpha} = - \sum_{\beta \neq N} \mathbf{D}_{\xi, \text{diff}}^{\alpha\beta} \left[\theta_{\mathcal{G}} \nabla_{\mathbf{x}} \left(\frac{L_{\xi}^{\beta} - L_{\xi}^N}{\theta_{\mathcal{G}}} \right) + (z_{\xi}^{\beta} - z_{\xi}^N) \nabla_{\mathbf{x}} \varphi \right], \quad \xi \in \mathcal{G}, \quad \alpha \neq N. \tag{117}$$

The two reference-component fluxes follow from (110). The entropy inequality in Section 5 then checks that these Onsager force–rate laws are dissipative and records the positivity assumptions that make the closures admissible.

4.3.2 Saturation-redistribution Onsager variation

The $|\mathcal{F}| - 1$ independent saturation rates are varied at fixed current state. Their contribution is the first line of the global stationarity statement (114). Stationarity gives the force–rate relation

$$\mathcal{L}_f^{\text{sat}} - \mathcal{L}_{f_{\star}}^{\text{sat}} = \sum_{g \neq f_{\star}} \mathcal{T}_{fg} \dot{S}_g, \quad f \neq f_{\star}. \tag{118a}$$

The resistance entries $\mathcal{T}_{fg}$ have units of pressure times time. They may depend on saturation, capillary history, temperature, deformation, and other current pore-structure variables. Their state dependence is held fixed during the Onsager rate variation. The force on the left of (118a) is the

difference of the coefficients used in the d'Alembert work (51). Equation (88) identifies it with the corresponding pressure-force difference. The entropy inequality in Section 5 determines the admissibility conditions on the resistance and verifies that the adopted resistance renders saturation redistribution dissipative.

5 Constitutive models and the entropy inequality

Section 4 supplies the coordinate and field balances and the Onsager rate statements. This section completes the porous-medium constitutive theory for stress, pressure, reaction, transport, and plastic response. It first defines the common solid motion, the fluid and solid thermal subsystems, the constitutive state variables, and the stored energies. The entropy inequality then supplies the reversible stress and pressure relations and restricts the dissipative laws. The electroquasistatic approximation has already been imposed; electromagnetic-wave dynamics are outside the model.

Cauchy stress is tension-positive, so the momentum balance uses $+\nabla_{\mathbf{x}} \cdot \boldsymbol{\sigma}$. Thermodynamic phase pressures, capillary pressures, and the equivalent pore pressure are positive in compression and therefore enter the total stress as negative spherical contributions, opposite to the tension-positive stress. A single prime marks the material stress at fixed intrinsic density, a double prime the fixed-pressure effective stress, and a superscript $+$ the electrical stress contribution. The Coleman–Noll analysis below uses these conventions throughout.

Every phase may contain multiple components. Each solid phase $s \in \mathcal{S}$ is a load-bearing multicomponent solid with mass fractions η_s^α , and all solid phases share the skeleton trajectory

$$\mathbf{x} = \boldsymbol{\chi}(\mathbf{X}, t), \quad \mathbf{F} = \nabla_{\mathbf{X}} \boldsymbol{\chi}, \quad J = \det \mathbf{F}. \quad (119)$$

Adsorbed species, host minerals, hydrate cages, bound water, and hydrate guest molecules move with this common skeleton motion. Their distinct mechanical effects enter through the composition dependence of the free energy, stress-free swelling, thermal expansion, elastic moduli, and plastic flow.

The thermal model distinguishes an equilibrated mobile-fluid subsystem from the solid skeleton,

$$\theta_\xi = \begin{cases} \theta_{\mathcal{F}}, & \xi = f \in \mathcal{F}, \\ \theta_{\mathcal{S}}, & \xi = s \in \mathcal{S}. \end{cases} \quad (120)$$

All mobile phases share $\theta_{\mathcal{F}}$, and all load-bearing solid phases share $\theta_{\mathcal{S}}$. Heat exchange between the subsystems is retained, so either temperature may be larger. Multiphase geothermal models use the same fluid/rock temperature grouping [23], whereas constituent mixture theory permits a separate temperature for every phase [21, 34]. Local thermal equilibrium is the limit $\theta_{\mathcal{F}} = \theta_{\mathcal{S}}$.

Constitutive rates are evaluated in the frame moving with the solid skeleton. For a spatial state field Γ , define the skeleton velocity and the skeleton-following (heavy-dot) rate by

$$\mathbf{v}_{\mathcal{S}} = \left. \frac{\partial \boldsymbol{\chi}}{\partial t} \right|_{\mathbf{X}}, \quad \dot{\Gamma} \equiv \frac{D_{\mathcal{S}} \Gamma}{Dt} = \frac{\partial \Gamma}{\partial t} + \mathbf{v}_{\mathcal{S}} \cdot \nabla_{\mathbf{x}} \Gamma. \quad (121)$$

The heavy dot applies to $\theta_{\mathcal{F}}$, $\theta_{\mathcal{S}}$, each ϕ_ξ , $\bar{\rho}_\xi$, η_ξ^α , the phase thermodynamic potentials, and the solid kinematic fields and internal variables $\mathbf{A}_s$ and $\bar{\mathbf{F}}_s$. The ordinary dot marks a rate following phase ξ , as in the component-insertion rates $\dot{\mathcal{C}}_\xi^\alpha$ and $\dot{c}_\xi^\alpha$. Because all solid phases share the skeleton trajectory, $D_s/Dt = D_{\mathcal{S}}/Dt$, while mobile phases retain their own phase velocities. For any phase field Γ_ξ , the phase-following and skeleton-following rates are related by

$$\dot{\Gamma}_\xi = \dot{\Gamma}_\xi + (\mathbf{v}_\xi - \mathbf{v}_{\mathcal{S}}) \cdot \nabla_{\mathbf{x}} \Gamma_\xi. \quad (122)$$

Thus $\mathbf{v}_\xi - \mathbf{v}_S$ is the bulk velocity of phase ξ relative to the skeleton, while the relative component fluxes describe the motion of components within the phase. This solid-observer convention appears in thermodynamic formulations of multicomponent multiphase poroelastic flow [52, eq. (2)] and is consistent with the solid-observed saturation rate used by Hassanizadeh and Gray [36, eq. (35)].

Summing (29) over α , using the zero-sum relative component flux (34), and rewriting in the skeleton frame gives the phase mass balance

$$\dot{\rho}_\xi + \rho_\xi \nabla_{\mathbf{x}} \cdot \mathbf{v}_S + \nabla_{\mathbf{x}} \cdot [\rho_\xi (\mathbf{v}_\xi - \mathbf{v}_S)] = \sum_{\alpha} \dot{c}_\xi^\alpha. \quad (123)$$

For any phase-specific quantity Γ_ξ , expand $\partial_t(\rho_\xi \Gamma_\xi) + \nabla_{\mathbf{x}} \cdot (\rho_\xi \Gamma_\xi \mathbf{v}_\xi)$ by product rules, substitute (123), and then use (122). This gives the conservative transport identity

$$\begin{aligned} \frac{\partial}{\partial t} (\rho_\xi \Gamma_\xi) + \nabla_{\mathbf{x}} \cdot (\rho_\xi \Gamma_\xi \mathbf{v}_\xi) &= \frac{D_S}{Dt} (\rho_\xi \Gamma_\xi) + \rho_\xi \Gamma_\xi \nabla_{\mathbf{x}} \cdot \mathbf{v}_S + \nabla_{\mathbf{x}} \cdot [\rho_\xi \Gamma_\xi (\mathbf{v}_\xi - \mathbf{v}_S)] \\ &= \rho_\xi \dot{\Gamma}_\xi + \Gamma_\xi \sum_{\alpha} \dot{c}_\xi^\alpha + \rho_\xi (\mathbf{v}_\xi - \mathbf{v}_S) \cdot \nabla_{\mathbf{x}} \Gamma_\xi \\ &= \rho_\xi \dot{\Gamma}_\xi + \Gamma_\xi \sum_{\alpha} \dot{c}_\xi^\alpha. \end{aligned} \quad (124)$$

The source term $\Gamma_\xi \sum_{\alpha} \dot{c}_\xi^\alpha$ is the mass-transfer source from (123), scaled by Γ_ξ . The divergence term in (124) measures transport through a control surface moving with the skeleton. For a solid phase, $\mathbf{v}_\xi = \mathbf{v}_S$, so this relative-transport contribution is zero. For a mobile phase, $\mathbf{v}_\xi \neq \mathbf{v}_S$, so the term is generally nonzero.

In the same observer frame, the rate of the pointwise volume-fraction constraint is

$$\dot{\phi}_\xi \equiv \frac{D_S \phi_\xi}{Dt} = \frac{\partial \phi_\xi}{\partial t} + \mathbf{v}_S \cdot \nabla_{\mathbf{x}} \phi_\xi, \quad \sum_{\xi} \dot{\phi}_\xi = 0. \quad (125)$$

Each volume fraction may change, but the rates must sum to zero. The skeleton-following rates above apply to phase-indexed fields, whereas several fields in the formulation are shared by the mixture as a whole and take a single value. The mechanism rate $r_{(m)}$ is one local process rate common to all phases participating in mechanism (m) . The electric potential φ is one Eulerian field for the mixture. The transfer multiplier τ is likewise one scalar field shared by all phases, and its material rate $D_\xi \tau / Dt$ is evaluated along the phase trajectory in the component-insertion relation.

5.1 Solid kinematics and state variables

The Coleman–Noll procedure in §5.2 requires the solid kinematic fields, their rate relations, and the constitutive state arguments. This subsection defines each. Extending Drumheller’s distension/true-deformation split for reacting mixtures [21] and its porous-media form in Foster et al. [24], the solid kinematic split is phase-specific but uses the common skeleton deformation,

$$\mathbf{F} = \mathbf{A}_s \bar{\mathbf{F}}_s, \quad J = a_s \bar{J}_s, \quad a_s = \det \mathbf{A}_s, \quad \bar{J}_s = \det \bar{\mathbf{F}}_s, \quad s \in \mathcal{S}. \quad (126)$$

The distension tensor $\mathbf{A}_s$ maps the true deformation of solid phase s into the common skeleton deformation. It represents the pore-space allocation and packing needed to accommodate swelling and reaction-induced volume change between phases. Extending Drumheller’s elastic–plastic treatment of true deformation and distension [21], the elastic, plastic, and stress-free factors are

$$\mathbf{A}_s = \mathbf{A}_s^e \mathbf{A}_s^p \mathbf{A}_s^0, \quad s \in \mathcal{S}, \quad (127a)$$

$$\bar{\mathbf{F}}_s = \bar{\mathbf{F}}_s^e \bar{\mathbf{F}}_s^p \bar{\mathbf{F}}_s^0, \quad s \in \mathcal{S}. \quad (127b)$$

Here $\mathbf{A}_s^e$ and $\bar{\mathbf{F}}_s^e$ are elastic factors, $\mathbf{A}_s^p$ and $\bar{\mathbf{F}}_s^p$ are plastic internal variables, and $\mathbf{A}_s^0$ and $\bar{\mathbf{F}}_s^0$ are reversible stress-free maps that can include temperature and solid-composition effects,

$$\mathbf{A}_s^0 = \mathbf{A}_s^0(\theta_S, \{\eta_s^\alpha\}), \quad \bar{\mathbf{F}}_s^0 = \bar{\mathbf{F}}_s^0(\theta_S, \{\eta_s^\alpha\}), \quad s \in \mathcal{S}. \quad (128)$$

The stress-free maps capture composition- and temperature-driven changes of the stress-free state, including adsorption swelling and shrinkage, hydrate-cage volume changes, and composition-dependent thermal expansion. A shared θ_S remains compatible with phase-specific thermal expansion: each phase retains its own functions $\mathbf{A}_s^0$ and $\bar{\mathbf{F}}_s^0$, and therefore its own derivative with respect to θ_S . A plastic internal state vector $\mathbf{p}_s$ per solid phase augments these plastic internal variables; its evolution (207c) carries hardening, softening, and rate dependence in the plastic closures of §5.4.5. Thermo-poroelastic models make the same physical distinction by assigning pore volume, fluid, and grain thermal expansions separately [49, 28, 27]. As in standard finite-strain multiplicative plasticity [54, 53] and Drummheller's mixture treatment [21], the true-plastic flow is assumed isochoric,

$$\det \bar{\mathbf{F}}_s^p = 1, \quad \text{tr} \left[\dot{\bar{\mathbf{F}}}_s^p (\bar{\mathbf{F}}_s^p)^{-1} \right] = 0, \quad s \in \mathcal{S}. \quad (129)$$

The dependent elastic arguments are

$$\mathbf{A}_s^e = \mathbf{A}_s(\mathbf{A}_s^0)^{-1}(\mathbf{A}_s^p)^{-1}, \quad \bar{\mathbf{F}}_s^e = \bar{\mathbf{F}}_s(\bar{\mathbf{F}}_s^0)^{-1}(\bar{\mathbf{F}}_s^p)^{-1}, \quad s \in \mathcal{S}. \quad (130)$$

The solid distension rate $\dot{a}_s/a_s$ enters the Coleman–Noll dissipation. The solid-phase mass-balance relations supply this rate. Summing the component material measure (32) over α for the solid phase gives

$$J\phi_s\bar{\rho}_s = \phi_{s0}\bar{\rho}_{s0} + \mathcal{C}_s, \quad \mathcal{C}_s = \sum_{\alpha} \mathcal{C}_s^{\alpha}, \quad s \in \mathcal{S}. \quad (131)$$

With true local conservation in the solid material,

$$\bar{J}_s\bar{\rho}_s = \bar{\rho}_{s0}, \quad s \in \mathcal{S}, \quad (132)$$

(131) becomes

$$a_s\phi_s\bar{\rho}_{s0} = \phi_{s0}\bar{\rho}_{s0} + \mathcal{C}_s, \quad s \in \mathcal{S}. \quad (133)$$

The rate form follows by taking the natural logarithm of $J = a_s\bar{J}_s$ and applying the solid-following material derivative, using the kinematic identity $\dot{J}/J = \nabla_{\mathbf{x}} \cdot \mathbf{v}_S$ and true mass conservation (132),

$$\boxed{\frac{\dot{a}_s}{a_s} = \nabla_{\mathbf{x}} \cdot \mathbf{v}_S + \frac{\dot{\bar{\rho}}_s}{\bar{\rho}_s}, \quad s \in \mathcal{S}.} \quad (134)$$

The entropy inequality is exploited with all other constitutive arguments held fixed. The nonelectrical state sets are

$$\mathcal{X}_s = \{\bar{\mathbf{F}}_s^e, \mathbf{A}_s^e, \bar{\rho}_s, \{\eta_s^\alpha\}, \theta_S\}, \quad \mathcal{X}_f = \{\bar{\rho}_f, \{\eta_f^\alpha\}, \theta_{\mathcal{F}}\}, \quad f \in \mathcal{F}, \quad s \in \mathcal{S}. \quad (135)$$

The interfacial state set is

$$\mathcal{X}_\gamma = \{\{S_f\}_{f \in \mathcal{F}}, \mathbf{h}, \theta_{\mathcal{F}}\}, \quad \mathbf{h} \in \mathbb{R}^{N_h}. \quad (136)$$

The phase energies use $\mathcal{X}_f$ and $\mathcal{X}_s$, while $\mathcal{X}_\gamma$ controls the shared pore-scale interfacial storage and therefore the stored capillary-pressure contribution. The capillary-history variables are therefore internal variables of the fluid subsystem rather than additional composition coordinates of an

individual fluid phase. The saturation rates $\dot{S}_f$ are process rates and are not members of $\mathcal{X}_\gamma$. The resistance $\mathcal{T}$ belongs to the dissipative closure, not to the stored energy. It may depend on the current constitutive and pore-structure state, but it is held fixed while the instantaneous saturation rates are varied by Onsager stationarity.

The intrinsic density rate needed in the Coleman–Noll analysis follows from (127b), isochoric plastic flow, and the composition-dependent stress-free true deformation. In the derivatives below, the subscript $\mathcal{X}_s$ indicates that all other members of the solid state set are held fixed:

$$\begin{aligned} \frac{\dot{\bar{\rho}}_s}{\bar{\rho}_s} = & -\text{tr} \left[\dot{\bar{\mathbf{F}}}_s^e (\bar{\mathbf{F}}_s^e)^{-1} \right] \\ & - \text{tr} \left[\left(\frac{\partial \bar{\mathbf{F}}_s^0}{\partial \theta_S} \Big|_{\mathcal{X}_s} \dot{\theta}_S + \sum_{\beta} \frac{\partial \bar{\mathbf{F}}_s^0}{\partial \eta_s^\beta} \Big|_{\mathcal{X}_s} \dot{\eta}_s^\beta \right) (\bar{\mathbf{F}}_s^0)^{-1} \right], \quad s \in \mathcal{S}. \end{aligned} \quad (137)$$

The Helmholtz free energies that supply the stored-energy terms are

$$\begin{aligned} \psi_f &= \psi_f(\bar{\rho}_f, \{\eta_f^\alpha\}, \theta_{\mathcal{F}}), & f \in \mathcal{F}, \\ \psi_s &= \psi_s(\bar{\mathbf{F}}_s^e, \mathbf{A}_s^e, \bar{\rho}_s, \{\eta_s^\alpha\}, \theta_{\mathcal{S}}), & s \in \mathcal{S}. \end{aligned} \quad (138)$$

The same held-fixed convention applies to derivatives annotated by $\mathcal{X}_f$. Because the mass fractions in each phase sum to one, only $N - 1$ composition rates are independent. The reversible composition relations below are therefore written as differences from component N .

Electrical storage is represented by the phase electric-enthalpy densities ω_ξ^+ introduced in §4. Because ω_ξ^+ is measured per current phase volume, phase ξ contributes $\phi_\xi \omega_\xi^+$ per current mixture volume. The interfacial Helmholtz energy has a different normalization: γ is measured per current fluid volume and contributes $\phi\gamma$ to the mixture. All phases experience the same electric field, but each phase may have a different dielectric response. The phase and mixture electric displacements $\mathbf{d}_\xi$ and $\mathbf{d}$ are defined in (73) with the minus sign characteristic of the electric-enthalpy representation [19]. As stated there, $\mathbf{E}$ is the electrical state variable and $\mathbf{d}_\xi$ is obtained by differentiating ω_ξ^+ .

For a fluid phase, $\omega_f^+ = \omega_f^+(\mathbf{E}, \bar{\rho}_f, \{\eta_f^\alpha\}, \theta_{\mathcal{F}})$. Its density, composition, and temperature dependence permits the scalar effective permittivity and dielectric pressure to change with fluid state. Such changes are relevant in porous rocks: the dielectric response of saturated sandstone depends on porosity and pore-fluid salinity, while measurements on fluid-saturated artificial shales show dependence on clay content and pore-fluid salinity and cation composition [40, 4]. The solid phase has the analogous dependence on the field, intrinsic density, solid composition, and $\theta_{\mathcal{S}}$. These dependencies contribute to the solid dielectric pressure and to the density, composition, and temperature coefficients collected in the entropy inequality.

As shown in Appendix A, objectivity of a potential with only one spatial-vector electrical argument makes ω_ξ^+ even in $\mathbf{E}$ and makes $\mathbf{d}_\xi$ parallel to $\mathbf{E}$. The present electrical response is therefore isotropic and excludes permanent polarization at zero field, bedding-directed dielectric anisotropy, and independent dielectric relaxation. Bedding-direction effects would require an additional objective structural argument and corresponding stress and torque terms. Electrical coupling retained here includes Maxwell stress, phase equilibrium, electrochemical transport, and electro-osmotic cross-coupling. This choice is consistent with laboratory water-driven hydraulic-fracture self-potential signals in saturated granite for which the response was dominated by electrokinetic coupling [46]. Plastic evolution depends on the phase material stress and composition, so electrical loading affects plastic response through the coupled Maxwell momentum solution.

The phase Maxwell stress $\boldsymbol{\sigma}_\xi^+$, defined in (75), contributes to the phase momentum balance through the total reversible stress $\boldsymbol{\sigma}_\xi^{'+}$. The density, composition, and temperature derivatives of ω_ξ^+

enter the corresponding coefficients in the entropy inequality. This separation assigns each electrical power contribution to a single governing equation.

The derivation first allows a general composition-dependent phase Helmholtz energy ψ_ξ . The later additive specialization in §5.8 is optional and resolves the solid energy into component contributions without changing the common solid motion.

5.2 Coleman–Noll procedure

The Coleman–Noll procedure tests the constitutive assumptions against the local entropy inequality. The balance laws and kinematic constraints restrict the admissible rates; after those restrictions are imposed, coefficients of the remaining independent reversible rates must vanish and the residual force–rate products must be nonnegative [14].

The three variational or thermodynamic steps used in the manuscript have different purposes. Hamilton–d’Alembert stationarity supplies the phase coordinate equations and multiplier relations, including any d’Alembert work specified for a dissipative force. The Onsager construction then supplies near-equilibrium choices for saturation redistribution, reaction, and relative-transport kinetics. Finally, Coleman–Noll determines which constitutive stresses, pressures, entropies, and force–rate products are compatible with the entropy inequality, and therefore which of the Onsager dissipative laws are admissible. Relations obtained independently from the stored energy variation and the entropy inequality must agree because both use the same energies and constraints.

The Coleman–Noll exploitation uses the absolute component potential defined by the constituent-mass derivative of the phase material and electric enthalpy storage at fixed phase volume fraction,

$$\hat{\mu}_\xi^\alpha \equiv \left. \frac{\partial (\rho_\xi \psi_\xi + \phi_\xi \omega_\xi^+)}{\partial \rho_\xi^\alpha} \right|_{\phi_\xi, \theta_\xi, \mathbf{E}, \{\rho_\xi^\beta\}_{\beta \neq \alpha}, \text{kinematic and internal fields}}, \quad \xi \in \mathcal{G}. \quad (139)$$

The corresponding electrochemical potential is

$$\mu_\xi^\alpha = \hat{\mu}_\xi^\alpha + z_\xi^\alpha \varphi. \quad (140)$$

Here φ has units of energy per charge and z_ξ^α has units of charge per component mass. These are constitutive state quantities, not variational multipliers. For a solid phase, the kinematic and internal fields held fixed in (139) are $\mathbf{A}_s$, $\bar{\mathbf{F}}_s$, $\mathbf{A}_s^p$, and $\bar{\mathbf{F}}_s^p$. For a fluid phase, the same definition reduces to the fixed-volume Helmholtz constituent potential, augmented by the composition and density dependence of ω_f^+ .

Let e_ξ denote the specific internal energy of phase ξ , and let $\mathfrak{s}_\xi$ denote its specific entropy. For fluid phases,

$$e_f = \psi_f + \theta_{\mathcal{F}} \mathfrak{s}_f, \quad \psi_f = \psi_f(\bar{\rho}_f, \{\eta_f^\alpha\}, \theta_{\mathcal{F}}), \quad f \in \mathcal{F}. \quad (141)$$

For multicomponent solid phases,

$$e_s = \psi_s + \theta_{\mathcal{S}} \mathfrak{s}_s, \quad \psi_s = \psi_s(\bar{\mathbf{F}}_s^e, \mathbf{A}_s^e, \bar{\rho}_s, \{\eta_s^\alpha\}, \theta_{\mathcal{S}}), \quad s \in \mathcal{S}. \quad (142)$$

The unresolved interface carries the corresponding caloric quantities per current fluid-subsystem volume. Let u_γ denote its internal-energy density and let $\mathfrak{s}_\gamma$ denote its entropy density. Their Legendre relation is

$$u_\gamma = \gamma + \theta_{\mathcal{F}} \mathfrak{s}_\gamma. \quad (143)$$

Thus ϕu_γ and $\phi \mathfrak{s}_\gamma$ are the corresponding internal-energy and entropy densities per current mixture volume. They belong to the fluid thermal subsystem and follow the skeleton control volume. The phase quantities e_f and $\mathfrak{s}_f$ contain only the caloric storage assigned to phase f .

The free-energy rates are

$$\sum_{f \in \mathcal{F}} \rho_f \dot{\psi}_f = \sum_{f \in \mathcal{F}} \rho_f \left(\left. \frac{\partial \psi_f}{\partial \bar{\rho}_f} \right|_{\mathcal{X}_f} \dot{\bar{\rho}}_f + \sum_{\beta} \left. \frac{\partial \psi_f}{\partial \eta_f^\beta} \right|_{\mathcal{X}_f} \dot{\eta}_f^\beta + \left. \frac{\partial \psi_f}{\partial \theta_{\mathcal{F}}} \right|_{\mathcal{X}_f} \dot{\theta}_{\mathcal{F}} \right), \quad (144)$$

$$\begin{aligned} \sum_{s \in \mathcal{S}} \rho_s \dot{\psi}_s = \sum_{s \in \mathcal{S}} \rho_s & \left[\left. \frac{\partial \psi_s}{\partial \mathbf{F}_s^e} \right|_{\mathcal{X}_s} : \dot{\mathbf{F}}_s^e + \left. \frac{\partial \psi_s}{\partial \mathbf{A}_s^e} \right|_{\mathcal{X}_s} : \dot{\mathbf{A}}_s^e \right. \\ & \left. + \left. \frac{\partial \psi_s}{\partial \bar{\rho}_s} \right|_{\mathcal{X}_s} \dot{\bar{\rho}}_s + \sum_{\beta} \left. \frac{\partial \psi_s}{\partial \eta_s^\beta} \right|_{\mathcal{X}_s} \dot{\eta}_s^\beta + \left. \frac{\partial \psi_s}{\partial \theta_{\mathcal{S}}} \right|_{\mathcal{X}_s} \dot{\theta}_{\mathcal{S}} \right]. \end{aligned} \quad (145)$$

The fluid Helmholtz energy has no elastic-deformation argument, so its material elastic stress is

$$\boldsymbol{\sigma}'_f = \mathbf{0}, \quad f \in \mathcal{F}. \quad (146)$$

Pressure is retained separately through the intrinsic-density coefficient. The remaining reversible stress in the fluid momentum equation is therefore the Maxwell stress,

$$\boldsymbol{\sigma}_f^+ = \boldsymbol{\sigma}_f^+, \quad f \in \mathcal{F}. \quad (147)$$

The interfacial Helmholtz density γ , like u_γ , is measured per current fluid-subsystem volume and has the state set (136). Temperature dependence permits the stored capillary pressure to vary with fluid temperature, as in the nonisothermal porous-media formulation of Hassanizadeh and Gray [36]. The internal-variable construction makes the stored pressure contribution depend on the drainage–imbibition path [57]. The mixture stores $\phi\gamma$ per current volume. Differentiating this quantity along the skeleton trajectory and using the interfacial potentials γ_f from (70) gives

$$\frac{D_S}{Dt} [\phi\gamma] = \sum_{f \in \mathcal{F}} \gamma_f \dot{\phi}_f + \phi \left. \frac{\partial \gamma}{\partial \mathbf{h}} \right|_{\{S_f\}_{f \in \mathcal{F}, \theta_{\mathcal{F}}}} \cdot \dot{\mathbf{h}} + \phi \left. \frac{\partial \gamma}{\partial \theta_{\mathcal{F}}} \right|_{\{S_f\}_{f \in \mathcal{F}, \mathbf{h}}} \dot{\theta}_{\mathcal{F}}. \quad (148)$$

This term is the interfacial Helmholtz-storage rate obtained after the fluid-subsystem energy and entropy balances are combined through (143). The first and second laws separately carry $D_S(\phi u_\gamma)/Dt$ and $D_S(\phi \mathfrak{s}_\gamma)/Dt$. The history rate records the change in interfacial storage as the pore-scale fluid arrangement changes; its dissipative restriction is derived below. The density $\phi\gamma$ represents unresolved interfaces; no sharp interface or interface velocity is introduced. A sharp-interface theory would instead require separate surface balances of energy and entropy [20, 9].

The material-source convention follows Drmheller’s constituent balance and adopts local-equilibrium insertion: mass inserted into or removed from phase ξ carries the recipient-phase specific internal energy e_ξ and specific entropy $\mathfrak{s}_\xi$. Isolating the source-carried parts of the corresponding conservative storage rates gives

$$\left[\frac{D_S}{Dt} (\rho_\xi e_\xi) + \rho_\xi e_\xi \nabla_{\mathbf{x}} \cdot \mathbf{v}_S + \nabla_{\mathbf{x}} \cdot [\rho_\xi e_\xi (\mathbf{v}_\xi - \mathbf{v}_S)] \right] \Big|_{\dot{e}_\xi=0} = e_\xi \sum_{\alpha} \dot{c}_\xi^\alpha, \quad (149a)$$

$$\left[\frac{D_S}{Dt} (\rho_\xi \mathfrak{s}_\xi) + \rho_\xi \mathfrak{s}_\xi \nabla_{\mathbf{x}} \cdot \mathbf{v}_S + \nabla_{\mathbf{x}} \cdot [\rho_\xi \mathfrak{s}_\xi (\mathbf{v}_\xi - \mathbf{v}_S)] \right] \Big|_{\dot{\mathfrak{s}}_\xi=0} = \mathfrak{s}_\xi \sum_{\alpha} \dot{c}_\xi^\alpha. \quad (149b)$$

$\mathfrak{s}_\xi$, the d’Alembert conversion power (51) uses $\psi_\xi + L_\xi^\alpha$, where ψ_ξ is the recipient-phase Helmholtz storage and L_ξ^α is the specific generalized transfer-work potential; $-L_\xi^\alpha \dot{c}_\xi^\alpha$ is the corresponding transfer-work rate. A non-equilibrium source state would require additional source energy and

entropy data and a corresponding entropy-production restriction; it is outside the adopted closure. Equivalently, setting $\Gamma_\xi = e_\xi$ in (124) produces the phase-following storage $\rho_\xi \dot{e}_\xi + e_\xi \sum_\alpha \dot{c}_\xi^\alpha$. The present convention therefore transports internal energy, together with pressure and other constraint powers kept explicit on the right-hand side, with bulk phase mass. Let $\mathbf{L}_\xi = \nabla_{\mathbf{x}} \mathbf{v}_\xi$ be the phase velocity gradient, $\mathbf{q}_\xi$ the total nonadvective material-energy flux assigned to phase ξ , $\rho_\xi r_\xi$ the external heat supply, and $\rho_\xi e_\xi^{\text{int}}$ the internal-energy supply from the other phases, all per unit current mixture volume where appropriate. Thus $\mathbf{q}_\xi$ collects the gauge-invariant nonadvective material-energy transport that remains after bulk phase convection has been separated; it accommodates conduction, interdiffusion energy transport, and any other nonadvective contribution. A charged component flux relative to its phase also receives the electrical work $z_\xi^\alpha \mathbf{j}_\xi^\alpha \cdot \mathbf{E}$. This work is written directly in terms of the electric field so that both the energy balance and the nonisothermal transport force are independent of the arbitrary zero of φ . The uncoupled Fourier specialization adopted below neglects Dufour and other heat–component-transport cross effects. The source-carried phase energy and entropy exclude the interfacial quantities u_γ and $\mathfrak{s}_\gamma$. Conversion changes the interfacial storage through its induced saturation, capillary-history, and temperature rates.

One energy balance is assigned to the fluid thermal subsystem and one to the solid thermal subsystem, following the constituent structure of Drumheller and Bedford [22]. Conversion work follows the generalized form of Drumheller [21, eq. (50)]. The fluid balance contains the averaged interfacial energy, and the solid balance contains the solid-phase energies. Storage rates are evaluated in the skeleton frame (121), as in the solid-following balances of Seguin and Walkington [52, eqs. (10)–(12)]. Consistently with those balances, bulk phase motion transports internal energy through the skeleton control surface and transports entropy in the entropy inequality below. These bulk convective fluxes are distinct from the nonadvective energy flux $\mathbf{q}_\xi$ and from the component-relative molecular-diffusion and mechanical-dispersion fluxes. Internal energy exchanged between phases cancels by mechanism. The later closures impose equal-and-opposite ordinary heat and reaction-associated transfers; the mechanical contribution cancels against interphase momentum power only after the subsystem balances are combined with the phase kinetic-energy balances.

Electrical storage is written in the electric-enthalpy representation [45]. Phase ξ contributes $\phi_\xi \omega_\xi^+$, while the shared interfacial internal energy ϕu_γ appears only in the fluid-subsystem balance. Expanding the electric-enthalpy rate exposes material-state, Maxwell mechanical-power, and common electric-potential-rate contributions. In particular, $\mathbf{d}_\xi = -\partial \omega_\xi^+ / \partial \mathbf{E}$ makes $-\phi_\xi \mathbf{d}_\xi \cdot \dot{\mathbf{E}}$ the constitutive electric-field-rate power; current-volume transport separates its geometric part into $\sigma_\xi^+ : \mathbf{L}_\xi$ and leaves $\phi_\xi \mathbf{d}_\xi \cdot \nabla_{\mathbf{x}} \dot{\varphi}$ as the shared field-coordinate part. The relative material flux in the energy balance written below therefore carries $\rho_\xi e_\xi$; the electrostatic field energy is Eulerian storage whose boundary power is supplied by the global identity below, not an additional material advective flux.

The field rates $\dot{\mathbf{E}}$ and $\dot{\varphi}$ are evaluated in the skeleton frame. The electric field and potential are spatial fields with no reference configuration; the skeleton frame is chosen because the free charge coupled to them is carried by the component material measures, and the balances below are written on skeleton-moving control volumes, so the skeleton velocity supplies the convective part of the field rates.

The last contribution cannot be assigned independently to the fluid and solid thermal subsystems because φ is one shared field. Summing it over all phases and using Gauss' law gives the global electrostatic power identity

$$\begin{aligned} \sum_{g \in \{\mathcal{F}, \mathcal{S}\}} \sum_{\xi \in \mathcal{G}} \phi_\xi \mathbf{d}_\xi \cdot \nabla_{\mathbf{x}} \dot{\varphi} &= \mathbf{d} \cdot \nabla_{\mathbf{x}} \dot{\varphi} \\ &= \nabla_{\mathbf{x}} \cdot (\dot{\varphi} \mathbf{d}) - \varrho \dot{\varphi}. \end{aligned} \quad (150)$$

The bulk term $-\varrho\dot{\varphi}$ is the rate form of the free-charge source work in (51), and the divergence gives the electrical boundary power. In particular, its flux is $\dot{\varphi}\bar{q}$ on $\Gamma_{\bar{q}}$. Equation (150) is an entropy-free field-power identity that separates the shared electric-potential-rate work from the two thermal-subsystem balances. It is applied globally before either thermal-subsystem balance is divided by its temperature. Here ϱ is the material-carried charge density defined by (39).

The two thermal-subsystem balances therefore retain the material-state rate of each phase electric enthalpy at fixed $\mathbf{E}$ and its Maxwell mechanical power, while the shared electric-potential-rate term is carried by (150). The resulting balance for $\mathcal{G} \in \{\mathcal{F}, \mathcal{S}\}$ is

$$\begin{aligned}
& \sum_{\xi \in \mathcal{G}} \left[\frac{D\mathcal{S}}{Dt} (\rho_{\xi} e_{\xi}) + \rho_{\xi} e_{\xi} \nabla_{\mathbf{x}} \cdot \mathbf{v}_{\mathcal{S}} + \nabla_{\mathbf{x}} \cdot [\rho_{\xi} e_{\xi} (\mathbf{v}_{\xi} - \mathbf{v}_{\mathcal{S}})] + \omega_{\xi}^{+} \dot{\phi}_{\xi} + \phi_{\xi} \frac{\partial \omega_{\xi}^{+}}{\partial \bar{\rho}_{\xi}} \Big|_{\mathcal{X}_{\xi}, \mathbf{E}} \dot{\bar{\rho}}_{\xi} \right. \\
& \quad \left. + \phi_{\xi} \sum_{\alpha} \frac{\partial \omega_{\xi}^{+}}{\partial \eta_{\xi}^{\alpha}} \Big|_{\mathcal{X}_{\xi}, \mathbf{E}} \dot{\eta}_{\xi}^{\alpha} + \phi_{\xi} \frac{\partial \omega_{\xi}^{+}}{\partial \theta_{\mathcal{G}}} \Big|_{\mathcal{X}_{\xi}, \mathbf{E}} \dot{\theta}_{\mathcal{G}} + \boldsymbol{\sigma}_{\xi}^{+} : \mathbf{L}_{\xi} \right] \\
& \quad + \delta_{\mathcal{G}\mathcal{F}} \frac{D\mathcal{S}}{Dt} (\phi u_{\gamma}) \\
& = \sum_{\xi \in \mathcal{G}} \left[\boldsymbol{\sigma}_{\xi}^{\prime+} : \mathbf{L}_{\xi} + \phi_{\xi} \bar{p}_{\xi} \frac{\dot{\bar{\rho}}_{\xi}}{\bar{\rho}_{\xi}} + \bar{p}_{\xi} \dot{\phi}_{\xi} + \lambda \dot{\phi}_{\xi} + \sum_{\alpha} \frac{\pi_{\xi}^{\alpha}}{\eta_{\xi}^{\alpha}} \dot{\eta}_{\xi}^{\alpha} - \sum_{\alpha} L_{\xi}^{\alpha} \dot{c}_{\xi}^{\alpha} \right. \\
& \quad \left. - \nabla_{\mathbf{x}} \cdot \mathbf{q}_{\xi} + \sum_{\alpha} z_{\xi}^{\alpha} (\mathbf{j}_{\xi, \text{disp}}^{\alpha} + \mathbf{j}_{\xi, \text{diff}}^{\alpha}) \cdot \mathbf{E} + \rho_{\xi} r_{\xi} + \rho_{\xi} e_{\xi}^{\text{int}} \right].
\end{aligned} \tag{151}$$

Here $\delta_{\mathcal{G}\mathcal{F}}$ is the Kronecker selector, $\delta_{\mathcal{G}\mathcal{F}} = 1$ when $\mathcal{G} = \mathcal{F}$ and zero otherwise, so the interfacial storage term enters only the fluid balance. The symbol δ is also used for variational displacements; the $\mathcal{G}\mathcal{F}$ subscript always distinguishes the selector. Also $e_{\xi} = \psi_{\xi} + \theta_{\xi} \mathfrak{s}_{\xi}$. By (124), the first three terms in each phase contribution simplify to $\rho_{\xi} \dot{e}_{\xi} + e_{\xi} \sum_{\alpha} \dot{c}_{\xi}^{\alpha}$; the source-carried energy convention is exact. The material-plus-field first law consists of the two instances of (151), the phase kinetic-energy balances obtained from momentum balance, and the global field-power identity (150). The field-power identity carries the shared power $\mathbf{d} \cdot \nabla_{\mathbf{x}} \dot{\varphi}$ and its source $-\varrho \dot{\varphi}$ outside the thermal balances, so each subsystem balance uses only its own temperature. For $\mathcal{G} = \mathcal{F}$, the final storage term on the left is the skeleton-following interfacial internal-energy rate. The unresolved-interface specialization assigns it no separate interface-relative advective flux. The electrical transport term in (151) is the work of the electric field on component charge transported relative to phase ξ . It is not a potential-energy flux. Both $\mathbf{E} = -\nabla_{\mathbf{x}} \varphi$ and $\mathbf{q}_{\xi}$ are unchanged under $\varphi \mapsto \varphi + c_{\varphi}(t)$, so each subsystem balance is gauge invariant term by term. Phase-advective electrical work belongs to the Maxwell mechanical and global field-power block; the term displayed here is only the additional work on charge moving relative to that phase and therefore does not duplicate the phase mechanical power. The direct observer-and-gauge test for this term is

$$\begin{aligned}
\sum_{\alpha} z_{\xi}^{\alpha} \left((\mathbf{j}_{\xi, \text{disp}}^{\alpha})^{\star} + (\mathbf{j}_{\xi, \text{diff}}^{\alpha})^{\star} \right) \cdot \mathbf{E}^{\star} &= \left[\mathbf{Q} \sum_{\alpha} z_{\xi}^{\alpha} (\mathbf{j}_{\xi, \text{disp}}^{\alpha} + \mathbf{j}_{\xi, \text{diff}}^{\alpha}) \right] \cdot \mathbf{Q}\mathbf{E} \\
&= \sum_{\alpha} z_{\xi}^{\alpha} (\mathbf{j}_{\xi, \text{disp}}^{\alpha} + \mathbf{j}_{\xi, \text{diff}}^{\alpha}) \cdot \mathbf{E}.
\end{aligned} \tag{152}$$

The additive gauge function does not appear because $\mathbf{E}^{\star} = -\nabla_{\mathbf{x}^{\star}} \varphi^{\star} = \mathbf{Q}\mathbf{E}$. The other occurrences of φ in the material-plus-field first law are only through $\mathbf{E}$, $\dot{\mathbf{E}}$, and the globally closed identity (150). Thus the complete energy equation, not only its final constitutive reduction, passes the gauge test. When the two subsystem equations are summed, the relative material-energy transport

remains $\sum_{\xi} \nabla_{\mathbf{x}} \cdot [\rho_{\xi} e_{\xi} (\mathbf{v}_{\xi} - \mathbf{v}_S)]$, as it must in a skeleton-moving control volume. Adding the phase kinetic-energy balances makes the mechanical interaction contribution cancel by its later equal-and-opposite allocation; ordinary heat and reaction-associated transfers cancel in the same way. In the nonporous single-phase limit the phase follows the skeleton, so the relative flux vanishes and the limit derived below is unchanged. Thus the observer transformation introduces neither an artificial source nor a loss of total energy.

The multiplier power $\lambda \sum_{\xi \in \mathcal{G}} \dot{\phi}_{\xi}$ transfers reversible work between the two thermal subsystems. It vanishes only after the subsystem balances are summed, because $\sum_{\xi} \dot{\phi}_{\xi} = 0$. Retaining this power in each subsystem balance is necessary when $\theta_{\mathcal{F}} \neq \theta_S$, since the two balances are divided by different temperatures in the entropy inequality.

The mechanical power uses the total reversible stress $\sigma'_{\xi}{}^{+}$. The electric-enthalpy rate contains the corresponding Maxwell power explicitly; subtracting it from the total mechanical power leaves the material stress power used in the constitutive restrictions. The electric-potential-gradient, bulk-source, and boundary-power terms have already been separated through (150); they are not included in either local thermal entropy supply.

The connection with a conventional thermo-electroelastic energy balance is most transparent in the nonporous, single-phase limit. Let $\mathcal{G} = \{\xi\}$, set $\phi_{\xi} = 1$, suppress conversion, composition, interfacial, and interphase-exchange terms, and let the skeleton observer follow phase ξ . Phase mass conservation then gives $\dot{\rho}_{\xi}/\rho_{\xi} = -\text{tr } \mathbf{L}_{\xi}$. Using $\mathbf{E} = -\nabla_{\mathbf{x}}\varphi$, $\dot{\mathbf{E}} = -\nabla_{\mathbf{x}}\dot{\varphi} - \mathbf{L}_{\xi}^T \mathbf{E}$, and (75), the electrical terms in (151) and (150) combine into the material-volume rate of ω_{ξ}^{+} , and the balance reduces to

$$\begin{aligned} \rho_{\xi} \frac{D_{\xi}}{Dt} \left(e_{\xi} + \frac{\omega_{\xi}^{+}}{\rho_{\xi}} \right) &= \rho_{\xi} \dot{e}_{\xi} + \dot{\omega}_{\xi}^{+} + \omega_{\xi}^{+} \text{tr } \mathbf{L}_{\xi} \\ &= \left(\sigma'_{\xi}{}^{+} - \bar{p}_{\xi} \mathbf{I} \right) : \mathbf{L}_{\xi} - \nabla_{\mathbf{x}} \cdot \mathbf{q}_{\xi} + \nabla_{\mathbf{x}} \cdot (\dot{\varphi} \mathbf{d}) - \varrho \dot{\varphi} + \rho_{\xi} r_{\xi}. \end{aligned} \quad (153)$$

Reference [45] instead writes its equation (12) for the material internal energy ε , with electrical power $\mathbf{E}^M \cdot \rho \dot{\boldsymbol{\pi}}$, where $\boldsymbol{\pi} = \mathbf{P}/\rho$ is the polarization per unit mass. Combining that balance with the electric-work term in its Helmholtz free-energy definition, equation (16), gives

$$\rho \frac{D}{Dt} \left(\varepsilon - \mathbf{E}^M \cdot \boldsymbol{\pi} \right) = \boldsymbol{\tau} : \mathbf{L} - \nabla_{\mathbf{x}} \cdot \mathbf{q} - \mathbf{P} \cdot \dot{\mathbf{E}}^M + \rho r. \quad (154)$$

Equations (153) and (154) are equivalent descriptions of the same single-phase thermo-electroelastic energy balance under the energy-density and stress identifications derived in Appendix C. Reference [45] writes the polarization work $-\mathbf{P} \cdot \dot{\mathbf{E}}^M$ on the right-hand side and treats polarization as a state variable. The present formulation instead uses the total electric displacement $\mathbf{d}$, which Gauss' law relates directly to free charge, and the electric enthalpy ω_{ξ}^{+} , whose dependence on density, saturation, composition, and temperature represents the effective dielectric response of the porous medium. The Maxwell stress enters the mechanical power through $\sigma'_{\xi}{}^{+}$, and the free-charge source and electrical boundary flux appear explicitly on the right-hand side of (153). The field-power identity (150), vacuum-displacement split, and associated isotropic stress shift convert between the two accounting conventions and relate the polarization-work term $-\mathbf{P} \cdot \dot{\mathbf{E}}$ used by Montanaro to the free-charge and boundary-flux terms displayed here. Polarization is therefore recovered constitutively from $\mathbf{P} = \mathbf{d} - \varepsilon_0 \mathbf{E}$ and is not an additional state variable. An independent polarization evolution law would be required only for relaxation, hysteresis, ferroelectricity, or other additional dielectric physics.

The solid stress power is decomposed by $\mathbf{F} = \mathbf{A}_s \bar{\mathbf{F}}_s$,

$$\mathbf{L}_s = \dot{\mathbf{A}}_s \mathbf{A}_s^{-1} + \mathbf{A}_s \dot{\bar{\mathbf{F}}}_s \bar{\mathbf{F}}_s^{-1} \mathbf{A}_s^{-1}, \quad s \in \mathcal{S}. \quad (155)$$

Using (127), the solid stress power is

$$\begin{aligned}
\sum_{s \in \mathcal{S}} \boldsymbol{\sigma}_s'^+ : \mathbf{L}_s &= \sum_{s \in \mathcal{S}} \text{tr} \left[(\boldsymbol{\sigma}_s'^+)^T \dot{\mathbf{A}}_s^e (\mathbf{A}_s^e)^{-1} \right] \\
&+ \sum_{s \in \mathcal{S}} \text{tr} \left[(\mathbf{A}_s^e)^{-1} (\boldsymbol{\sigma}_s'^+)^T \mathbf{A}_s^e \dot{\mathbf{A}}_s^p (\mathbf{A}_s^p)^{-1} \right] \\
&+ \sum_{s \in \mathcal{S}} \text{tr} \left[(\mathbf{A}_s^p)^{-1} (\mathbf{A}_s^e)^{-1} (\boldsymbol{\sigma}_s'^+)^T \mathbf{A}_s^e \mathbf{A}_s^p \frac{\partial \mathbf{A}_s^0}{\partial \theta_S} \bigg|_{\mathcal{X}_s} (\mathbf{A}_s^0)^{-1} \right] \dot{\theta}_S \\
&+ \sum_{s \in \mathcal{S}} \sum_{\beta} \text{tr} \left[(\mathbf{A}_s^p)^{-1} (\mathbf{A}_s^e)^{-1} (\boldsymbol{\sigma}_s'^+)^T \mathbf{A}_s^e \mathbf{A}_s^p \frac{\partial \mathbf{A}_s^0}{\partial \eta_s^\beta} \bigg|_{\mathcal{X}_s} (\mathbf{A}_s^0)^{-1} \right] \dot{\eta}_s^\beta \\
&+ \sum_{s \in \mathcal{S}} \text{tr} \left[\mathbf{A}_s^{-1} (\boldsymbol{\sigma}_s'^+)^T \mathbf{A}_s \dot{\mathbf{F}}_s^e (\bar{\mathbf{F}}_s^e)^{-1} \right] \\
&+ \sum_{s \in \mathcal{S}} \text{tr} \left[(\bar{\mathbf{F}}_s^e)^{-1} \mathbf{A}_s^{-1} (\boldsymbol{\sigma}_s'^+)^T \mathbf{A}_s \bar{\mathbf{F}}_s^e \dot{\mathbf{F}}_s^p (\bar{\mathbf{F}}_s^p)^{-1} \right] \\
&+ \sum_{s \in \mathcal{S}} \text{tr} \left[(\bar{\mathbf{F}}_s^p)^{-1} (\bar{\mathbf{F}}_s^e)^{-1} \mathbf{A}_s^{-1} (\boldsymbol{\sigma}_s'^+)^T \mathbf{A}_s \bar{\mathbf{F}}_s^e \bar{\mathbf{F}}_s^p \frac{\partial \bar{\mathbf{F}}_s^0}{\partial \theta_S} \bigg|_{\mathcal{X}_s} (\bar{\mathbf{F}}_s^0)^{-1} \right] \dot{\theta}_S \\
&+ \sum_{s \in \mathcal{S}} \sum_{\beta} \text{tr} \left[(\bar{\mathbf{F}}_s^p)^{-1} (\bar{\mathbf{F}}_s^e)^{-1} \mathbf{A}_s^{-1} (\boldsymbol{\sigma}_s'^+)^T \mathbf{A}_s \bar{\mathbf{F}}_s^e \bar{\mathbf{F}}_s^p \frac{\partial \bar{\mathbf{F}}_s^0}{\partial \eta_s^\beta} \bigg|_{\mathcal{X}_s} (\bar{\mathbf{F}}_s^0)^{-1} \right] \dot{\eta}_s^\beta. \tag{156}
\end{aligned}$$

The local entropy inequality is written in the same skeleton frame as the subsystem energy balances. Its entropy flux contains entropy convected through the skeleton control surface, entropy transported by the gauge-invariant material-energy flux, and the chemical-potential-weighted contribution of component-relative transport. Electrical work on the relative charge flux enters through the gauge-invariant volume power in (151), not through a potential-dependent entropy flux. In the $N - 1$ independent component coordinates, the neutral contribution is written in potential-difference form. This is the phasewise zero-sum analogue of the mixture entropy flux of Bothe and Dreyer [10, eq. (60)],

$$\begin{aligned}
0 \leq & \sum_{\mathcal{G} \in \{\mathcal{F}, \mathcal{S}\}} \sum_{\xi \in \mathcal{G}} \left[\frac{D_S}{Dt} (\rho_\xi \mathfrak{s}_\xi) + \rho_\xi \mathfrak{s}_\xi \nabla_{\mathbf{x}} \cdot \mathbf{v}_S \right. \\
& + \nabla_{\mathbf{x}} \cdot \left(\rho_\xi \mathfrak{s}_\xi (\mathbf{v}_\xi - \mathbf{v}_S) + \frac{\mathbf{q}_\xi}{\theta_G} \right) \\
& - \nabla_{\mathbf{x}} \cdot \left[\sum_{\alpha \neq N} \frac{\hat{\mu}_\xi^\alpha - \hat{\mu}_\xi^N}{\theta_G} (\mathbf{j}_{\xi, \text{disp}}^\alpha + \mathbf{j}_{\xi, \text{diff}}^\alpha) \right] - \frac{\rho_\xi r_\xi}{\theta_G} \Big] \\
& + \frac{D_S}{Dt} (\phi \mathfrak{s}_\gamma). \tag{157}
\end{aligned}$$

The last term is interfacial entropy storage on the skeleton trajectory. It has no separate relative flux at the present averaging level; unresolved interfacial conduction is included in the fluid-subsystem nonadvective energy-flux sum $\sum_{f \in \mathcal{F}} \mathbf{q}_f$.

The admissible rates in this inequality already satisfy the four constraints introduced in §4, the component charge balance (42), and the global electrostatic power identity (150). The C_1 multiplier power is present in (151); C_2 is enforced by the augmented component material measure and its density and composition kinematics; and C_4 imposes zero net insertion. Stoichiometrically

conservative conversion and zero-sum relative transport satisfy the latter constraint. Constraint C_3 is handled explicitly by adding $\Pi_\xi \sum_\alpha \dot{\eta}_\xi^\alpha = 0$, which permits all N mass-fraction rates to be retained until the composition coefficients are reduced to $N - 1$ independent differences by subtracting the reference-component coefficient.

Substituting (151) eliminates the external heat supply from each thermal group. The common electric-potential rate and its bulk and boundary powers were separated globally in (150), before the remaining terms are divided by $\theta_{\mathcal{F}}$ or $\theta_{\mathcal{S}}$. Thus Gauss' law is not applied separately to temperature-weighted fluid and solid field powers. Maxwell power is removed from the total mechanical power at the same step, leaving the material stress σ'_ξ . The result is

$$\begin{aligned}
0 \leq & \sum_{\mathcal{G} \in \{\mathcal{F}, \mathcal{S}\}} \sum_{\xi \in \mathcal{G}} \frac{1}{\theta_{\mathcal{G}}} \left(\sigma'_\xi : \mathbf{L}_\xi + \phi_\xi \bar{p}_\xi \frac{\dot{\rho}_\xi}{\rho_\xi} - \rho_\xi \left(\dot{\psi}_\xi + \mathfrak{s}_\xi \dot{\theta}_{\mathcal{G}} \right) - \sum_\alpha \dot{c}_\xi^\alpha \left(\psi_\xi + L_\xi^\alpha \right) + \rho_\xi e_\xi^{\text{int}} \right) \\
& - \sum_{\mathcal{G} \in \{\mathcal{F}, \mathcal{S}\}} \sum_{\xi \in \mathcal{G}} \frac{\rho_\xi}{\theta_{\mathcal{G}}} (\mathbf{v}_\xi - \mathbf{v}_{\mathcal{S}}) \cdot (\nabla_{\mathbf{x}} \psi_\xi + \mathfrak{s}_\xi \nabla_{\mathbf{x}} \theta_{\mathcal{G}}) \\
& - \sum_{\mathcal{G} \in \{\mathcal{F}, \mathcal{S}\}} \sum_{\xi \in \mathcal{G}} \frac{\mathbf{q}_\xi \cdot \nabla_{\mathbf{x}} \theta_{\mathcal{G}}}{\theta_{\mathcal{G}}^2} \\
& + \sum_{\mathcal{G} \in \{\mathcal{F}, \mathcal{S}\}} \sum_{\xi \in \mathcal{G}} \frac{1}{\theta_{\mathcal{G}}} \sum_\alpha z_\xi^\alpha \left(\mathbf{j}_{\xi, \text{disp}}^\alpha + \mathbf{j}_{\xi, \text{diff}}^\alpha \right) \cdot \mathbf{E} \\
& - \sum_{\mathcal{G} \in \{\mathcal{F}, \mathcal{S}\}} \sum_{\xi \in \mathcal{G}} \sum_{\alpha \neq N} \nabla_{\mathbf{x}} \cdot \left[\frac{\hat{\mu}_\xi^\alpha - \hat{\mu}_\xi^N}{\theta_{\mathcal{G}}} \left(\mathbf{j}_{\xi, \text{disp}}^\alpha + \mathbf{j}_{\xi, \text{diff}}^\alpha \right) \right] \\
& + \sum_{\mathcal{G} \in \{\mathcal{F}, \mathcal{S}\}} \frac{1}{\theta_{\mathcal{G}}} \sum_{\xi \in \mathcal{G}} \left((\lambda + \bar{p}_\xi) \dot{\phi}_\xi + \sum_\alpha \frac{\pi_\xi^\alpha}{\eta_\xi^\alpha} \dot{\eta}_\xi^\alpha + \Pi_\xi \sum_\alpha \dot{\eta}_\xi^\alpha \right) \\
& - \frac{1}{\theta_{\mathcal{F}}} \left[\sum_{f \in \mathcal{F}} \gamma_f \dot{\phi}_f + \phi \frac{\partial \gamma}{\partial \mathbf{h}} \Big|_{\{S_f\}_{f \in \mathcal{F}, \theta_{\mathcal{F}}}} \cdot \dot{\mathbf{h}} + \phi \frac{\partial \gamma}{\partial \theta_{\mathcal{F}}} \Big|_{\{S_f\}_{f \in \mathcal{F}, \mathbf{h}}} \dot{\theta}_{\mathcal{F}} + \phi \mathfrak{s}_\gamma \dot{\theta}_{\mathcal{F}} \right] \\
& + \sum_{\mathcal{G} \in \{\mathcal{F}, \mathcal{S}\}} \frac{1}{\theta_{\mathcal{G}}} \left[- \sum_{\xi \in \mathcal{G}} \left(\omega_\xi^+ \dot{\phi}_\xi + \phi_\xi \frac{\partial \omega_\xi^+}{\partial \rho_\xi} \Big|_{\mathcal{X}_\xi, \mathbf{E}} \dot{\rho}_\xi \right) \right. \\
& \left. - \sum_{\xi \in \mathcal{G}} \phi_\xi \sum_\beta \frac{\partial \omega_\xi^+}{\partial \eta_\xi^\beta} \Big|_{\mathcal{X}_\xi, \mathbf{E}} \dot{\eta}_\xi^\beta - \sum_{\xi \in \mathcal{G}} \phi_\xi \frac{\partial \omega_\xi^+}{\partial \theta_{\mathcal{G}}} \Big|_{\mathcal{X}_\xi, \mathbf{E}} \dot{\theta}_{\mathcal{G}} \right]. \tag{158}
\end{aligned}$$

The skeleton-rate free-energy term in (158) and the separate term containing the Helmholtz-energy and temperature gradients are generated together when a phase-following thermodynamic rate is expressed in the skeleton frame. Indeed, (122) gives the exact identity

$$-\frac{\rho_\xi}{\theta_{\mathcal{G}}} \left(\dot{\psi}_\xi + \mathfrak{s}_\xi \dot{\theta}_{\mathcal{G}} \right) - \frac{\rho_\xi}{\theta_{\mathcal{G}}} (\mathbf{v}_\xi - \mathbf{v}_{\mathcal{S}}) \cdot (\nabla_{\mathbf{x}} \psi_\xi + \mathfrak{s}_\xi \nabla_{\mathbf{x}} \theta_{\mathcal{G}}) = -\frac{\rho_\xi}{\theta_{\mathcal{G}}} \left(\dot{\psi}_\xi + \mathfrak{s}_\xi \dot{\theta}_{\mathcal{G}} \right). \tag{159}$$

Consequently, the second term on the left is not an additional constitutive force conjugate to bulk phase velocity. Separating it from the first term is only an observer-dependent expansion of the single phase-following rate on the right. Treating that term as an independent dissipative force would count the same thermodynamic rate twice: once through the Coleman–Noll coefficients of the phase state variables and again through a bulk interaction law.

In (158), the interfacial contribution is the negative of the storage rate (148). The remaining derivatives of ω_ξ^+ measure how electrical storage changes with density, composition, and temperature.

The explicit relative-velocity term is retained in the intermediate skeleton-rate form so that the change of observer remains visible. Equation (159) does not state that this term vanishes. It states that the term must be recombined with the skeleton-rate free-energy contribution before the collected inequality is separated into reversible and residual parts. The explicit reassembly is given after the collected inequality; applying the reversible restrictions to its residual block alone would use the identity incorrectly. The Maxwell part of the stress power is removed from the total mechanical power by

$$\boldsymbol{\sigma}'_{\xi} : \mathbf{L}_{\xi} - \boldsymbol{\sigma}_{\xi}^+ : \mathbf{L}_{\xi} = \boldsymbol{\sigma}'_{\xi} : \mathbf{L}_{\xi}. \quad (160)$$

The material stress $\boldsymbol{\sigma}'_{\xi}$ is therefore conjugate to the material Helmholtz-energy rate, while the momentum equation continues to use the total stress $\boldsymbol{\sigma}_{\xi}^+$. This is the same division obtained from an electromagnetic energy-flux balance: the field contribution supplies Maxwell power, and the remaining mechanical power acts on the material free energy [48]. Both the displacement relation $\mathbf{d}_{\xi} = -\partial\omega_{\xi}^+/\partial\mathbf{E}$ and the Maxwell stress (75) are generated from the same phase electric enthalpy [19].

To expose the independent constitutive rates, substitute the fluid and solid free-energy rates (144)–(145), the solid density rate (137), and the stress-power split (156). Next use (31) to separate component insertion into conversion and relative-flux contributions. The neutral component-source term and entropy-flux divergence combine by the product rule, while the direct relative-current work in (151) supplies the electric-field part of the transport force. A charge-rate projection derived with the source terms below records the equivalent potential-charge accounting separately. The divergence terms are retained in the strong form and contribute the corresponding boundary fluxes in the integrated statement. Collecting the volume-fraction, capillary-history, composition, temperature, reaction, and transport rates gives one inequality organized into five labelled blocks. The first block contains the elastic, distension, volume-fraction, and capillary-history rates. Each subsequent display continues the right-hand side of the first, so its leading sign belongs to the same sum. All five blocks therefore form the single inequality (161).

Elastic, distension, and volume-fraction rates.

$$\begin{aligned} 0 \leq & \frac{1}{\theta_S} \sum_{s \in \mathcal{S}} \text{tr} \left[\left((\boldsymbol{\sigma}'_s)^T - \rho_s \mathbf{A}_s^e \left(\frac{\partial \psi_s}{\partial \mathbf{A}_s^e} \Big|_{\chi_s} \right)^T \right) \dot{\mathbf{A}}_s^e (\mathbf{A}_s^e)^{-1} \right] \\ & + \frac{1}{\theta_S} \sum_{s \in \mathcal{S}} \text{tr} \left[\left(\mathbf{A}_s^{-1} (\boldsymbol{\sigma}'_s)^T \mathbf{A}_s - \rho_s \bar{\mathbf{F}}_s^e \left(\frac{\partial \psi_s}{\partial \bar{\mathbf{F}}_s^e} \Big|_{\chi_s} \right)^T \right. \right. \\ & \left. \left. + \left(\rho_s \frac{\partial \psi_s}{\partial \bar{\rho}_s} \Big|_{\chi_s} \bar{\rho}_s + \phi_s \frac{\partial \omega_s^+}{\partial \bar{\rho}_s} \Big|_{\chi_s, \mathbf{E}} \bar{\rho}_s - \phi_s \bar{p}_s \right) \mathbf{I} \right) \dot{\bar{\mathbf{F}}}_s^e (\bar{\mathbf{F}}_s^e)^{-1} \right] \\ & + \frac{1}{\theta_S} \sum_{s \in \mathcal{S}} \left(\lambda + \bar{p}_s - \omega_s^+ \right) \dot{\phi}_s + \frac{1}{\theta_{\mathcal{F}}} \sum_{f \in \mathcal{F}} \left(\lambda + \bar{p}_f - \omega_f^+ - \gamma_f \right) \dot{\phi}_f - \frac{\phi}{\theta_{\mathcal{F}}} \frac{\partial \gamma}{\partial \mathbf{h}} \Big|_{\{S_f\}_{f \in \mathcal{F}}, \theta_{\mathcal{F}}} \cdot \dot{\mathbf{h}} \quad (161a) \end{aligned}$$

Density and composition rates.

$$\begin{aligned}
& + \frac{1}{\theta_{\mathcal{F}}} \sum_{f \in \mathcal{F}} \left[\frac{\phi_f \bar{p}_f}{\bar{\rho}_f} - \rho_f \frac{\partial \psi_f}{\partial \bar{\rho}_f} \Big|_{\mathcal{X}_f} - \phi_f \frac{\partial \omega_f^+}{\partial \bar{\rho}_f} \Big|_{\mathcal{X}_f, \mathbf{E}} \right] \dot{\bar{\rho}}_f \\
& + \frac{1}{\theta_{\mathcal{F}}} \sum_{f \in \mathcal{F}} \sum_{\beta} \left[\frac{\pi_f^\beta}{\eta_f^\beta} + \Pi_f - \rho_f \frac{\partial \psi_f}{\partial \eta_f^\beta} \Big|_{\mathcal{X}_f} - \phi_f \frac{\partial \omega_f^+}{\partial \eta_f^\beta} \Big|_{\mathcal{X}_f, \mathbf{E}} \right] \dot{\eta}_f^\beta \\
& + \frac{1}{\theta_{\mathcal{S}}} \sum_{s \in \mathcal{S}} \sum_{\beta} \left[\frac{\pi_s^\beta}{\eta_s^\beta} + \Pi_s - \rho_s \frac{\partial \psi_s}{\partial \eta_s^\beta} \Big|_{\mathcal{X}_s} - \phi_s \frac{\partial \omega_s^+}{\partial \eta_s^\beta} \Big|_{\mathcal{X}_s, \mathbf{E}} \right. \\
& + \text{tr} \left[(\mathbf{A}_s^p)^{-1} (\mathbf{A}_s^e)^{-1} (\boldsymbol{\sigma}'_s)^T \mathbf{A}_s^e \mathbf{A}_s^p \frac{\partial \mathbf{A}_s^0}{\partial \eta_s^\beta} \Big|_{\mathcal{X}_s} (\mathbf{A}_s^0)^{-1} \right] \\
& + \text{tr} \left[\left((\bar{\mathbf{F}}_s^p)^{-1} (\bar{\mathbf{F}}_s^e)^{-1} \mathbf{A}_s^{-1} (\boldsymbol{\sigma}'_s)^T \mathbf{A}_s \bar{\mathbf{F}}_s^e \bar{\mathbf{F}}_s^p \right. \right. \\
& \left. \left. + \left(\rho_s \frac{\partial \psi_s}{\partial \bar{\rho}_s} \Big|_{\mathcal{X}_s} \bar{\rho}_s + \phi_s \frac{\partial \omega_s^+}{\partial \bar{\rho}_s} \Big|_{\mathcal{X}_s, \mathbf{E}} \bar{\rho}_s - \phi_s \bar{p}_s \right) \mathbf{I} \right) \frac{\partial \bar{\mathbf{F}}_s^0}{\partial \eta_s^\beta} \Big|_{\mathcal{X}_s} (\bar{\mathbf{F}}_s^0)^{-1} \right] \dot{\eta}_s^\beta \quad (161b)
\end{aligned}$$

Temperature rates.

$$\begin{aligned}
& + \frac{1}{\theta_{\mathcal{F}}} \left[- \sum_{f \in \mathcal{F}} \rho_f \left(\mathfrak{s}_f + \frac{\partial \psi_f}{\partial \theta_{\mathcal{F}}} \Big|_{\mathcal{X}_f} \right) - \sum_{f \in \mathcal{F}} \phi_f \frac{\partial \omega_f^+}{\partial \theta_{\mathcal{F}}} \Big|_{\mathcal{X}_f, \mathbf{E}} - \phi \left(\mathfrak{s}_\gamma + \frac{\partial \gamma}{\partial \theta_{\mathcal{F}}} \Big|_{\{S_f\}_{f \in \mathcal{F}, \mathbf{h}}} \right) \right] \dot{\theta}_{\mathcal{F}} \\
& + \frac{1}{\theta_{\mathcal{S}}} \left[- \sum_{s \in \mathcal{S}} \rho_s \left(\mathfrak{s}_s + \frac{\partial \psi_s}{\partial \theta_{\mathcal{S}}} \Big|_{\mathcal{X}_s} \right) - \sum_{s \in \mathcal{S}} \phi_s \frac{\partial \omega_s^+}{\partial \theta_{\mathcal{S}}} \Big|_{\mathcal{X}_s, \mathbf{E}} \right. \\
& + \sum_{s \in \mathcal{S}} \text{tr} \left[(\mathbf{A}_s^p)^{-1} (\mathbf{A}_s^e)^{-1} (\boldsymbol{\sigma}'_s)^T \mathbf{A}_s^e \mathbf{A}_s^p \frac{\partial \mathbf{A}_s^0}{\partial \theta_{\mathcal{S}}} \Big|_{\mathcal{X}_s} (\mathbf{A}_s^0)^{-1} \right] \\
& + \sum_{s \in \mathcal{S}} \text{tr} \left[\left((\bar{\mathbf{F}}_s^p)^{-1} (\bar{\mathbf{F}}_s^e)^{-1} \mathbf{A}_s^{-1} (\boldsymbol{\sigma}'_s)^T \mathbf{A}_s \bar{\mathbf{F}}_s^e \bar{\mathbf{F}}_s^p \right. \right. \\
& \left. \left. + \left(\rho_s \frac{\partial \psi_s}{\partial \bar{\rho}_s} \Big|_{\mathcal{X}_s} \bar{\rho}_s + \phi_s \frac{\partial \omega_s^+}{\partial \bar{\rho}_s} \Big|_{\mathcal{X}_s, \mathbf{E}} \bar{\rho}_s - \phi_s \bar{p}_s \right) \mathbf{I} \right) \frac{\partial \bar{\mathbf{F}}_s^0}{\partial \theta_{\mathcal{S}}} \Big|_{\mathcal{X}_s} (\bar{\mathbf{F}}_s^0)^{-1} \right] \dot{\theta}_{\mathcal{S}} \quad (161c)
\end{aligned}$$

Reaction and relative-transport rates.

$$\begin{aligned}
& - \sum_m \left[\frac{1}{\theta_{\mathcal{F}}} \sum_{f \in \mathcal{F}} \sum_{\alpha} \nu_{f(m)}^\alpha (\psi_f + L_f^\alpha) + \frac{1}{\theta_{\mathcal{S}}} \sum_{s \in \mathcal{S}} \sum_{\alpha} \nu_{s(m)}^\alpha (\psi_s + L_s^\alpha) \right] r_{(m)} \\
& - \sum_{\mathcal{G} \in \{\mathcal{F}, \mathcal{S}\}} \sum_{\xi \in \mathcal{G}} \sum_{\alpha \neq N} \left(\mathbf{j}_{\xi, \text{disp}}^\alpha + \mathbf{j}_{\xi, \text{diff}}^\alpha \right) \cdot \left[\nabla_{\mathbf{x}} \left(\frac{\hat{\mu}_\xi^\alpha - \hat{\mu}_\xi^N}{\theta_{\mathcal{G}}} \right) + \frac{z_\xi^\alpha - z_\xi^N}{\theta_{\mathcal{G}}} \nabla_{\mathbf{x}} \varphi \right] \quad (161d)
\end{aligned}$$

Plastic, interaction-energy, heat, and intermediate observer-conversion terms.

$$\begin{aligned}
& + \frac{1}{\theta_S} \sum_{s \in \mathcal{S}} \text{tr} \left[(\mathbf{A}_s^e)^{-1} (\boldsymbol{\sigma}'_s)^T \mathbf{A}_s^e \dot{\mathbf{A}}_s^p (\mathbf{A}_s^p)^{-1} \right] \\
& + \frac{1}{\theta_S} \sum_{s \in \mathcal{S}} \text{tr} \left[(\bar{\mathbf{F}}_s^e)^{-1} \mathbf{A}_s^{-1} (\boldsymbol{\sigma}'_s)^T \mathbf{A}_s \bar{\mathbf{F}}_s^e \dot{\bar{\mathbf{F}}}_s^p (\bar{\mathbf{F}}_s^p)^{-1} \right] \\
& + \sum_{g \in \{\mathcal{F}, \mathcal{S}\}} \frac{1}{\theta_g} \sum_{\xi \in \mathcal{G}} \left[\rho_\xi e_\xi^{\text{int}} - \rho_\xi (\mathbf{v}_\xi - \mathbf{v}_S) \cdot (\nabla_{\mathbf{x}} \psi_\xi + \mathbf{s}_\xi \nabla_{\mathbf{x}} \theta_g) \right] - \sum_{g \in \{\mathcal{F}, \mathcal{S}\}} \sum_{\xi \in \mathcal{G}} \frac{\mathbf{q}_\xi \cdot \nabla_{\mathbf{x}} \theta_g}{\theta_g^2}. \quad (161e)
\end{aligned}$$

Equation (161) is an audit expansion in skeleton-rate coordinates that groups the collected entropy into the mechanism blocks below; the reversible–residual division is applied after the observer reassembly. In particular, the first term on the left of (159) has been distributed among the density, composition, temperature, and solid-kinematic coefficients in (161a)–(161c), while its observer correction appears intact in (161e). To show the required operation explicitly, solve (159) for that correction and sum over the phases:

$$\begin{aligned}
& - \sum_{g \in \{\mathcal{F}, \mathcal{S}\}} \frac{1}{\theta_g} \sum_{\xi \in \mathcal{G}} \rho_\xi (\mathbf{v}_\xi - \mathbf{v}_S) \cdot (\nabla_{\mathbf{x}} \psi_\xi + \mathbf{s}_\xi \nabla_{\mathbf{x}} \theta_g) \\
& = - \sum_{g \in \{\mathcal{F}, \mathcal{S}\}} \frac{1}{\theta_g} \sum_{\xi \in \mathcal{G}} \rho_\xi (\dot{\psi}_\xi + \mathbf{s}_\xi \dot{\theta}_g) + \sum_{g \in \{\mathcal{F}, \mathcal{S}\}} \frac{1}{\theta_g} \sum_{\xi \in \mathcal{G}} \rho_\xi (\dot{\psi}_\xi + \mathbf{s}_\xi \dot{\theta}_g). \quad (162)
\end{aligned}$$

The final positive sum in (162) cancels the negative skeleton-rate free-energy contribution that was expanded into the preceding blocks of (161). This is an algebraic reassembly of the complete collected inequality; both contributions remain in the entropy inequality through their phase-following replacement in the second line. What remains from the pair is the phase-following rate in the second line. For a mobile fluid phase its constitutive chain rule is

$$\dot{\psi}_f = \left. \frac{\partial \psi_f}{\partial \bar{\rho}_f} \right|_{\mathcal{X}_f} \dot{\bar{\rho}}_f + \sum_{\beta} \left. \frac{\partial \psi_f}{\partial \eta_f^\beta} \right|_{\mathcal{X}_f} \dot{\eta}_f^\beta + \left. \frac{\partial \psi_f}{\partial \theta_{\mathcal{F}}} \right|_{\mathcal{X}_f} \dot{\theta}_{\mathcal{F}}, \quad f \in \mathcal{F}. \quad (163)$$

For every solid phase, $\mathbf{v}_s = \mathbf{v}_S$, so the phase-following and skeleton-following rates coincide and (145) already supplies this chain rule. Only after (162) is substituted into the whole of (161) are the reversible restrictions applied. If the coefficients in the first four blocks were set to zero before this reassembly, the observer correction in the residual block would incorrectly survive as an independent force–flux product.

After this ordering is enforced, coefficients of elastic deformation, intrinsic density, composition, temperature, and volume-fraction rates give the reversible constitutive restrictions. Reaction rates, component-relative fluxes, plastic rates, interphase energy exchange, and heat flux remain as dissipative force–rate products. The resulting residual is treated in the subsequent source-and-closure subsection.

5.3 Reversible restrictions

After the observer correction has been reassembled according to (162), the reversible restrictions are obtained by setting to zero the coefficients of rates that can vary independently at a fixed constitutive state. The stress appearing in these coefficients is the material stress $\boldsymbol{\sigma}'_\xi$. The total stress in the momentum equation is $\boldsymbol{\sigma}'_\xi^+ = \boldsymbol{\sigma}'_\xi + \boldsymbol{\sigma}_\xi^+$.

The coefficient of $\dot{\bar{\mathbf{F}}}_s^e (\bar{\mathbf{F}}_s^e)^{-1}$ gives

$$\begin{aligned} \mathbf{A}_s^{-1} (\boldsymbol{\sigma}'_s)^T \mathbf{A}_s &= \rho_s \bar{\mathbf{F}}_s^e \left(\frac{\partial \psi_s}{\partial \bar{\mathbf{F}}_s^e} \bigg|_{\mathcal{X}_s} \right)^T \\ &\quad - \left(\rho_s \frac{\partial \psi_s}{\partial \bar{\rho}_s} \bigg|_{\mathcal{X}_s} \bar{\rho}_s + \phi_s \frac{\partial \omega_s^+}{\partial \bar{\rho}_s} \bigg|_{\mathcal{X}_s, \mathbf{E}} \bar{\rho}_s - \phi_s \bar{p}_s \right) \mathbf{I}, \quad s \in \mathcal{S}. \end{aligned} \quad (164)$$

For a fluid, $\boldsymbol{\sigma}'_f = \mathbf{0}$ because the Helmholtz energy has no elastic deformation argument. After the isotropic Maxwell contribution is combined with the pressure relation, the remaining nonpressure reversible stress enters the fluid momentum balance with dynamic pressure lag (103) through $\phi_f \mathbf{E} \otimes \mathbf{d}_f$; the fluid pressure is determined separately by the intrinsic-density coefficient.

Setting the intrinsic-density coefficients to zero defines the fluid and solid phase pressures,

$$\bar{p}_f = \bar{\rho}_f^2 \frac{\partial \psi_f}{\partial \bar{\rho}_f} \bigg|_{\mathcal{X}_f} + \bar{\rho}_f \frac{\partial \omega_f^+}{\partial \bar{\rho}_f} \bigg|_{\mathcal{X}_f, \mathbf{E}}, \quad f \in \mathcal{F}, \quad (165a)$$

$$\bar{p}_s = \bar{\rho}_s^2 \frac{\partial \psi_s}{\partial \bar{\rho}_s} \bigg|_{\mathcal{X}_s} + \bar{\rho}_s \frac{\partial \omega_s^+}{\partial \bar{\rho}_s} \bigg|_{\mathcal{X}_s, \mathbf{E}}, \quad s \in \mathcal{S}. \quad (165b)$$

Using the solid pressure relation in the elastic-deformation coefficient removes the spherical density term and gives the material solid stress,

$$\boldsymbol{\sigma}'_s = \mathbf{A}_s^{-T} \left(\rho_s \frac{\partial \psi_s}{\partial \bar{\mathbf{F}}_s^e} \bigg|_{\mathcal{X}_s} (\bar{\mathbf{F}}_s^e)^T \right) \mathbf{A}_s^T, \quad s \in \mathcal{S}. \quad (166)$$

The electrical part of the solid phase-map variation supplies the solid Maxwell stress,

$$\boldsymbol{\sigma}_s^+ = \boldsymbol{\sigma}_\xi^+ \big|_{\xi=s}, \quad s \in \mathcal{S}, \quad (167)$$

The total solid stress is $\boldsymbol{\sigma}_s'^+ = \boldsymbol{\sigma}'_s + \boldsymbol{\sigma}_s^+$. This total stress enters momentum balance, whereas only $\boldsymbol{\sigma}'_s$ is conjugate to the solid material free-energy rate.

For the linear dielectric choice $\omega_\xi^+ = -\frac{1}{2} \mathbf{E} \cdot \mathbf{d}_\xi$, the sum of the phase-attributed electrical stresses is the usual Maxwell stress $\mathbf{E} \otimes \mathbf{d} - \frac{1}{2} (\mathbf{E} \cdot \mathbf{d}) \mathbf{I}$, with $\mathbf{d} = \sum_\xi \phi_\xi \mathbf{d}_\xi$.

The coefficient of the elastic distension rate gives

$$\boldsymbol{\sigma}'_s = \rho_s \frac{\partial \psi_s}{\partial \mathbf{A}_s^e} \bigg|_{\mathcal{X}_s} (\mathbf{A}_s^e)^T, \quad s \in \mathcal{S}. \quad (168)$$

The solid and fluid volume-fraction rates are constrained by $\sum_\xi \dot{\phi}_\xi = 0$, so their reversible coefficients are determined up to the common multiplier λ . The multiplier power was retained in both subsystem energy balances; consequently, the same λ appears in the solid and fluid coefficients even when their temperatures differ.

For the fluid phases, let $\dot{\phi} = D_S \phi / Dt$ and use $\dot{\phi}_f = S_f \dot{\phi} + \phi \dot{S}_f$, with $\sum_f \dot{S}_f = 0$. The fluid volume-fraction power then separates into a pore-volume part and a saturation-redistribution part:

$$\begin{aligned} &\sum_{f \in \mathcal{F}} \left(\lambda + \bar{p}_f - \omega_f^+ - \gamma_f \right) \dot{\phi}_f \\ &= \left[\lambda + \sum_{f \in \mathcal{F}} S_f \left(\bar{p}_f - \omega_f^+ - \gamma_f \right) \right] \dot{\phi} + \phi \sum_{f \in \mathcal{F}} \left(\bar{p}_f - \omega_f^+ - \gamma_f \right) \dot{S}_f. \end{aligned} \quad (169)$$

The solid volume-fraction rates and the total fluid pore-volume rate remain reversible. Setting their coefficients to zero gives

$$0 = \lambda + \bar{p}_s - \omega_s^+, \quad s \in \mathcal{S}, \quad (170a)$$

$$0 = \lambda + \sum_{f \in \mathcal{F}} S_f (\bar{p}_f - \omega_f^+ - \gamma_f). \quad (170b)$$

The second relation and $\sum_f S_f \gamma_f = \gamma$ preserve the equivalent-pressure identity for the actual phase pressures (93). The final term in (169) is retained in the residual inequality and closed by the dynamic pressure-lag Onsager relation. If $\mathcal{T} = \mathbf{0}$, that closure makes the phase coefficients equal; the common pore-volume relation then recovers the individual reversible fluid relations. This split does not require $\theta_{\mathcal{F}} = \theta_{\mathcal{S}}$.

Only $N - 1$ composition rates are independent in each fluid phase. Subtracting the component- N coefficient from the other coefficients gives

$$\boxed{\begin{aligned} & \rho_f \left(\frac{\partial \psi_f}{\partial \eta_f^\beta} \Big|_{\mathcal{X}_f} - \frac{\partial \psi_f}{\partial \eta_f^N} \Big|_{\mathcal{X}_f} \right) + \phi_f \left(\frac{\partial \omega_f^+}{\partial \eta_f^\beta} \Big|_{\mathcal{X}_f, \mathbf{E}} - \frac{\partial \omega_f^+}{\partial \eta_f^N} \Big|_{\mathcal{X}_f, \mathbf{E}} \right) \\ &= \frac{\pi_f^\beta}{\eta_f^\beta} - \frac{\pi_f^N}{\eta_f^N}, \quad \beta = 1, \dots, N - 1, \quad f \in \mathcal{F}. \end{aligned}} \quad (171)$$

The corresponding component differences for a solid phase also contain the composition dependence of its stress-free maps,

$$\boxed{\begin{aligned} & \rho_s \left(\frac{\partial \psi_s}{\partial \eta_s^\beta} \Big|_{\mathcal{X}_s} - \frac{\partial \psi_s}{\partial \eta_s^N} \Big|_{\mathcal{X}_s} \right) + \phi_s \left(\frac{\partial \omega_s^+}{\partial \eta_s^\beta} \Big|_{\mathcal{X}_s, \mathbf{E}} - \frac{\partial \omega_s^+}{\partial \eta_s^N} \Big|_{\mathcal{X}_s, \mathbf{E}} \right) \\ & - \text{tr} \left[(\mathbf{A}_s^p)^{-1} (\mathbf{A}_s^e)^{-1} (\boldsymbol{\sigma}'_s)^T \mathbf{A}_s^e \mathbf{A}_s^p \left(\frac{\partial \mathbf{A}_s^0}{\partial \eta_s^\beta} \Big|_{\mathcal{X}_s} - \frac{\partial \mathbf{A}_s^0}{\partial \eta_s^N} \Big|_{\mathcal{X}_s} \right) (\mathbf{A}_s^0)^{-1} \right] \\ & - \text{tr} \left[((\bar{\mathbf{F}}_s^p)^{-1} (\bar{\mathbf{F}}_s^e)^{-1} \mathbf{A}_s^{-1} (\boldsymbol{\sigma}'_s)^T \mathbf{A}_s \bar{\mathbf{F}}_s^e \bar{\mathbf{F}}_s^p) \right. \\ & \quad \left. \left(\frac{\partial \bar{\mathbf{F}}_s^0}{\partial \eta_s^\beta} \Big|_{\mathcal{X}_s} - \frac{\partial \bar{\mathbf{F}}_s^0}{\partial \eta_s^N} \Big|_{\mathcal{X}_s} \right) (\bar{\mathbf{F}}_s^0)^{-1} \right] \\ &= \frac{\pi_s^\beta}{\eta_s^\beta} - \frac{\pi_s^N}{\eta_s^N}, \quad \beta = 1, \dots, N - 1, \quad s \in \mathcal{S}. \end{aligned}} \quad (172)$$

Finally, $\dot{\theta}_{\mathcal{F}}$ and $\dot{\theta}_{\mathcal{S}}$ are independent, so their coefficients determine the total entropy of each thermal subsystem. The phasewise caloric energies transported by phases with distinct velocities require an allocation within those totals. A sufficient constitutive specialization assigns the temperature derivative of each phase energy to that phase and retains the interfacial entropy as separate

fluid-subsystem storage:

$$\rho_f \mathfrak{s}_f = -\rho_f \left. \frac{\partial \psi_f}{\partial \theta_{\mathcal{F}}} \right|_{\mathcal{X}_f} - \phi_f \left. \frac{\partial \omega_f^+}{\partial \theta_{\mathcal{F}}} \right|_{\mathcal{X}_f, \mathbf{E}}, \quad f \in \mathcal{F}, \quad (173a)$$

$$\mathfrak{s}_\gamma = - \left. \frac{\partial \gamma}{\partial \theta_{\mathcal{F}}} \right|_{\{S_f\}_{f \in \mathcal{F}, \mathbf{h}}}, \quad (173b)$$

$$\begin{aligned} \rho_s \mathfrak{s}_s = & -\rho_s \left. \frac{\partial \psi_s}{\partial \theta_{\mathcal{S}}} \right|_{\mathcal{X}_s} - \phi_s \left. \frac{\partial \omega_s^+}{\partial \theta_{\mathcal{S}}} \right|_{\mathcal{X}_s, \mathbf{E}} \\ & + \text{tr} \left[(\mathbf{A}_s^p)^{-1} (\mathbf{A}_s^e)^{-1} (\boldsymbol{\sigma}'_s)^T \mathbf{A}_s^e \mathbf{A}_s^p \left. \frac{\partial \mathbf{A}_s^0}{\partial \theta_{\mathcal{S}}} \right|_{\mathcal{X}_s} (\mathbf{A}_s^0)^{-1} \right] \\ & + \text{tr} \left[(\bar{\mathbf{F}}_s^p)^{-1} (\bar{\mathbf{F}}_s^e)^{-1} \mathbf{A}_s^{-1} (\boldsymbol{\sigma}'_s)^T \mathbf{A}_s \bar{\mathbf{F}}_s^e \bar{\mathbf{F}}_s^p \left. \frac{\partial \bar{\mathbf{F}}_s^0}{\partial \theta_{\mathcal{S}}} \right|_{\mathcal{X}_s} (\bar{\mathbf{F}}_s^0)^{-1} \right], \quad s \in \mathcal{S}. \end{aligned} \quad (173c)$$

Summing (173a) over the mobile phases and adding ϕ times (173b) recovers the fluid-subsystem temperature coefficient. Summing (173c) recovers the solid-subsystem coefficient. The phasewise relations are the caloric allocation used by the transport terms, while their subsystem sums are the Coleman–Noll restrictions.

5.4 Sources, residual dissipation, and closures

The reversible restrictions of §5.3 settle the reversible stress, pressure, and energy relations. This subsection assembles what remains. It first converts the component-supply terms into the thermodynamic potentials and forces that appear in the source projection: the within-phase transfer-work potential L_ξ^α , the conversion affinity, and the relative-transport force (§5.4.1). Substituting the reversible restrictions and these forces into the collected entropy inequality then leaves the residual dissipation inequality (§5.4.2). The remaining subsections close each dissipative mechanism admitted by that inequality: dynamic pressure lag and capillary history (§5.4.3), reaction and relative transport (§5.4.4), plastic flow (§5.4.5), interphase mechanical interaction (§5.4.6), and thermal exchange and conduction (§5.4.7). The mechanism index (m) covers chemical reaction, phase transformation, sorption or desorption, and ion exchange; “conversion” is the generic term for any such local process. Three reference choices recur: the reference component N , the phase transfer-work potentials L_ξ^N , and the solid transfer reference $s_\star$, each introduced where first needed.

5.4.1 Component supply and thermodynamic forces

The material increment $\mathcal{C}_\xi^\alpha$ records both conversion and component transport relative to phase ξ . Its variational coefficient (98) contains the specific generalized transfer-work potential L_ξ^α , while the entropy inequality contains the combination $\psi_\xi + L_\xi^\alpha$ multiplying the component-supply rate.

The stress-free maps of a solid phase vary with composition, and (130) gives

$$\left. \frac{\partial \mathbf{A}_s^e}{\partial \eta_s^\beta} \right|_{\mathbf{A}_s, \mathbf{A}_s^p, \theta_{\mathcal{S}}} = - \mathbf{A}_s^e \mathbf{A}_s^p \left. \frac{\partial \mathbf{A}_s^0}{\partial \eta_s^\beta} \right|_{\mathcal{X}_s} (\mathbf{A}_s^0)^{-1} (\mathbf{A}_s^p)^{-1}, \quad s \in \mathcal{S}, \quad (174a)$$

$$\left. \frac{\partial \bar{\mathbf{F}}_s^e}{\partial \eta_s^\beta} \right|_{\bar{\mathbf{F}}_s, \bar{\mathbf{F}}_s^p, \theta_{\mathcal{S}}} = - \bar{\mathbf{F}}_s^e \bar{\mathbf{F}}_s^p \left. \frac{\partial \bar{\mathbf{F}}_s^0}{\partial \eta_s^\beta} \right|_{\mathcal{X}_s} (\bar{\mathbf{F}}_s^0)^{-1} (\bar{\mathbf{F}}_s^p)^{-1}, \quad s \in \mathcal{S}. \quad (174b)$$

The component potential introduces no new primary field: an equation of state or free-energy material evaluates it algebraically.

Using $\rho_\xi = \sum_\alpha \rho_\xi^\alpha = \phi_\xi \bar{\rho}_\xi$, the constituent-mass chain rule together with the density relation (83) and the component stationarity relation (96) gives the phase Euler identity

$$\hat{\mu}_\xi^\alpha = \psi_\xi + \frac{\pi_\xi^\alpha}{\phi_\xi \bar{\rho}_\xi \eta_\xi^\alpha}. \quad (175)$$

Appendix B gives the complete constituent-mass chain rule leading to (175). For solids, (174) and the material-stress relations convert the implicit elastic derivatives into the two stress-power terms in (172), so the same cancellation applies.

Only the within-phase differences of the single specific generalized transfer-work potential are fixed at this stage. Subtracting the reference-component form of (98) from its component- α form gives

$$\boxed{\begin{aligned} L_\xi^\alpha - L_\xi^N &= \frac{\pi_\xi^\alpha}{\phi_\xi \bar{\rho}_\xi \eta_\xi^\alpha} - \frac{\pi_\xi^N}{\phi_\xi \bar{\rho}_\xi \eta_\xi^N} \\ &= \hat{\mu}_\xi^\alpha - \hat{\mu}_\xi^N, \quad \alpha = 1, \dots, N-1. \end{aligned}} \quad (176)$$

The second equality subtracts the constituent derivatives (139); the common density and normalization terms cancel and leave the chemical-potential difference supplied by the composition restrictions (171) and (172). Consequently,

$$\left(\psi_\xi + L_\xi^\alpha + z_\xi^\alpha \varphi \right) - \left(\psi_\xi + L_\xi^N + z_\xi^N \varphi \right) = \mu_\xi^\alpha - \mu_\xi^N. \quad (177)$$

The generalized transfer potentials therefore retain the usual within-phase electrochemical-potential differences even though their absolute values need not equal the electrochemical potentials away from phase equilibrium. At nonuniform temperature the transport force uses the equivalent gauge-invariant split into a component-potential thermal gradient and the electric field, derived with the relative-transport force below.

Equations (98) and (175) also identify the common within-phase offset explicitly:

$$\left(\psi_\xi + L_\xi^\alpha + z_\xi^\alpha \varphi \right) - \mu_\xi^\alpha = \frac{D_\xi \tau}{Dt} - \frac{1}{2} \mathbf{v}_\xi \cdot \mathbf{v}_\xi. \quad (178)$$

The right-hand side is independent of the component index, which is the absolute counterpart of (177). Equivalently, every specific generalized transfer-work potential is closed by the explicit algebraic recovery

$$\boxed{L_\xi^\alpha = \hat{\mu}_\xi^\alpha - \psi_\xi + \frac{D_\xi \tau}{Dt} - \frac{1}{2} \mathbf{v}_\xi \cdot \mathbf{v}_\xi.} \quad (179)$$

The phase free-energy model supplies ψ_ξ and $\hat{\mu}_\xi^\alpha$, and the transfer-potential equation determines the component-independent offset $D_\xi \tau / Dt - \mathbf{v}_\xi \cdot \mathbf{v}_\xi / 2$.

To make the retained- τ system square, choose one solid phase $s_\star$ as the transfer reference. All solid phases follow the skeleton, so $D_{s_\star} / Dt = D_S / Dt$. The normalization

$$\psi_{s_\star} + L_{s_\star}^N = \hat{\mu}_{s_\star}^N, \quad s_\star \in \mathcal{S}. \quad (180)$$

fixes the common additive level of the specific transfer-work potentials. The reference-component form of (98) then supplies the single evolution equation

$$\begin{aligned} \frac{D_S \tau}{Dt} &= \frac{1}{2} \mathbf{v}_S \cdot \mathbf{v}_S + \hat{\mu}_{s_\star}^N - \psi_{s_\star} - \frac{\pi_{s_\star}^N}{\phi_{s_\star} \bar{\rho}_{s_\star} \eta_{s_\star}^N} \\ &= \frac{1}{2} \mathbf{v}_S \cdot \mathbf{v}_S, \quad s_\star \in \mathcal{S}. \end{aligned} \quad (181)$$

Equation (181) evolves τ by integration along each skeleton trajectory; for a stationary skeleton $D_S\tau/Dt = 0$ and τ retains its initial value. Appendix A states the corresponding additive normalization of that initial value. The second equality follows from (175); the expanded first line records the thermodynamic normalization used by the general phase equations. Once τ is known, the remaining $P - 1$ phase transfer-work potentials are recovered algebraically from

$$L_\xi^N = \frac{D_\xi\tau}{Dt} - \frac{1}{2}\mathbf{v}_\xi \cdot \mathbf{v}_\xi + \frac{\pi_\xi^N}{\phi_\xi \bar{\rho}_\xi \eta_\xi^N}, \quad \xi \neq s_\star. \quad (182)$$

Equation (179), or equivalently (176), then reconstructs every L_ξ^α with $\alpha \neq N$. Thus one scalar evolution determines τ , $P - 1$ algebraic equations determine the remaining phase transfer-work potentials, and the component-difference restrictions introduce no additional primary fields.

Substituting the component material-rate identity (31) into the temperature-weighted supply power separates conversion from transport relative to the phase,

$$\begin{aligned} & - \sum_{\mathcal{G} \in \{\mathcal{F}, \mathcal{S}\}} \frac{1}{\theta_{\mathcal{G}}} \sum_{\xi \in \mathcal{G}} \sum_{\alpha} \dot{c}_\xi^\alpha (\psi_\xi + L_\xi^\alpha) \\ & = - \sum_m \left[\sum_{\mathcal{G} \in \{\mathcal{F}, \mathcal{S}\}} \frac{1}{\theta_{\mathcal{G}}} \sum_{\xi \in \mathcal{G}} \sum_{\alpha} (\psi_\xi + L_\xi^\alpha) \nu_{\xi(m)}^\alpha \right] r_{(m)} \\ & \quad + \sum_{\mathcal{G} \in \{\mathcal{F}, \mathcal{S}\}} \sum_{\xi \in \mathcal{G}} \sum_{\alpha} \frac{\psi_\xi + L_\xi^\alpha}{\theta_{\mathcal{G}}} \nabla_{\mathbf{x}} \cdot (\mathbf{j}_{\xi, \text{disp}}^\alpha + \mathbf{j}_{\xi, \text{diff}}^\alpha). \end{aligned} \quad (183)$$

The traditional electrochemical affinity of mechanism m is

$$\mathcal{A}_{(m)} \equiv - \sum_{\xi} \sum_{\alpha} \mu_\xi^\alpha \nu_{\xi(m)}^\alpha. \quad (184)$$

For a mechanism satisfying (45), the explicit electrical term cancels from the affinity:

$$\begin{aligned} \mathcal{A}_{(m)} & = - \sum_{\xi} \sum_{\alpha} \mu_\xi^\alpha \nu_{\xi(m)}^\alpha \\ & = - \sum_{\xi} \sum_{\alpha} \hat{\mu}_\xi^\alpha \nu_{\xi(m)}^\alpha - \varphi \sum_{\xi} \sum_{\alpha} z_\xi^\alpha \nu_{\xi(m)}^\alpha \\ & = - \sum_{\xi} \sum_{\alpha} \hat{\mu}_\xi^\alpha \nu_{\xi(m)}^\alpha. \end{aligned} \quad (185)$$

Charge conservation for each mechanism cancels the common electric-potential term from its traditional affinity. Electrical effects nevertheless remain in the constitutive state dependence of $\hat{\mu}_\xi^\alpha$, in the field force on charged transport, and in electrochemical phase equilibrium.

Substituting the phase offset (178) into the generalized stoichiometric sum and using the affinity definition (184) gives

$$\mathcal{A}_{(m)} = - \sum_{\xi} \sum_{\alpha} (\psi_\xi + L_\xi^\alpha + z_\xi^\alpha \varphi) \nu_{\xi(m)}^\alpha + \sum_{\xi} \left(\frac{D_\xi\tau}{Dt} - \frac{1}{2}\mathbf{v}_\xi \cdot \mathbf{v}_\xi \right) \sum_{\alpha} \nu_{\xi(m)}^\alpha. \quad (186)$$

Equation (186) is an identity that expresses the conversion driving force in two equivalent representations. When the transfer-work term vanishes, the identity reduces to the usual generalized-coefficient representation of $\mathcal{A}_{(m)}$, whose value is fixed separately by the thermodynamic-equilibrium condition.

The transfer-work term is associated with net mass insertion into a phase; it vanishes for a chemical reaction that conserves mass separately within every phase and at full reversible equilibrium, and it contributes for phase-change, dissolution, precipitation, and pore-filling mechanisms that move net mass between phases.

For a mechanism confined to one thermal subsystem, the conversion contribution in (183) equals $\mathcal{A}_{(m)}r_{(m)}/\theta_{\mathcal{G}}$ when the mechanism conserves mass separately within every participating phase; a phase-changing mechanism retains the transfer-work term in (186). A fluid–solid mechanism spans two different temperatures, so its contribution is written as the temperature-weighted sum

$$-r_{(m)} \sum_{\mathcal{G} \in \{\mathcal{F}, \mathcal{S}\}} \frac{1}{\theta_{\mathcal{G}}} \sum_{\xi \in \mathcal{G}} \sum_{\alpha} (\psi_{\xi} + L_{\xi}^{\alpha}) \nu_{\xi(m)}^{\alpha}. \quad (187)$$

This neutral reaction contribution is gauge invariant for every mechanism; the charge-rate identity below records the corresponding gauge accounting. When a mechanism transfers net charge between the fluid and solid subsystems, the reaction-energy transfer is carried as a separate contribution, a local bulk representative-volume effect, and is coupled to the neutral reaction force through the mechanismwise admissibility condition of §5.4.4.

Multiplying the complete component-rate balance by $\varphi z_{\xi}^{\alpha}/\theta_{\mathcal{G}}$, applying the product rule to the relative charge flux, and summing gives the temperature-weighted charge-rate identity

$$\begin{aligned} 0 = & \sum_{\mathcal{G} \in \{\mathcal{F}, \mathcal{S}\}} \sum_{\xi \in \mathcal{G}} \sum_{\alpha} \left\{ \frac{\varphi z_{\xi}^{\alpha}}{\theta_{\mathcal{G}}} \left[\dot{c}_{\xi}^{\alpha} - \sum_m \nu_{\xi(m)}^{\alpha} r_{(m)} \right] \right. \\ & \left. + \frac{1}{\theta_{\mathcal{G}}} \nabla_{\mathbf{x}} \cdot \left[\varphi z_{\xi}^{\alpha} (\mathbf{j}_{\xi, \text{disp}}^{\alpha} + \mathbf{j}_{\xi, \text{diff}}^{\alpha}) \right] - \frac{z_{\xi}^{\alpha}}{\theta_{\mathcal{G}}} (\mathbf{j}_{\xi, \text{disp}}^{\alpha} + \mathbf{j}_{\xi, \text{diff}}^{\alpha}) \cdot \nabla_{\mathbf{x}} \varphi \right\}. \end{aligned} \quad (188)$$

Equation (188) is gauge invariant as a whole. Under $\varphi \mapsto \varphi + c_{\varphi}(t)$, its change is $c_{\varphi}(t)/\theta_{\mathcal{G}}$ times the complete charge-weighted component balance and therefore vanishes. The energy representation retains the direct, gauge-invariant relative-current work of (151), so the divergence and electric-field pieces of the identity enter the first law only through that combined work. The charge-rate identity therefore serves as an alternative accounting check, and the reaction coefficient is the neutral coefficient $\psi_{\xi} + L_{\xi}^{\alpha}$ for every mechanism. When charge is conserved separately within each thermal subsystem, the temperature-weighted stoichiometric sum may equivalently be written with electrochemical coefficients, because the added electrical sum vanishes. For charge transfer between subsystems, gauge invariance requires the neutral form; its physical reaction-energy transfer is coupled through the mechanismwise admissibility condition of §5.4.4.

In the local-thermal-equilibrium limit, $\theta_{\mathcal{F}} = \theta_{\mathcal{S}} = \theta$, total charge conservation permits the common electric-potential term to be restored inside the full stoichiometric sum, and this expression becomes

$$\begin{aligned} -r_{(m)} \sum_{\mathcal{G} \in \{\mathcal{F}, \mathcal{S}\}} \frac{1}{\theta_{\mathcal{G}}} \sum_{\xi \in \mathcal{G}} \sum_{\alpha} (\psi_{\xi} + L_{\xi}^{\alpha}) \nu_{\xi(m)}^{\alpha} &= -\frac{r_{(m)}}{\theta} \sum_{\xi} \sum_{\alpha} (\psi_{\xi} + L_{\xi}^{\alpha} + z_{\xi}^{\alpha} \varphi) \nu_{\xi(m)}^{\alpha} \\ &= \frac{r_{(m)}}{\theta} \left[\mathcal{A}_{(m)} - \sum_{\xi} \left(\frac{D_{\xi} \tau}{Dt} - \frac{1}{2} \mathbf{v}_{\xi} \cdot \mathbf{v}_{\xi} \right) \sum_{\alpha} \nu_{\xi(m)}^{\alpha} \right]. \end{aligned} \quad (189)$$

For phasewise mass-conserving chemistry, or when the transfer-work offsets vanish at reversible equilibrium, this is the usual affinity power $\mathcal{A}_{(m)}r_{(m)}/\theta$. Thus chemical conversion and interphase energy exchange remain distinct contributions to the two-temperature entropy inequality, as in

Drumheller's constituent formulation [21, eq. (88)]. Their closures may be uncoupled or Onsager-coupled, subject to the combined dissipation inequality and the interaction-energy conservation condition of §5.4.6.

The remaining part of (183) is the power of component transport relative to a phase. Select the same reference component N used in the Onsager calculation; the separate zero-sum convention (35) converts the full component sum to $N - 1$ independent potential differences. Combining the component-relative term already present in the entropy flux (157), the transport part of (183), and the direct relative-current work in (151), the product rule cancels the neutral flux divergence pointwise and leaves the electric-field work unchanged:

$$\begin{aligned}
& - \sum_{\mathcal{G} \in \{\mathcal{F}, \mathcal{S}\}} \sum_{\xi \in \mathcal{G}} \sum_{\alpha \neq N} \nabla_{\mathbf{x}} \cdot \left[\frac{\hat{\mu}_{\xi}^{\alpha} - \hat{\mu}_{\xi}^N}{\theta_{\mathcal{G}}} (\mathbf{j}_{\xi, \text{disp}}^{\alpha} + \mathbf{j}_{\xi, \text{diff}}^{\alpha}) \right] \\
& + \sum_{\mathcal{G} \in \{\mathcal{F}, \mathcal{S}\}} \sum_{\xi \in \mathcal{G}} \sum_{\alpha \neq N} \frac{\hat{\mu}_{\xi}^{\alpha} - \hat{\mu}_{\xi}^N}{\theta_{\mathcal{G}}} \nabla_{\mathbf{x}} \cdot (\mathbf{j}_{\xi, \text{disp}}^{\alpha} + \mathbf{j}_{\xi, \text{diff}}^{\alpha}) \\
& - \sum_{\mathcal{G} \in \{\mathcal{F}, \mathcal{S}\}} \sum_{\xi \in \mathcal{G}} \sum_{\alpha \neq N} \frac{z_{\xi}^{\alpha} - z_{\xi}^N}{\theta_{\mathcal{G}}} (\mathbf{j}_{\xi, \text{disp}}^{\alpha} + \mathbf{j}_{\xi, \text{diff}}^{\alpha}) \cdot \nabla_{\mathbf{x}} \varphi \\
& = - \sum_{\mathcal{G} \in \{\mathcal{F}, \mathcal{S}\}} \sum_{\xi \in \mathcal{G}} \sum_{\alpha \neq N} (\mathbf{j}_{\xi, \text{disp}}^{\alpha} + \mathbf{j}_{\xi, \text{diff}}^{\alpha}) \cdot \left[\nabla_{\mathbf{x}} \left(\frac{\hat{\mu}_{\xi}^{\alpha} - \hat{\mu}_{\xi}^N}{\theta_{\mathcal{G}}} \right) + \frac{z_{\xi}^{\alpha} - z_{\xi}^N}{\theta_{\mathcal{G}}} \nabla_{\mathbf{x}} \varphi \right].
\end{aligned} \tag{190}$$

The divergence terms are retained in the strong form and contribute the corresponding boundary fluxes in the integrated statement, while the product rule reduces the volume part to the local production density. The local entropy production from relative transport is

$$- \sum_{\mathcal{G} \in \{\mathcal{F}, \mathcal{S}\}} \sum_{\xi \in \mathcal{G}} \sum_{\alpha \neq N} (\mathbf{j}_{\xi, \text{disp}}^{\alpha} + \mathbf{j}_{\xi, \text{diff}}^{\alpha}) \cdot \left[\nabla_{\mathbf{x}} \left(\frac{\hat{\mu}_{\xi}^{\alpha} - \hat{\mu}_{\xi}^N}{\theta_{\mathcal{G}}} \right) + \frac{z_{\xi}^{\alpha} - z_{\xi}^N}{\theta_{\mathcal{G}}} \nabla_{\mathbf{x}} \varphi \right]. \tag{191}$$

After the zero-sum reduction, the first part is the standard neutral molecular-diffusion force in nonisothermal mixture thermodynamics [10, 11]; the second is the electric force per temperature. The complete force uses $\nabla_{\mathbf{x}} \varphi = -\mathbf{E}$ rather than the gauge-dependent combination $\varphi \nabla_{\mathbf{x}} (1/\theta_{\mathcal{G}})$, so it is invariant under $\varphi \mapsto \varphi + c_{\varphi}(t)$. The present theory adopts the same force for mechanical dispersion as a constitutive analogy to the molecular-diffusion force. At uniform local temperature, the two parts combine into $\nabla_{\mathbf{x}} (\mu_{\xi}^{\alpha} - \mu_{\xi}^N)/\theta_{\mathcal{G}}$. The observer and gauge rules collected in Appendix A confirm that the force is equivariant under the Euclidean observer transformation and invariant under $\varphi \mapsto \varphi + c_{\varphi}(t)$, since $c_{\varphi}(t)$ carries no spatial gradient.

5.4.2 Residual inequality

Plastic flow is driven by the material stress $\boldsymbol{\sigma}'_s$. Mapping $\boldsymbol{\sigma}'_s$ through the current distension and elastic true-deformation factors gives the stress conjugate to the true-plastic rate. Because true-plastic flow is isochoric, only the deviatoric part performs plastic work. Define that driving stress by

$$\mathbf{S}_s \equiv (\bar{\mathbf{F}}_s^e)^{-1} \mathbf{A}_s^{-1} \left((\boldsymbol{\sigma}'_s)^T - \frac{1}{3} \text{tr}(\boldsymbol{\sigma}'_s) \mathbf{I} \right) \mathbf{A}_s \bar{\mathbf{F}}_s^e, \quad s \in \mathcal{S}. \tag{192}$$

The trace of $\mathbf{S}_s$ vanishes, so it performs no work on a spherical plastic rate and is conjugate to the isochoric rate $\dot{\bar{\mathbf{F}}}_s^p (\bar{\mathbf{F}}_s^p)^{-1}$. Equation (192) extends Drumheller's deviatoric true-plastic driving stress through the phase distension map [21, eqs. (108)–(112)].

Applying the reversible pressure, stress, distension, composition, entropy, and common pore-volume relations from §5.3 removes their rate coefficients from (161). The saturation-redistribution term from (169) remains dissipative. The coordinate-stationarity relation (88) replaces its pressure-force differences by the generalized saturation-force differences; their common scalar performs no power because $\sum_f \dot{S}_f = 0$. The component-supply terms are then replaced by the temperature-weighted reaction and relative-transport powers derived in (187) and (191). Gauss' law was already used in the global field-power identity (150). The component charge balance constrains the admissible rates and is recorded by (188); its potential-dependent terms are accounted through that balance and the field-power identity, so charge accumulation and the field rate enter the residual only through the admissible rates.

The bulk-translation term is removed from the residual only through the ordering displayed in (162). Substituting that identity into the complete inequality first cancels the skeleton-rate free-energy contribution recovered from (161a)–(161c). The remaining member of the pair is the phase-following rate, whose fluid chain rule is (163). The reversible relations from §5.3 are then substituted into this reassembled form. Every term in (161e) is carried through the reassembly and settled by those reversible restrictions; the identity itself supplies the bulk-translation elimination.

This change of rate coordinates preserves the physical phase forces: pressure, capillary, Maxwell, body-force, inertia, and conversion-insertion powers remain in the phase momentum equations. The observer correction enters once, through the phase-following rate, and the reassembly absorbs the coefficient $\nabla_{\mathbf{x}}\psi_\xi + \mathfrak{s}_\xi \nabla_{\mathbf{x}}\theta_{\mathcal{G}}$ into that rate. The remaining bulk-translation constitutive mechanism is interphase mechanical interaction, whose dissipated power is converted to the internal-energy supplies below. What remains is the residual dissipation inequality

$$\begin{aligned}
0 \leq & \sum_m \left[- \sum_{\mathcal{G} \in \{\mathcal{F}, \mathcal{S}\}} \frac{1}{\theta_{\mathcal{G}}} \sum_{\xi \in \mathcal{G}} \sum_{\alpha} \left(\psi_\xi + L_\xi^\alpha \right) \nu_{\xi(m)}^\alpha \right] r_{(m)} \\
& + \frac{\phi}{\theta_{\mathcal{F}}} \sum_{f \in \mathcal{F}} \mathcal{L}_f^{\text{sat}} \dot{S}_f \\
& - \sum_{\mathcal{G} \in \{\mathcal{F}, \mathcal{S}\}} \sum_{\xi \in \mathcal{G}} \sum_{\alpha \neq N} \left(\mathbf{j}_{\xi, \text{disp}}^\alpha + \mathbf{j}_{\xi, \text{diff}}^\alpha \right) \cdot \left[\nabla_{\mathbf{x}} \left(\frac{\hat{\mu}_\xi^\alpha - \hat{\mu}_\xi^N}{\theta_{\mathcal{G}}} \right) + \frac{z_\xi^\alpha - z_\xi^N}{\theta_{\mathcal{G}}} \nabla_{\mathbf{x}} \varphi \right] \\
& - \frac{\phi}{\theta_{\mathcal{F}}} \frac{\partial \gamma}{\partial \mathbf{h}} \Big|_{\{S_f\}_{f \in \mathcal{F}, \theta_{\mathcal{F}}}} \cdot \dot{\mathbf{h}} \\
& + \frac{1}{\theta_{\mathcal{S}}} \sum_{s \in \mathcal{S}} \boldsymbol{\sigma}'_s : \mathbf{A}_s^e \dot{\mathbf{A}}_s^p (\mathbf{A}_s^p)^{-1} (\mathbf{A}_s^e)^{-1} \\
& + \frac{1}{\theta_{\mathcal{S}}} \sum_{s \in \mathcal{S}} \text{tr} \left[\mathbf{S}_s \dot{\mathbf{F}}_s^p (\bar{\mathbf{F}}_s^p)^{-1} \right] \\
& + \sum_{\mathcal{G} \in \{\mathcal{F}, \mathcal{S}\}} \frac{1}{\theta_{\mathcal{G}}} \sum_{\xi \in \mathcal{G}} \rho_\xi e_\xi^{\text{int}} - \sum_{\mathcal{G} \in \{\mathcal{F}, \mathcal{S}\}} \sum_{\xi \in \mathcal{G}} \frac{\mathbf{q}_\xi \cdot \nabla_{\mathbf{x}} \theta_{\mathcal{G}}}{\theta_{\mathcal{G}}^2}.
\end{aligned} \tag{193}$$

Equation (193) retains the saturation pressure-lag and capillary-history force–rate products together with the other dissipative mechanisms. The bulk velocity is set by the phase momentum balance together with the interphase drag law; pressure, capillarity, electrostatics, gravity, inertia, and conversion all drive a moving phase through those balances, and the residual inequality carries only the dissipative mechanisms listed. Chemical-potential differences drive component-relative diffusion and dispersion through (191) and remain distinct from the bulk drag force. Thermo-osmotic or other cross effects enter through an explicit positive-semidefinite coupled closure, separate from the

observer-conversion term in (159).

5.4.3 Dynamic pressure lag and capillary-history closures

The global Onsager statement (112) and its collected variation (114) include the independent saturation rates. The same generalized force supplies the d'Alembert work in (51), and coordinate stationarity identifies its phase differences through (88). Substitution of the Onsager closure (118) into the saturation term in (193) gives

$$\begin{aligned} \frac{\phi}{\theta_{\mathcal{F}}} \sum_{f \in \mathcal{F}} \mathcal{L}_f^{\text{sat}} \dot{S}_f \\ = \frac{\phi}{\theta_{\mathcal{F}}} \sum_{f \neq f_{\star}} \sum_{g \neq f_{\star}} \mathcal{T}_{fg} \dot{S}_f \dot{S}_g \geq 0. \end{aligned} \quad (194)$$

The nonnegativity holds for every saturation-rate vector when the resistance is symmetric and positive semidefinite:

$$\mathcal{T}_{fg} = \mathcal{T}_{gf}, \quad \sum_{f \neq f_{\star}} \sum_{g \neq f_{\star}} y_f \mathcal{T}_{fg} y_g \geq 0 \quad \text{for all real } \{y_f\}_{f \neq f_{\star}}. \quad (195)$$

For two fluid phases, take $f_{\star} = w$ and write $\mathcal{T}_{nw} \equiv \mathcal{T}_{nn}$. Equations (71) and (88), together with (118a) give

$$\boxed{\bar{p}_n - \bar{p}_w = p_{c,nw} + \omega_n^+ - \omega_w^+ + \mathcal{T}_{nw} \dot{S}_n, \quad \mathcal{T}_{nw} \geq 0, \quad (w, n) \in \mathcal{I}.} \quad (196)$$

Because $\dot{S}_n = -\dot{S}_w$, the final term may equivalently be written $-\mathcal{T}_{nw} \dot{S}_w$. Setting $\mathcal{T} = \mathbf{0}$ recovers the zero-rate electrocapillary relation obtained from (88). Imposing electrical neutrality as well gives (89). This closure adds rate dependence to the dissipative pressure response while the stored interfacial energy retains only its saturation and history dependence. The thermodynamic distinction between the phase-pressure difference and stored capillary pressure, followed by a linear saturation-rate closure, is developed by Hassanizadeh and Gray and Hassanizadeh, Celia, and Dahle [36, 35]. Laboratory measurements support rate-dependent pressure differences and show that the coefficient may depend on grain size and on the drainage–imbibition path [13, 44].

The reversible coordinate variation holds $\mathbf{h}$ fixed, so the capillary-history state has no Euler–Lagrange equation. Its skeleton-following rate is an internal dissipative rate. When it is uncoupled from the other residual mechanisms, a sufficient pointwise restriction is

$$0 \leq -\frac{\phi}{\theta_{\mathcal{F}}} \left. \frac{\partial \gamma}{\partial \mathbf{h}} \right|_{\{S_f\}_{f \in \mathcal{F}, \theta_{\mathcal{F}}}} \cdot \dot{\mathbf{h}}. \quad (197)$$

A material model supplies N_h evolution equations for $\mathbf{h}$ that satisfy (197), with $\dot{\mathbf{h}} = D_S \mathbf{h} / Dt$. Drainage–imbibition rules may use the saturation-rate direction to select loading or unloading and store reversal and trapping data in $\mathbf{h}$. Between switching events the state is continuous, so the capillary pressure may follow primary, secondary, and higher-order scanning paths [57]. The same history state may also enter a separately calibrated relative-permeability closure. Setting $N_h = 0$, or holding $\mathbf{h}$ fixed, recovers the single-valued stored capillary law and removes the history-dissipation term. The displayed dynamic and history laws are uncoupled. A joint Onsager block coupling $\dot{S}_f$ and $\dot{\mathbf{h}}$ is admissible when its symmetric resistance is positive semidefinite; loading–unloading switches may instead retain the present nonsmooth history rule. Coupled capillary, transport, and thermal kinetics are admissible when their combined force–rate form remains nonnegative.

5.4.4 Reaction and relative-transport closures

The source-carried energy in (149a) accounts for the energy of mass inserted into each recipient phase. Any additional reaction-associated internal-energy supply only reallocates energy among phases and must conserve mixture energy mechanism by mechanism:

$$\sum_{\xi} \rho_{\xi} e_{\xi}^{\text{int}} \Big|_{\text{rxn},(m)} = 0, \quad (198a)$$

$$\sum_{f \in \mathcal{F}} \rho_f e_f^{\text{int}} \Big|_{\text{rxn},(m)} = - \sum_{s \in \mathcal{S}} \rho_s e_s^{\text{int}} \Big|_{\text{rxn},(m)}. \quad (198b)$$

For a mechanism confined to one thermal subsystem, the reaction-associated allocation may be set to zero because the source-carried terms already enter that subsystem balance. For a mechanism spanning the two thermal subsystems, (198b) constitutively allocates the latent or reaction heat between the two subsystem balances.

Inequality (193) is the admissibility condition restricting the admissible kinetic laws. The quadratic Onsager potential in §4.3 supplies the following uncoupled near-equilibrium choice for any mechanism:

$$r_{(m)} = -K_{(m)} \left[\sum_{\mathcal{G} \in \{\mathcal{F}, \mathcal{S}\}} \frac{1}{\theta_{\mathcal{G}}} \sum_{\xi \in \mathcal{G}} \sum_{\alpha} \left(\psi_{\xi} + L_{\xi}^{\alpha} \right) \nu_{\xi(m)}^{\alpha} \right], \quad K_{(m)} > 0. \quad (199)$$

The force in (199) is gauge invariant. For a mechanism that conserves charge separately within each thermal subsystem, it may equivalently be evaluated with electrochemical coefficients. A mechanism that transfers charge between the thermal subsystems may couple its reaction rate to the physical reaction-energy transfer, but the pair must satisfy the mechanismwise condition

$$\begin{aligned} 0 \leq & \left[- \sum_{\mathcal{G} \in \{\mathcal{F}, \mathcal{S}\}} \frac{1}{\theta_{\mathcal{G}}} \sum_{\xi \in \mathcal{G}} \sum_{\alpha} \left(\psi_{\xi} + L_{\xi}^{\alpha} \right) \nu_{\xi(m)}^{\alpha} \right] r_{(m)} \\ & + \left(\frac{1}{\theta_{\mathcal{F}}} - \frac{1}{\theta_{\mathcal{S}}} \right) \sum_{f \in \mathcal{F}} \rho_f e_f^{\text{int}} \Big|_{\text{rxn},(m)}. \end{aligned} \quad (200)$$

The second term follows directly from the equal-and-opposite allocation in (198b). A positive-semidefinite Onsager matrix acting on these two force–rate pairs is one coupled closure; block-diagonal choices are also admissible when each term is nonnegative. Both forces are gauge invariant in the direct-field energy representation.

Stationarity with respect to the dispersion and diffusion fluxes gives

$$\sum_{\beta \neq N} \left(\mathbf{D}_{\xi, \text{disp}}^{-1} \right)^{\alpha\beta} \mathbf{j}_{\xi, \text{disp}}^{\beta} + \theta_{\mathcal{G}} \nabla_{\mathbf{x}} \left(\frac{\hat{\mu}_{\xi}^{\alpha} - \hat{\mu}_{\xi}^N}{\theta_{\mathcal{G}}} \right) + \left(z_{\xi}^{\alpha} - z_{\xi}^N \right) \nabla_{\mathbf{x}} \varphi = \mathbf{0}, \quad \xi \in \mathcal{G}, \quad \alpha \neq N, \quad (201)$$

$$\sum_{\beta \neq N} \left(\mathbf{D}_{\xi, \text{diff}}^{-1} \right)^{\alpha\beta} \mathbf{j}_{\xi, \text{diff}}^{\beta} + \theta_{\mathcal{G}} \nabla_{\mathbf{x}} \left(\frac{\hat{\mu}_{\xi}^{\alpha} - \hat{\mu}_{\xi}^N}{\theta_{\mathcal{G}}} \right) + \left(z_{\xi}^{\alpha} - z_{\xi}^N \right) \nabla_{\mathbf{x}} \varphi = \mathbf{0}, \quad \xi \in \mathcal{G}, \quad \alpha \neq N. \quad (202)$$

The diffusion row is the inverse-mobility form of the reduced $N - 1$ -component Fick–Onsager closure [10, 11]. For charged species, Dreyer, Gohlke, and Müller write the chemical-potential

gradient and electric force separately; under isothermal electrostatics their force combines into the electrochemical-potential difference used here [20]. The nonisothermal closure keeps those two parts separate: the absolute component potential is divided by $\theta_{\mathcal{G}}$ before differentiation, whereas the electric force is $(z_{\xi}^{\alpha} - z_{\xi}^N) \nabla_{\mathbf{x}} \varphi$. This ordering is required for electric-gauge invariance.

Solving these relations in the $N - 1$ independent flux coordinates gives

$$\mathbf{j}_{\xi, \text{disp}}^{\alpha} = - \sum_{\beta \neq N} \mathbf{D}_{\xi, \text{disp}}^{\alpha\beta} \left[\theta_{\mathcal{G}} \nabla_{\mathbf{x}} \left(\frac{\hat{\mu}_{\xi}^{\beta} - \hat{\mu}_{\xi}^N}{\theta_{\mathcal{G}}} \right) + (z_{\xi}^{\beta} - z_{\xi}^N) \nabla_{\mathbf{x}} \varphi \right], \quad \xi \in \mathcal{G}, \quad \alpha \neq N, \quad (203)$$

$$\mathbf{j}_{\xi, \text{diff}}^{\alpha} = - \sum_{\beta \neq N} \mathbf{D}_{\xi, \text{diff}}^{\alpha\beta} \left[\theta_{\mathcal{G}} \nabla_{\mathbf{x}} \left(\frac{\hat{\mu}_{\xi}^{\beta} - \hat{\mu}_{\xi}^N}{\theta_{\mathcal{G}}} \right) + (z_{\xi}^{\beta} - z_{\xi}^N) \nabla_{\mathbf{x}} \varphi \right], \quad \xi \in \mathcal{G}, \quad \alpha \neq N, \quad (204)$$

$$\mathbf{j}_{\xi, k}^N = - \sum_{\alpha \neq N} \mathbf{j}_{\xi, k}^{\alpha}, \quad k \in \{\text{disp}, \text{diff}\}. \quad (205)$$

The final row reconstructs the reference-component flux and enforces the separate zero-sum specialization (35). The reduced mobilities and their inverses act only on the $N - 1$ independent component coordinates. Consequently the laws use component-potential differences and the electric field and are invariant under both a common phasewise component-potential shift and $\varphi \mapsto \varphi + c_{\varphi}(t)$. At uniform temperature they reduce to the familiar electrochemical-potential-gradient form. Substitution of (199) and (205) into the reaction and transport part of (193) gives

$$\begin{aligned} & \sum_m \left[- \sum_{\mathcal{G} \in \{\mathcal{F}, \mathcal{S}\}} \frac{1}{\theta_{\mathcal{G}}} \sum_{\xi \in \mathcal{G}} \sum_{\alpha} (\psi_{\xi} + L_{\xi}^{\alpha}) \nu_{\xi(m)}^{\alpha} \right] r_{(m)} \\ & - \sum_{\mathcal{G} \in \{\mathcal{F}, \mathcal{S}\}} \sum_{\xi \in \mathcal{G}} \sum_{\alpha \neq N} (\mathbf{j}_{\xi, \text{disp}}^{\alpha} + \mathbf{j}_{\xi, \text{diff}}^{\alpha}) \cdot \left[\nabla_{\mathbf{x}} \left(\frac{\hat{\mu}_{\xi}^{\alpha} - \hat{\mu}_{\xi}^N}{\theta_{\mathcal{G}}} \right) + \frac{z_{\xi}^{\alpha} - z_{\xi}^N}{\theta_{\mathcal{G}}} \nabla_{\mathbf{x}} \varphi \right] \\ & = \sum_m \frac{r_{(m)}^2}{K_{(m)}} \\ & + \sum_{\mathcal{G} \in \{\mathcal{F}, \mathcal{S}\}} \frac{1}{\theta_{\mathcal{G}}} \sum_{\xi \in \mathcal{G}} \sum_{\alpha \neq N} \sum_{\beta \neq N} \mathbf{j}_{\xi, \text{disp}}^{\alpha} \cdot (\mathbf{D}_{\xi, \text{disp}}^{-1})^{\alpha\beta} \mathbf{j}_{\xi, \text{disp}}^{\beta} \\ & + \sum_{\mathcal{G} \in \{\mathcal{F}, \mathcal{S}\}} \frac{1}{\theta_{\mathcal{G}}} \sum_{\xi \in \mathcal{G}} \sum_{\alpha \neq N} \sum_{\beta \neq N} \mathbf{j}_{\xi, \text{diff}}^{\alpha} \cdot (\mathbf{D}_{\xi, \text{diff}}^{-1})^{\alpha\beta} \mathbf{j}_{\xi, \text{diff}}^{\beta} \geq 0. \end{aligned} \quad (206)$$

Thus the reaction and relative-transport terms are dissipative when each $\mathbf{D}_{\xi, k}$ is symmetric positive definite on the $N - 1$ independent component coordinates. Diffusion and dispersion may use different mobilities under the same gauge-invariant nonisothermal force; the neutral limit follows by setting $z_{\xi}^{\alpha} = 0$. Dispersion may depend on resolved flow and pore geometry [51, 31]. Reaction, diffusion, and dispersion may also be cross-coupled, provided their combined force-rate form remains nonnegative [18, 56]. When reaction and reaction-energy transfer are cross-coupled, their additional block must satisfy (200).

5.4.5 Plastic-flow closures

The two plastic powers in (193) admit the following uncoupled associated closures, analogous to Drumbheller's sufficient construction [21]. A plastic internal state vector $\mathbf{p}_s$ per solid phase carries hardening, softening, and rate dependence through the flow-rule mobilities; because the state set $\mathcal{X}_s$

contains the composition $\{\eta_s^\alpha\}$, these are single phase-level laws acting on the phase mixture as a whole rather than on individual components:

$$\dot{\bar{\mathbf{F}}}_s^p (\bar{\mathbf{F}}_s^p)^{-1} = \Lambda_{\bar{\mathbf{F}}_s}(\mathcal{X}_s, \mathbf{p}_s) (\mathbf{S}_s)^T, \quad s \in \mathcal{S}, \quad (207a)$$

$$\dot{\mathbf{A}}_s^p (\mathbf{A}_s^p)^{-1} = \Lambda_{\mathbf{A}_s}(\mathcal{X}_s, \mathbf{p}_s) (\mathbf{A}_s^e)^T \boldsymbol{\sigma}'_s (\mathbf{A}_s^e)^{-T}, \quad s \in \mathcal{S}, \quad (207b)$$

$$\dot{\mathbf{p}}_s = \mathbf{g}_s(\mathcal{X}_s, \mathbf{p}_s, \mathbf{S}_s, \boldsymbol{\sigma}'_s), \quad s \in \mathcal{S}, \quad (207c)$$

$$\Lambda_{\bar{\mathbf{F}}_s}(\mathcal{X}_s, \mathbf{p}_s) \geq 0, \quad s \in \mathcal{S}, \quad (207d)$$

$$\Lambda_{\mathbf{A}_s}(\mathcal{X}_s, \mathbf{p}_s) \geq 0, \quad s \in \mathcal{S}. \quad (207e)$$

Because $\text{tr } \mathbf{S}_s = 0$, the first closure preserves isochoric true-plastic flow. The nonnegative scalar mobilities make both plastic powers nonnegative separately. The mobilities depend on the equilibrium state set $\mathcal{X}_s$ and the plastic internal state vector $\mathbf{p}_s$, whose evolution (207c) carries hardening, softening, and rate dependence inside the plastic closure. The additive specialization retains these single phase-level laws. Coupled or non-associated plastic deformation–distension laws may replace (207), but their combined conjugate power in (193) must remain nonnegative. This combined criterion also permits a frictional dilation specialization: under compressive mean stress, plastic dilation gives a negative plastic-distension power that is supported by positive true-plastic dissipation. A shared rate constraint and stress-dependent dissipation can then retain normality in the generalized forces while producing a non-associated pressure-dependent rule after reduction to true-stress space [15].

5.4.6 Interphase mechanical interaction

The component-relative diffusion and dispersion fluxes were closed in §5.4.4. The interaction considered here is different: it is the momentum exchange caused by relative motion of the bulk phases. Conservation of total mixture energy requires the phase interaction supplies associated with mechanical momentum exchange to satisfy [22]

$$\sum_{\xi} \left(\rho_{\xi} e_{\xi}^{\text{int}} \Big|_{\text{mech}} + \mathbf{b}_{\xi} \cdot \mathbf{v}_{\xi} \right) = 0. \quad (208)$$

Here $\mathbf{b}_{\xi}$ is the momentum supplied to phase ξ , while $\rho_{\xi} e_{\xi}^{\text{int}} \Big|_{\text{mech}}$ is the associated internal-energy supply. The full e_{ξ}^{int} in the subsystem energy balance is the sum of this mechanical contribution, ordinary heat exchange, and any reaction-associated interphase energy transfer. The reversible solid and pore-volume constraint powers are absent because their coefficients have already vanished through (170); the saturation-redistribution power remains separately in (194). Because the free-energy convection term has been recombined with the phase-following reversible rate, the entropy contribution of this mechanism is the temperature-weighted mechanical internal-energy supply. When it is closed separately from reaction, plasticity, component-relative transport, and heat conduction, its sufficient thermodynamic admissibility condition is

$$\sum_{\mathcal{G} \in \{\mathcal{F}, \mathcal{S}\}} \frac{1}{\theta_{\mathcal{G}}} \sum_{\xi \in \mathcal{G}} \rho_{\xi} e_{\xi}^{\text{int}} \Big|_{\text{mech}} \geq 0. \quad (209)$$

The cited mixture theories support complementary parts of this construction, which (209) assembles. Drumheller and Bedford’s two-temperature inequality couples interaction-energy transfer to relative mechanical power, and together with their total energy balance it is the basis for requiring (208) and temperature-weighted interaction heating simultaneously [22, eq. (4.8)]. Gray’s porous-medium

inequalities pair solid-relative velocities with combined interaction and thermodynamic forces, and his slow-flow example closes the phase momentum through the pressure-gradient equation [30, eqs. (33), (37), (44), (47), and (77)]. Seguin and Walkington provide the closest common-temperature analogue, whose reduction yields a pressure-driven force balance, a drag law, and Darcy flow [52, eqs. (15), (32), (33), (35), (37), (40), and (41)]. Bothe and Dreyer make a related combined-force rearrangement for constituent diffusion in a common-temperature miscible fluid, a comparison that concerns diffusion and Gibbs–Duhem reduction [10, eqs. (88)–(93)].

Equation (209) and the energy-conservation identity (208) must hold simultaneously. A more general Onsager model may couple mechanical interaction heating to heat transfer or reaction; then nonnegativity of the coupled block is the operative requirement.

In a general multiphase closure, the momentum supply may be written as the sum of antisymmetric pairwise forces,

$$\mathbf{b}_\xi = \sum_{\zeta \neq \xi} \mathbf{b}_{\zeta\xi}, \quad \mathbf{b}_{\zeta\xi} = -\mathbf{b}_{\xi\zeta}, \quad (210)$$

where $\mathbf{b}_{\zeta\xi}$ is the force exerted on phase ξ by phase ζ . The pairwise mechanical power is therefore

$$\sum_{\xi < \zeta} \mathbf{b}_{\zeta\xi} \cdot (\mathbf{v}_\xi - \mathbf{v}_\zeta). \quad (211)$$

For a concrete reservoir-oriented closure, retain fluid–skeleton exchange, use the common solid velocity, and neglect direct fluid–fluid drag. The fluid and aggregate solid momentum supplies are prescribed by

$$\mathbf{b}_f = -\mathbf{k}_{fS}^{-1}(\mathbf{v}_f - \mathbf{v}_S), \quad f \in \mathcal{F}, \quad (212a)$$

$$\sum_{s \in \mathcal{S}} \mathbf{b}_s = -\sum_{f \in \mathcal{F}} \mathbf{b}_f, \quad (212b)$$

$$\mathbf{k}_{fS} = \mathbf{k}_{fS}^T > 0, \quad f \in \mathcal{F}. \quad (212c)$$

Equation (212a) is a purely dissipative drag law; the reversible pressure, capillary, Maxwell, body-force, inertia, and conversion-insertion terms remain in the phase momentum balance, and $\mathbf{b}_f$ carries only the dissipative drag. Here $\mathbf{y} \cdot \mathbf{k}_{fS}^{-1}\mathbf{y} > 0$ for every $\mathbf{y} \neq \mathbf{0}$. Because all solid phases have velocity $\mathbf{v}_S$, (212b) is sufficient to determine the total solid interaction power. A constituent model may partition the aggregate solid supply among the solid phases without changing the following result.

The associated internal-energy supplies are closed by

$$\rho_f e_f^{\text{int}} \Big|_{\text{mech}} = \frac{1}{2} (\mathbf{v}_f - \mathbf{v}_S) \cdot \mathbf{k}_{fS}^{-1} (\mathbf{v}_f - \mathbf{v}_S), \quad f \in \mathcal{F}, \quad (213a)$$

$$\sum_{s \in \mathcal{S}} \rho_s e_s^{\text{int}} \Big|_{\text{mech}} = \frac{1}{2} \sum_{f \in \mathcal{F}} (\mathbf{v}_f - \mathbf{v}_S) \cdot \mathbf{k}_{fS}^{-1} (\mathbf{v}_f - \mathbf{v}_S). \quad (213b)$$

Thus the nonnegative drag heating is divided equally between the fluid and solid thermal subsystems. This equal partition is a sufficient closure, not a required microscopic statement about where viscous heating occurs. Any other partition is admissible if it satisfies both (208) and (209). Summing (213a) and (213b), and using (212a) and (212b), gives

$$\sum_{\xi} \left(\rho_{\xi} e_{\xi}^{\text{int}} \Big|_{\text{mech}} + \mathbf{b}_{\xi} \cdot \mathbf{v}_{\xi} \right) = \sum_{f \in \mathcal{F}} \left[(\mathbf{v}_f - \mathbf{v}_S) \cdot \mathbf{k}_{fS}^{-1} (\mathbf{v}_f - \mathbf{v}_S) + \mathbf{b}_f \cdot (\mathbf{v}_f - \mathbf{v}_S) \right] = 0. \quad (214)$$

Hence (208) is satisfied exactly. Substitution of the same energy supplies into (209) leaves

$$\frac{1}{2} \sum_{f \in \mathcal{F}} \left(\frac{1}{\theta_{\mathcal{F}}} + \frac{1}{\theta_{\mathcal{S}}} \right) (\mathbf{v}_f - \mathbf{v}_{\mathcal{S}}) \cdot \mathbf{k}_{f\mathcal{S}}^{-1} (\mathbf{v}_f - \mathbf{v}_{\mathcal{S}}) \geq 0. \quad (215)$$

This proves the joint admissibility condition for arbitrary skeleton velocity: only the relative velocities enter. More general positive-semidefinite block closures may retain direct fluid–fluid drag or couple this mechanism to heat transfer, but (212)–(215) provide one complete local closure.

5.4.7 Thermal exchange and heat conduction

Ordinary heat exchange transfers internal energy between the fluid and solid thermal subsystems even when there is no phase-relative motion. It is distinct from the drag-generated heating above and from the reaction-associated energy exchange required by a charged cross-subsystem mechanism. The reaction-associated exchange remains paired with $r_{(m)}$ in the coupled closure described after (199); the heat-transfer coefficient below accounts for ordinary heat exchange.

A sufficient bulk fluid–solid heat-exchange law is

$$\begin{aligned} \sum_{f \in \mathcal{F}} \rho_f e_f^{\text{int}} \Big|_{\text{heat}} &= h_{\mathcal{FS}} (\theta_{\mathcal{S}} - \theta_{\mathcal{F}}), \\ \sum_{s \in \mathcal{S}} \rho_s e_s^{\text{int}} \Big|_{\text{heat}} &= -h_{\mathcal{FS}} (\theta_{\mathcal{S}} - \theta_{\mathcal{F}}), \quad h_{\mathcal{FS}} \geq 0. \end{aligned} \quad (216)$$

Together, the mechanical, ordinary-heat, and reaction-associated allocations give the explicit mixture cancellation

$$\begin{aligned} \sum_{\xi} \left(\rho_{\xi} e_{\xi}^{\text{int}} + \mathbf{b}_{\xi} \cdot \mathbf{v}_{\xi} \right) &= \sum_{\xi} \left(\rho_{\xi} e_{\xi}^{\text{int}} \Big|_{\text{mech}} + \mathbf{b}_{\xi} \cdot \mathbf{v}_{\xi} \right) \\ &\quad + \sum_{f \in \mathcal{F}} \rho_f e_f^{\text{int}} \Big|_{\text{heat}} + \sum_{s \in \mathcal{S}} \rho_s e_s^{\text{int}} \Big|_{\text{heat}} \\ &\quad + \sum_m \sum_{\xi} \rho_{\xi} e_{\xi}^{\text{int}} \Big|_{\text{rxn},(m)} \\ &= 0. \end{aligned} \quad (217)$$

The first group vanishes by (208), the second by (216), and each term in the final sum by (198a). Adding the global field-power identity (150) then completes the material-plus-field first-law accounting. The ordinary heat exchange contributes

$$h_{\mathcal{FS}} (\theta_{\mathcal{S}} - \theta_{\mathcal{F}}) \left(\frac{1}{\theta_{\mathcal{F}}} - \frac{1}{\theta_{\mathcal{S}}} \right) = h_{\mathcal{FS}} \frac{(\theta_{\mathcal{S}} - \theta_{\mathcal{F}})^2}{\theta_{\mathcal{F}} \theta_{\mathcal{S}}} \geq 0 \quad (218)$$

to the entropy production.

The simplest uncoupled closure represents the gauge-invariant material part of the nonadvective energy flux within phase $\xi \in \mathcal{G}$ by Fourier’s law,

$$\mathbf{q}_{\xi} = -\mathbf{K}_{\xi} \nabla_{\mathbf{x}} \theta_{\mathcal{G}}, \quad \xi \in \mathcal{G}, \quad \mathbf{K}_{\xi} = \mathbf{K}_{\xi}^T \geq 0, \quad (219)$$

where $\mathbf{y} \cdot \mathbf{K}_\xi \mathbf{y} \geq 0$ for every $\mathbf{y}$, and $\theta_{\mathcal{F}}, \theta_{\mathcal{S}} > 0$. More general closures may couple $\mathbf{q}_\xi$ to the component-relative thermodynamic forces, provided the combined heat-transport Onsager block remains positive semidefinite. The unresolved interfacial contribution is included in the fluid-subsystem sum $\sum_{f \in \mathcal{F}} \mathbf{q}_f$; no additional interfacial heat-flux field is introduced. The uncoupled closure gives the entropy contribution

$$- \sum_{\mathcal{G} \in \{\mathcal{F}, \mathcal{S}\}} \sum_{\xi \in \mathcal{G}} \frac{\mathbf{q}_\xi \cdot \nabla_{\mathbf{x}} \theta_{\mathcal{G}}}{\theta_{\mathcal{G}}^2} = \sum_{\mathcal{G} \in \{\mathcal{F}, \mathcal{S}\}} \sum_{\xi \in \mathcal{G}} \frac{\nabla_{\mathbf{x}} \theta_{\mathcal{G}} \cdot \mathbf{K}_\xi \nabla_{\mathbf{x}} \theta_{\mathcal{G}}}{\theta_{\mathcal{G}}^2} \geq 0. \quad (220)$$

The reaction and component-relative transport terms are controlled by (206); the fluid-skeleton interaction closure reduces the mechanical-interaction condition (209) to the nonnegative form (215); and ordinary heat exchange and conduction are controlled by (218) and (220). These are separate closures even though their entropy contributions appear in the same residual inequality.

5.5 Example mechanisms: reactions, phase transformations, sorption/desorption, and ion exchange

The mechanism index (m) covers any local conversion described by the phase/component stoichiometry $\nu_{\xi(m)}^\alpha$. The principal mechanism types differ only in whether conversion changes the component identity, the phase label, or both.

A true chemical reaction changes component identity. It may occur entirely within one phase or involve components from several phases. For example, aqueous carbonic-acid dissociation, $\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$, changes the aqueous component populations without transferring a component to another phase. On a molar progress basis, the signed molar coefficients are $(-1, +1, +1)$. If M_α denotes component molar mass, the mass coefficients used in the balance and affinity are

$$\begin{aligned} \left(\nu_{f(m)}^{\text{H}_2\text{CO}_3}, \nu_{f(m)}^{\text{H}^+}, \nu_{f(m)}^{\text{HCO}_3^-} \right) &= \left(-M_{\text{H}_2\text{CO}_3}, M_{\text{H}^+}, M_{\text{HCO}_3^-} \right), \\ \sum_{\alpha} \nu_{f(m)}^\alpha &= -M_{\text{H}_2\text{CO}_3} + M_{\text{H}^+} + M_{\text{HCO}_3^-} = 0, \\ \frac{1}{F_{\text{Far}}} \sum_{\alpha} z_f^\alpha \nu_{f(m)}^\alpha &= 0 + 1 - 1 = 0, \quad f \in \mathcal{F}. \end{aligned} \quad (221)$$

where $M_{\text{H}_2\text{CO}_3} = M_{\text{H}^+} + M_{\text{HCO}_3^-}$ and F_{Far} is the Faraday constant. Thus both mass and charge conservation are explicit before these coefficients enter the affinity and kinetic relations.

A pure phase transformation preserves component identity and changes only its phase label. Vaporization and condensation are examples. For a component g transferred from phase ξ to phase ζ , the one-to-one stoichiometry below uses a mass-progress basis: $r_{(m)}$ is mass transferred per current mixture volume per time, and the dimensionless mass yields are

$$\nu_{\zeta(m)}^g = 1, \quad \nu_{\xi(m)}^g = -1. \quad (222)$$

All other stoichiometric coefficients vanish. The corresponding affinity is

$$\mathcal{A}_{(m)} = \mu_\xi^g - \mu_\zeta^g. \quad (223)$$

The transformation can therefore change phase fractions and phase compositions even though the total mass of component g is unchanged. For the same charged component in both phases, charge conservation gives $z_\xi^g = z_\zeta^g$, so the explicit electric-potential terms cancel. The conversion power additionally contains the difference of the two phase-transfer offsets according to (186); it vanishes

at reversible phase equilibrium but need not vanish during a dynamic transformation with relative phase motion.

Sorption/desorption is treated by the same one-to-one transfer structure, with $\xi = f$ a mobile phase and $\zeta = s$ a solid phase whose constituents share the skeleton motion. It includes surface adsorption and bulk absorption without requiring those pore-scale processes to be represented separately. For a neutral component g , away from local thermal equilibrium an admissible kinetic law must satisfy

$$\left(\frac{\psi_f + L_f^g}{\theta_{\mathcal{F}}} - \frac{\psi_s + L_s^g}{\theta_{\mathcal{S}}} \right) r_{(m)} \geq 0, \quad f \in \mathcal{F}, \quad s \in \mathcal{S}. \quad (224)$$

Charged sorption that transfers net charge between the thermal subsystems uses the same gauge-invariant neutral reaction force and must satisfy (200); its reaction and reaction-energy rates may be Onsager-coupled. The sorbed amount η_s^g may also enter ψ_s , $\mathbf{A}_s^0$, $\bar{\mathbf{F}}_s^0$, and the plastic flow law. Thus adsorption, desorption, hydrate formation, and hydrate dissociation can change stiffness, swelling, compaction, and other solid properties through the evolving composition of the load-bearing phase.

Ion exchange is a coupled set of transfers between mobile ions and charged solid-site components. For example, calcium uptake accompanied by sodium release can be represented by $2\text{NaX}_s + \text{Ca}_f^{2+} \rightleftharpoons \text{CaX}_{2s} + 2\text{Na}_f^+$, where X^- denotes a monovalent solid exchange site, so NaX_s and CaX_{2s} are neutral solid components. The signed molar coefficients in the order $(\text{NaX}_s, \text{Ca}_f^{2+}, \text{CaX}_{2s}, \text{Na}_f^+)$ are $(-2, -1, +1, +2)$. The corresponding mass coefficients and conservation checks are

$$\begin{aligned} \left(\nu_{s(m)}^{\text{NaX}}, \nu_{f(m)}^{\text{Ca}^{2+}}, \nu_{s(m)}^{\text{CaX}_2}, \nu_{f(m)}^{\text{Na}^+} \right) &= (-2M_{\text{NaX}}, -M_{\text{Ca}^{2+}}, M_{\text{CaX}_2}, 2M_{\text{Na}^+}), \\ \sum_{\xi} \sum_{\alpha} \nu_{\xi(m)}^{\alpha} &= -2M_{\text{NaX}} - M_{\text{Ca}^{2+}} + M_{\text{CaX}_2} + 2M_{\text{Na}^+} = 0, \\ \frac{1}{F_{\text{Far}}} \sum_{\xi} \sum_{\alpha} z_{\xi}^{\alpha} \nu_{\xi(m)}^{\alpha} &= 0 - 2 + 0 + 2 = 0, \quad f \in \mathcal{F}, \quad s \in \mathcal{S}. \end{aligned} \quad (225)$$

Here $M_{\text{NaX}} = M_{\text{Na}^+} + M_{\text{X}}$ and $M_{\text{CaX}_2} = M_{\text{Ca}^{2+}} + 2M_{\text{X}}$. The mechanism therefore changes fluid composition and solid-site occupancy while satisfying both conservation restrictions. Its driving force is the corresponding electrochemical affinity; equilibrium or kinetic ion-exchange models provide the remaining closure.

5.6 Phase reaction-modified Biot coefficients

The entropy inequality gives the single-prime solid stress in intrinsic-density variables. Reservoir and poromechanics equations commonly use equivalent pore pressure as a controlled variable. A phase-level Legendre transform exchanges intrinsic specific volume for $\bar{p}_E$ and gives the corresponding double-prime stress [12]. We first apply this transformation to the general phase energy and then develop the additive component specialization.

The required current and reference specific volumes are

$$v_s = \frac{1}{\rho_s}, \quad v_{s0} = \frac{1}{\rho_{s0}}, \quad \bar{v}_s = \frac{1}{\bar{\rho}_s}, \quad \bar{v}_{s0} = \frac{1}{\bar{\rho}_{s0}}, \quad s \in \mathcal{S}. \quad (226)$$

The solid volume-fraction restriction identifies the thermodynamic variable conjugate to intrinsic specific volume,

$$\begin{aligned} \bar{p}_E &= \bar{p}_s - \omega_s^+ \\ &= - \left. \frac{\partial (\psi_s + \omega_s^+ \bar{v}_s)}{\partial \bar{v}_s} \right|_{\bar{\mathbf{F}}_s^e, \mathbf{A}_s^e, \{\eta_s^\alpha\}, \theta_s, \mathbf{E}}, \quad s \in \mathcal{S}, \end{aligned} \quad (227)$$

Here $\omega_s^+ \bar{v}_s$ is the electric enthalpy per unit intrinsic solid mass. Equation (227) gives $-\bar{p}_E$ as the coefficient of $d\bar{v}_s$ when the remaining state variables are fixed. The Legendre term $\bar{p}_E \bar{v}_s$ converts this coefficient into the pressure differential,

$$\begin{aligned} d\left(\psi_s + \omega_s^+ \bar{v}_s\right) \Big|_{\bar{\mathbf{F}}_s^e, \mathbf{A}_s^e, \{\eta_s^\alpha\}, \theta_S, \mathbf{E}} &= -\bar{p}_E d\bar{v}_s, \\ d\left(\psi_s + \omega_s^+ \bar{v}_s + \bar{p}_E \bar{v}_s\right) \Big|_{\bar{\mathbf{F}}_s^e, \mathbf{A}_s^e, \{\eta_s^\alpha\}, \theta_S, \mathbf{E}} &= \bar{v}_s d\bar{p}_E, \quad s \in \mathcal{S}. \end{aligned} \quad (228)$$

Thus $\bar{p}_E$ is conjugate to $\bar{v}_s$, and the phase pressure satisfies $\bar{p}_s = \bar{p}_E + \omega_s^+$. Define the transformed phase potential and its pressure derivative by

$$\tilde{\psi}_s = \psi_s + \omega_s^+ \bar{v}_s + \bar{p}_E \bar{v}_s, \quad s \in \mathcal{S}, \quad (229a)$$

$$\bar{v}_s = \frac{\partial \tilde{\psi}_s}{\partial \bar{p}_E} \Big|_{\bar{\mathbf{F}}_s^e, \mathbf{A}_s^e, \{\eta_s^\alpha\}, \theta_S, \mathbf{E}}, \quad s \in \mathcal{S}. \quad (229b)$$

At fixed equivalent pressure, the common skeleton Jacobian J parameterizes the specific-volume response. Through $J = a_s \bar{J}_s$, this response includes the concurrent allocation of volume between elastic true deformation and elastic distension. The Legendre identity and the kinematic split give

$$d\left[\tilde{\psi}_s - \left(\psi_s + \omega_s^+ \bar{v}_s\right)\right] \Big|_{\bar{p}_E, \theta_S, \{\eta_s^\alpha\}, \mathbf{E}} = \bar{p}_E \frac{\partial \bar{v}_s}{\partial J} \Big|_{\bar{p}_E, \theta_S, \{\eta_s^\alpha\}, \mathbf{E}} dJ, \quad s \in \mathcal{S}, \quad (230a)$$

$$dJ = a_s \bar{J}_s (\bar{\mathbf{F}}_s^e)^{-T} : d\bar{\mathbf{F}}_s^e + a_s \bar{J}_s (\mathbf{A}_s^e)^{-T} : d\mathbf{A}_s^e, \quad s \in \mathcal{S}. \quad (230b)$$

Equation (230a) evaluates the constitutive derivative with respect to the common volume. The kinematic identity (230b) resolves the corresponding differential into independent elastic true-deformation and elastic-distension contributions, with the plastic and stress-free states fixed. The coefficient of $d\bar{\mathbf{F}}_s^e$ determines the intrinsic Piola stress, and the coefficient of $d\mathbf{A}_s^e$ determines the distension force. The fixed-pressure derivative $\partial \bar{v}_s / \partial J$ contains the equilibrated response of a_s along this common-volume path. The Legendre identity gives two intrinsic Piola stresses. Differentiating the transformed potential at fixed $\bar{p}_E$ gives the single-prime stress and recovers its intrinsic-volume form. Differentiating the electrothermodynamic phase potential $\psi_s + \omega_s^+ \bar{v}_s$ along the same pressure path gives the double-prime stress,

$$\bar{\mathbf{P}}'_s = \bar{\rho}_{s0} \frac{\partial \tilde{\psi}_s}{\partial \bar{\mathbf{F}}_s^e} \Big|_{\bar{p}_E, \mathbf{A}_s^e, \theta_S, \{\eta_s^\alpha\}, \mathbf{E}}, \quad s \in \mathcal{S}, \quad (231a)$$

$$\bar{\rho}_{s0} \frac{\partial \tilde{\psi}_s}{\partial \bar{\mathbf{F}}_s^e} \Big|_{\bar{p}_E, \mathbf{A}_s^e, \theta_S, \{\eta_s^\alpha\}, \mathbf{E}} = \bar{\rho}_{s0} \frac{\partial \psi_s}{\partial \bar{\mathbf{F}}_s^e} \Big|_{\bar{v}_s, \mathbf{A}_s^e, \{\eta_s^\alpha\}, \theta_S, \mathbf{E}}, \quad s \in \mathcal{S}, \quad (231b)$$

$$\bar{\mathbf{P}}''_s = \bar{\rho}_{s0} \frac{\partial (\psi_s + \omega_s^+ \bar{v}_s)}{\partial \bar{\mathbf{F}}_s^e} \Big|_{\bar{p}_E, \mathbf{A}_s^e, \theta_S, \{\eta_s^\alpha\}, \mathbf{E}}, \quad s \in \mathcal{S}. \quad (231c)$$

To obtain the relation between the Piola stresses, set $d\mathbf{A}_s^e = \mathbf{0}$ in (230b). Substitute the resulting expression for dJ into (230a), then equate the coefficients of $d\bar{\mathbf{F}}_s^e$ using the stress definitions (231a) and (231c). This gives

$$\bar{\mathbf{P}}'_s = \bar{\mathbf{P}}''_s + \bar{p}_E \frac{a_s}{\bar{v}_{s0}} \frac{\partial \bar{v}_s}{\partial J} \Big|_{\bar{p}_E, \theta_S, \{\eta_s^\alpha\}, \mathbf{E}} \bar{J}_s (\bar{\mathbf{F}}_s^e)^{-T}, \quad s \in \mathcal{S}. \quad (232)$$

Define the phase nonlinear Biot coefficient by

$$\boxed{\bar{B}_s \equiv 1 - \frac{a_s}{\bar{v}_{s0}} \frac{\partial \bar{v}_s}{\partial J} \Big|_{\bar{p}_E, \theta_S, \{\eta_s^e\}, \mathbf{E}}}, \quad s \in \mathcal{S}. \quad (233)$$

The factor $1 - \bar{B}_s$ is the fraction of a common volumetric perturbation carried by the true-solid specific volume of phase s at the current reacted state. Its complement $\bar{B}_s$ measures the distension response. The factor a_s supplies the current allocation of skeleton volume to the phase, including packing and stress-free volume change. In the nonreacting single-solid specialization, aggregation of the intrinsic phase coefficient with the solid volume fraction and use of $a_s \phi_s = \phi_{s0}$ recover the nonlinear Biot coefficient of [25]. Substitution into (232) gives the intrinsic Piola-stress split,

$$\bar{\mathbf{P}}'_s = \bar{\mathbf{P}}''_s + (1 - \bar{B}_s) \bar{p}_E \bar{J}_s (\bar{\mathbf{F}}_s^e)^{-T}, \quad s \in \mathcal{S}. \quad (234)$$

Push-forward through the true volume ratio $\bar{J}_s$ and the distension map gives the intrinsic Cauchy stresses. Using $\bar{\rho}_{s0} = \bar{J}_s \bar{\rho}_s$ from (132), these maps are

$$\bar{\boldsymbol{\sigma}}'_s = \frac{1}{\bar{J}_s} \mathbf{A}_s^{-T} \bar{\mathbf{P}}'_s (\bar{\mathbf{F}}_s^e)^T \mathbf{A}_s^T, \quad s \in \mathcal{S}, \quad (235a)$$

$$\bar{\boldsymbol{\sigma}}''_s = \frac{1}{\bar{J}_s} \mathbf{A}_s^{-T} \bar{\mathbf{P}}''_s (\bar{\mathbf{F}}_s^e)^T \mathbf{A}_s^T, \quad s \in \mathcal{S}. \quad (235b)$$

Multiplication by the phase volume fraction gives the partial phase Cauchy stresses,

$$\boldsymbol{\sigma}'_s = \phi_s \bar{\boldsymbol{\sigma}}'_s, \quad \boldsymbol{\sigma}''_s = \phi_s \bar{\boldsymbol{\sigma}}''_s, \quad s \in \mathcal{S}. \quad (236)$$

Applying (235) and (236) to (234) converts the pressure correction into the partial Cauchy stress used in (166), giving

$$\boxed{\boldsymbol{\sigma}'_s = \boldsymbol{\sigma}''_s + \phi_s (1 - \bar{B}_s) \bar{p}_E \mathbf{I}}, \quad s \in \mathcal{S}. \quad (237)$$

Equation (237) applies to the general composition-dependent phase energy. The additive specialization in §5.8 resolves $\bar{B}_s$ and $\boldsymbol{\sigma}''_s$ into component contributions. The component pressure-redistribution path preserves the fixed- $\bar{p}_E$ derivative, and the resulting contributions sum to (233).

5.7 Solid phase and overall momentum from the Biot–Terzaghi effective-stress relation

The solid volume-fraction restriction gives the phase pressure in terms of the equivalent pore pressure $\bar{p}_E = -\lambda$,

$$\begin{aligned} \bar{p}_E &= -\lambda \\ &= \bar{p}_s - \omega_s^+, \quad s \in \mathcal{S}. \end{aligned} \quad (238)$$

Substituting the phase stress split into the solid momentum balance gives

$$\begin{aligned} \rho_s \mathbf{a}_s &= \nabla_{\mathbf{x}} \cdot \left[\boldsymbol{\sigma}''_s + \phi_s (1 - \bar{B}_s) \bar{p}_E \mathbf{I} + \boldsymbol{\sigma}_s^+ \right] - \phi_s \nabla_{\mathbf{x}} \bar{p}_E - \nabla_{\mathbf{x}} (\phi_s \omega_s^+) + \rho_s \mathbf{g} + \mathbf{b}_s \\ &\quad + \sum_{\alpha} \dot{c}_s^{\alpha} (\nabla_{\mathbf{x}} \tau - \mathbf{v}_s), \quad s \in \mathcal{S}. \end{aligned} \quad (239)$$

Plastic flow remains conjugate to $\boldsymbol{\sigma}'_s$. A constitutive model calibrated with the fixed-pressure stress $\boldsymbol{\sigma}''_s$ must first use (237) to reconstruct $\boldsymbol{\sigma}'_s$. Maxwell stress enters the momentum balance separately and affects plastic response indirectly through the resulting deformation and material stress.

After the solid partial stresses are summed, the solid-phase Biot terms combine as

$$\sum_{s \in \mathcal{S}} \boldsymbol{\sigma}'_s = \sum_{s \in \mathcal{S}} \boldsymbol{\sigma}''_s + \sum_{s \in \mathcal{S}} \phi_s (1 - \bar{B}_s) \bar{p}_E \mathbf{I}, \quad (240)$$

$$\boldsymbol{\sigma}'' \equiv \sum_{s \in \mathcal{S}} \boldsymbol{\sigma}''_s, \quad (241)$$

$$\boxed{B = 1 - \sum_{s \in \mathcal{S}} \phi_s (1 - \bar{B}_s)}. \quad (242)$$

Because the phase partial stresses are all measured per unit current skeleton volume, their pressure corrections add directly. The aggregate coefficient is therefore the combination in (242); in the single-solid limit it reduces to $B = 1 - \phi_s (1 - \bar{B}_s)$.

After summing the solid phase balances, the Biot-pressure and electrical parts in (239) can be rewritten using (241),

$$\begin{aligned} \sum_{s \in \mathcal{S}} \left[\nabla_{\mathbf{x}} \cdot \left(\phi_s (1 - \bar{B}_s) \bar{p}_E \mathbf{I} + \boldsymbol{\sigma}''_s \right) - \phi_s \nabla_{\mathbf{x}} \bar{p}_E - \nabla_{\mathbf{x}} \left(\phi_s \omega_s^+ \right) \right] \\ = \nabla_{\mathbf{x}} \cdot \left[-B \bar{p}_E \mathbf{I} + \sum_{s \in \mathcal{S}} \phi_s \mathbf{E} \otimes \mathbf{d}_s \right] + \left(1 - \sum_{s \in \mathcal{S}} \phi_s \right) \nabla_{\mathbf{x}} \bar{p}_E. \end{aligned} \quad (243)$$

Using the volume-fraction constraint, the coefficient of $\nabla_{\mathbf{x}} \bar{p}_E$ in the summed solid balance is the total fluid volume fraction $\phi = \sum_{f \in \mathcal{F}} \phi_f$.

For the summed fluid balance, apply the fluid stress restriction (146) to (103). Differentiating (92), using $\sum_f \nabla_{\mathbf{x}} S_f = \mathbf{0}$, and applying the saturation-derivative convention stated after (66) gives the interfacial state-gradient identity

$$\sum_{f \in \mathcal{F}} S_f \nabla_{\mathbf{x}} \gamma_f = \frac{\partial \gamma}{\partial \theta_{\mathcal{F}}} \Big|_{\{S_f\}_{f \in \mathcal{F}}, \mathbf{h}} \nabla_{\mathbf{x}} \theta_{\mathcal{F}} + (\nabla_{\mathbf{x}} \mathbf{h})^T \frac{\partial \gamma}{\partial \mathbf{h}} \Big|_{\{S_f\}_{f \in \mathcal{F}}, \theta_{\mathcal{F}}}. \quad (244)$$

Thus, writing $\phi_f = \phi S_f$, the summed fluid pressure and electrical terms give

$$\begin{aligned} \sum_{f \in \mathcal{F}} \left[\nabla_{\mathbf{x}} \cdot (\phi_f \mathbf{E} \otimes \mathbf{d}_f) - \phi_f \nabla_{\mathbf{x}} (\bar{p}_f - \omega_f^+) \right] &= \nabla_{\mathbf{x}} \cdot \left(\sum_{f \in \mathcal{F}} \phi_f \mathbf{E} \otimes \mathbf{d}_f \right) - \phi \nabla_{\mathbf{x}} \bar{p}_E \\ &\quad - \phi \frac{\partial \gamma}{\partial \theta_{\mathcal{F}}} \Big|_{\{S_f\}_{f \in \mathcal{F}}, \mathbf{h}} \nabla_{\mathbf{x}} \theta_{\mathcal{F}} \\ &\quad - \phi (\nabla_{\mathbf{x}} \mathbf{h})^T \frac{\partial \gamma}{\partial \mathbf{h}} \Big|_{\{S_f\}_{f \in \mathcal{F}}, \theta_{\mathcal{F}}} \\ &\quad + \phi \sum_{f \in \mathcal{F}} \left(\bar{p}_f - \bar{p}_E - \gamma_f - \omega_f^+ \right) \nabla_{\mathbf{x}} S_f. \end{aligned} \quad (245)$$

The final term follows from the common pore-volume restriction (170b). It vanishes in the reversible limit and carries the dynamic pressure lag through the summed momentum balance.

Adding the solid and fluid pressure terms and using $\sum_{\xi} \phi_{\xi} = 1$ and $\mathbf{d} = \sum_{\xi} \phi_{\xi} \mathbf{d}_{\xi}$ gives

$$\begin{aligned}
& \sum_{s \in \mathcal{S}} \left\{ \nabla_{\mathbf{x}} \cdot \left[\phi_s (1 - \bar{B}_s) \bar{p}_E \mathbf{I} + \boldsymbol{\sigma}_s^+ \right] - \phi_s \nabla_{\mathbf{x}} \bar{p}_E - \nabla_{\mathbf{x}} \left(\phi_s \omega_s^+ \right) \right\} \\
& + \sum_{f \in \mathcal{F}} \left[\nabla_{\mathbf{x}} \cdot (\phi_f \mathbf{E} \otimes \mathbf{d}_f) - \phi_f \nabla_{\mathbf{x}} (\bar{p}_f - \omega_f^+) \right] \\
& = \nabla_{\mathbf{x}} \cdot [-B \bar{p}_E \mathbf{I} + \mathbf{E} \otimes \mathbf{d}] \\
& - \phi \left. \frac{\partial \gamma}{\partial \theta_{\mathcal{F}}} \right|_{\{S_f\}_{f \in \mathcal{F}}, \mathbf{h}} \nabla_{\mathbf{x}} \theta_{\mathcal{F}} \\
& - \phi (\nabla_{\mathbf{x}} \mathbf{h})^T \left. \frac{\partial \gamma}{\partial \mathbf{h}} \right|_{\{S_f\}_{f \in \mathcal{F}}, \theta_{\mathcal{F}}} \\
& + \phi \sum_{f \in \mathcal{F}} (\bar{p}_f - \bar{p}_E - \gamma_f - \omega_f^+) \nabla_{\mathbf{x}} S_f.
\end{aligned} \tag{246}$$

The pairwise interaction forces cancel when all phase momentum balances are summed. Substituting (246) then gives the overall mixture momentum balance

$$\begin{aligned}
\sum_{\xi} \rho_{\xi} \mathbf{a}_{\xi} &= \nabla_{\mathbf{x}} \cdot [\boldsymbol{\sigma}'' - B \bar{p}_E \mathbf{I} + \mathbf{E} \otimes \mathbf{d}] + \rho \mathbf{g} + \sum_{\xi} \sum_{\alpha} \dot{c}_{\xi}^{\alpha} (\nabla_{\mathbf{x}} \boldsymbol{\tau} - \mathbf{v}_{\xi}) \\
& - \phi \left. \frac{\partial \gamma}{\partial \theta_{\mathcal{F}}} \right|_{\{S_f\}_{f \in \mathcal{F}}, \mathbf{h}} \nabla_{\mathbf{x}} \theta_{\mathcal{F}} \\
& - \phi (\nabla_{\mathbf{x}} \mathbf{h})^T \left. \frac{\partial \gamma}{\partial \mathbf{h}} \right|_{\{S_f\}_{f \in \mathcal{F}}, \theta_{\mathcal{F}}} \\
& + \phi \sum_{f \in \mathcal{F}} (\bar{p}_f - \bar{p}_E - \gamma_f - \omega_f^+) \nabla_{\mathbf{x}} S_f.
\end{aligned} \tag{247}$$

On a boundary portion where the phase virtual motions coincide with the common mixture virtual motion, the phase boundary powers add. Summing (100) and (104), then using (237), (242), (93), and $\boldsymbol{\sigma}'_f = \mathbf{0}$, gives the overall natural traction,

$$\begin{aligned}
\bar{\mathbf{t}} &\equiv \sum_{\xi} \mathbf{t}_{\xi} \\
&= \left\{ \sum_{s \in \mathcal{S}} [\boldsymbol{\sigma}'_s^+ - \phi_s (\bar{p}_E + \omega_s^+) \mathbf{I}] + \sum_{f \in \mathcal{F}} [\boldsymbol{\sigma}'_f^+ - \phi_f \bar{p}_f \mathbf{I}] \right\} \mathbf{n} \\
&= [\boldsymbol{\sigma}'' - B \bar{p}_E \mathbf{I} + \mathbf{E} \otimes \mathbf{d} - \phi \gamma \mathbf{I}] \mathbf{n} \quad \text{on } \Gamma_{\bar{\mathbf{t}}}.
\end{aligned} \tag{248}$$

The term $-\phi \gamma \mathbf{I}$ is the stored interfacial-energy contribution identified by the saturation-weighted phase-pressure relation. The thermocapillary, capillary-history-gradient, dynamic pressure-lag, and conversion terms in (247) remain bulk sources. Additional external-surface physics requires a separate surface model.

The term proportional to $\partial \gamma / \partial \theta_{\mathcal{F}}$ is the interfacial Gibbs–Duhem thermal contribution generated by the bulk free-energy aggregation. Indeed, $\mathfrak{s}_{\gamma} = -\partial \gamma / \partial \theta_{\mathcal{F}}$ is the interfacial entropy per current fluid-subsystem volume, so the sign agrees with the bulk Gibbs–Duhem identity [10, eq. (59)]. The contribution is therefore a bulk thermocapillary analogue of the sharp-interface Marangoni traction. In the sharp-interface description the Marangoni traction is the tangential surface force arising from gradients of surface tension along the interface; it is obtained from a surface momentum balance

using the interfacial normal and surface projector [38, 32]. The averaged description expresses the same physical effect through the bulk interfacial potential γ and the state variables $\theta_{\mathcal{F}}$, $\mathbf{h}$, and $\{S_f\}_{f \in \mathcal{F}}$, so the traction follows directly from the averaged state set. The bulk term vanishes in the isothermal limit or when the interfacial potential has no explicit temperature dependence. The capillary-history-gradient term records spatial variation of the drainage–imbibition state and vanishes when $\mathbf{h}$ is spatially uniform or γ is independent of it. The dynamic pressure-lag term vanishes when $\mathcal{T} = \mathbf{0}$ or when the saturation field is spatially uniform.

5.8 Additive solid component specialization

The general phase energy need not be additive. An additive representation is useful, however, when components share one solid motion but their stored-energy contributions can be distinguished. Examples include adsorbates and bound water in a mineral framework, lattice substitutions or defects, and guest occupancy in hydrate cages. The components share the solid velocity $\mathbf{v}_s$ and the phase-level elastic measures, the true deformation $\bar{\mathbf{F}}_s^e$ and the distension $\mathbf{A}_s^e$; the split applies only to the stored energy. Each component potential may depend on the full composition, so the model can retain nonideal interactions. When no meaningful component-energy split exists, the general phase energy (138) remains the appropriate model. The component decomposition below retains the phase electric enthalpy ω_s^+ and the equivalent pressure $\bar{p}_E = \bar{p}_s - \omega_s^+$. Electrical storage remains a phase-level constitutive quantity governed by (227)–(247).

Introduce component potentials ψ_s^α , intrinsic densities $\bar{\rho}_s^\alpha$, and pressures $\bar{p}_s^\alpha$. The component intrinsic densities and component solid volume fractions satisfy

$$\bar{\rho}_s = \sum_{\alpha} \phi_s^\alpha \bar{\rho}_s^\alpha, \quad s \in \mathcal{S}, \quad (249a)$$

$$\eta_s^\alpha = \frac{\phi_s^\alpha \bar{\rho}_s^\alpha}{\bar{\rho}_s}, \quad s \in \mathcal{S}, \quad (249b)$$

$$\phi_s^\alpha = \frac{\eta_s^\alpha \bar{\rho}_s}{\bar{\rho}_s^\alpha}, \quad \sum_{\alpha} \phi_s^\alpha = 1, \quad s \in \mathcal{S}. \quad (249c)$$

The additive phase energy is

$$\psi_s = \sum_{\alpha} \eta_s^\alpha \psi_s^\alpha(\bar{\mathbf{F}}_s^e, \mathbf{A}_s^e, \bar{\rho}_s^\alpha, \{\eta_s^\beta\}, \theta_s), \quad s \in \mathcal{S}. \quad (250)$$

Then the pressure average, stress, and distension restrictions become

$$\bar{p}_s = \sum_{\alpha} \phi_s^\alpha \bar{p}_s^\alpha, \quad s \in \mathcal{S}, \quad (251a)$$

$$\bar{\boldsymbol{\sigma}}'_s = \sum_{\alpha} \bar{\boldsymbol{\sigma}}_s'^{\alpha}, \quad s \in \mathcal{S}, \quad (251b)$$

$$\bar{\boldsymbol{\sigma}}_s'^{\alpha} = \phi_s^\alpha \bar{\rho}_s^\alpha \mathbf{A}_s^{-T} \left(\left. \frac{\partial \psi_s^\alpha}{\partial \bar{\mathbf{F}}_s^e} \right|_{\mathcal{X}_s} (\bar{\mathbf{F}}_s^e)^T \right) \mathbf{A}_s^T, \quad s \in \mathcal{S}, \quad (251c)$$

$$\bar{\boldsymbol{\sigma}}'_s = \bar{\rho}_s \sum_{\alpha} \eta_s^\alpha \left. \frac{\partial \psi_s^\alpha}{\partial \mathbf{A}_s^e} \right|_{\mathcal{X}_s} (\mathbf{A}_s^e)^T, \quad s \in \mathcal{S}. \quad (251d)$$

The corresponding partial phase stress is $\boldsymbol{\sigma}'_s = \phi_s \bar{\boldsymbol{\sigma}}'_s$, relating the intrinsic additive stresses to the momentum-balance stress (166). The storage multipliers provide the same component pressures. Since $\sum_{\alpha} \pi_s^\alpha / \phi_s = \bar{p}_s$, the additive model assigns component α the pressure share

$$\frac{\pi_s^\alpha}{\phi_s} = \phi_s^\alpha \bar{p}_s^\alpha, \quad \bar{p}_s^\alpha = \frac{\pi_s^\alpha}{\phi_s \phi_s^\alpha}, \quad s \in \mathcal{S}. \quad (252)$$

Summing over components recovers the phase pressure. Thus π_s^α and ϕ_s^α determine $\bar{p}_s^\alpha$ without introducing another pressure closure in the general additive energy representation.

The additive split of the stored energy does not extend to the plastic closure. The phase plastic law remains a single composition-dependent function of the solid phase: one mobility $\Lambda_{\mathbf{F}_s}$ and one $\Lambda_{\mathbf{A}_s}$ act on the phase plastic rates, and the composition $\{\eta_s^\alpha\}$ enters through the state set $\mathcal{X}_s$. Thus absorbed water, adsorbed species, or guest molecules modify the plastic response of the phase as a whole through the composition dependence of the common mobilities; the components share the single phase plastic deformation and its flow rule. The additive specialization therefore retains the phase-level closure of (207),

$$\dot{\mathbf{F}}_s^p (\bar{\mathbf{F}}_s^p)^{-1} = \Lambda_{\mathbf{F}_s}(\mathcal{X}_s, \mathbf{p}_s) (\mathbf{S}_s)^T, \quad s \in \mathcal{S}, \quad (253a)$$

$$\dot{\mathbf{A}}_s^p (\mathbf{A}_s^p)^{-1} = \Lambda_{\mathbf{A}_s}(\mathcal{X}_s, \mathbf{p}_s) (\mathbf{A}_s^e)^T \boldsymbol{\sigma}'_s (\mathbf{A}_s^e)^{-T}, \quad s \in \mathcal{S}. \quad (253b)$$

The mobilities are nonnegative as in (207d)–(207e), so each plastic power is separately dissipative, and the internal-state evolution follows (207c).

5.8.1 General additive component Biot decomposition

The additive Helmholtz energy admits a corresponding component decomposition of the phase electrical enthalpy. Introduce component electrical enthalpy densities $\omega_s^{\alpha+}$ satisfying

$$\psi_s + \omega_s^+ \bar{v}_s = \sum_{\alpha} \eta_s^\alpha \left(\psi_s^\alpha + \omega_s^{\alpha+} \bar{v}_s^\alpha \right), \quad s \in \mathcal{S}, \quad (254a)$$

$$\bar{v}_s = \sum_{\alpha} \eta_s^\alpha \bar{v}_s^\alpha, \quad \omega_s^+ = \sum_{\alpha} \phi_s^\alpha \omega_s^{\alpha+}, \quad s \in \mathcal{S}. \quad (254b)$$

The density rules (249) give $\eta_s^\alpha \bar{v}_s^\alpha = \phi_s^\alpha \bar{v}_s$, which establishes (254b). Combining this identity with the mechanical-pressure average (251a) gives the component equivalent pressures and their phase average,

$$\bar{p}_{E,s}^\alpha \equiv \bar{p}_s^\alpha - \omega_s^{\alpha+} = - \left. \frac{\partial (\psi_s^\alpha + \omega_s^{\alpha+} \bar{v}_s^\alpha)}{\partial \bar{v}_s^\alpha} \right|_{\bar{\mathbf{F}}_s^e, \mathbf{A}_s^e, \{\eta_s^\beta\}, \theta_S, \mathbf{E}}, \quad s \in \mathcal{S}, \quad (255a)$$

$$\bar{p}_E = \sum_{\alpha} \phi_s^\alpha \bar{p}_{E,s}^\alpha, \quad s \in \mathcal{S}. \quad (255b)$$

Each component may carry its own mechanical and equivalent pressures. The storage multipliers determine the mechanical-pressure shares through (252), and the component electrical enthalpies convert those shares to the conjugate equivalent pressures in (255a).

At fixed composition, the specific-volume conjugacy and its Legendre differential are

$$\begin{aligned} d \left(\psi_s^\alpha + \omega_s^{\alpha+} \bar{v}_s^\alpha \right) \Big|_{\bar{\mathbf{F}}_s^e, \mathbf{A}_s^e, \{\eta_s^\beta\}, \theta_S, \mathbf{E}} &= -\bar{p}_{E,s}^\alpha d\bar{v}_s^\alpha, \\ d \left(\psi_s^\alpha + \omega_s^{\alpha+} \bar{v}_s^\alpha + \bar{p}_{E,s}^\alpha \bar{v}_s^\alpha \right) \Big|_{\bar{\mathbf{F}}_s^e, \mathbf{A}_s^e, \{\eta_s^\beta\}, \theta_S, \mathbf{E}} &= \bar{v}_s^\alpha d\bar{p}_{E,s}^\alpha, \quad s \in \mathcal{S}. \end{aligned} \quad (256)$$

Since $\bar{p}_{E,s}^\alpha = \bar{p}_s^\alpha - \omega_s^{\alpha+}$, the transformed component potential has the equivalent forms

$$\tilde{\psi}_s^\alpha = \psi_s^\alpha + \omega_s^{\alpha+} \bar{v}_s^\alpha + \bar{p}_{E,s}^\alpha \bar{v}_s^\alpha = \psi_s^\alpha + \bar{p}_s^\alpha \bar{v}_s^\alpha, \quad s \in \mathcal{S}. \quad (257)$$

The form $\psi_s^\alpha + \bar{p}_s^\alpha \bar{v}_s^\alpha$ evaluates the transform directly from the component mechanical pressure. The transformed potential uses $\bar{p}_{E,s}^\alpha$ as its pressure variable, with $d\bar{p}_{E,s}^\alpha = d\bar{p}_s^\alpha - d\omega_s^{\alpha+}$.

Consider an instantaneous deformation at fixed composition, temperature, electric field, and component equivalent pressures. Along this path, the component Legendre identity gives

$$d \left[\tilde{\psi}_s^\alpha - \left(\psi_s^\alpha + \omega_s^{\alpha+} \bar{v}_s^\alpha \right) \right] \Big|_{\{\bar{p}_{E,s}^\beta\}, \theta_S, \{\eta_s^\beta\}, \mathbf{E}} = \bar{p}_{E,s}^\alpha \frac{\partial \bar{v}_s^\alpha}{\partial J} \Big|_{\{\bar{p}_{E,s}^\beta\}, \theta_S, \{\eta_s^\beta\}, \mathbf{E}} dJ, \quad s \in \mathcal{S}. \quad (258)$$

The double-prime component stress is the deformation response of the component electrothermodynamic potential at fixed component equivalent pressures,

$$\bar{\sigma}_s^{\prime\prime\alpha} \equiv \phi_s^\alpha \bar{\rho}_s^\alpha \mathbf{A}_s^{-T} \left[\frac{\partial \left(\psi_s^\alpha + \omega_s^{\alpha+} \bar{v}_s^\alpha \right)}{\partial \bar{\mathbf{F}}_s^e} \Big|_{\{\bar{p}_{E,s}^\beta\}, \mathbf{A}_s^e, \{\eta_s^\beta\}, \theta_S, \mathbf{E}} (\bar{\mathbf{F}}_s^e)^T \right] \mathbf{A}_s^T, \quad s \in \mathcal{S}. \quad (259)$$

For the component Piola-stress response, set $d\mathbf{A}_s^e = \mathbf{0}$ in (230b). Substitution of the resulting dJ into (258), followed by comparison of the coefficients of $d\bar{\mathbf{F}}_s^e$, gives the pressure contribution to the component Piola stress. The push-forward (235) converts this contribution to

$$\bar{\sigma}_s^{\prime\alpha} - \bar{\sigma}_s^{\prime\prime\alpha} = \bar{p}_{E,s}^\alpha \frac{a_s \eta_s^\alpha}{\bar{v}_{s0}} \frac{\partial \bar{v}_s^\alpha}{\partial J} \Big|_{\{\bar{p}_{E,s}^\beta\}, \theta_S, \{\eta_s^\beta\}, \mathbf{E}} \mathbf{I}, \quad s \in \mathcal{S}. \quad (260)$$

The additive specific-volume relation in (254b) gives the phase tangent along the same fixed-composition path,

$$\frac{\partial \bar{v}_s}{\partial J} \Big|_{\{\bar{p}_{E,s}^\beta\}, \theta_S, \{\eta_s^\beta\}, \mathbf{E}} = \sum_\alpha \eta_s^\alpha \frac{\partial \bar{v}_s^\alpha}{\partial J} \Big|_{\{\bar{p}_{E,s}^\beta\}, \theta_S, \{\eta_s^\beta\}, \mathbf{E}}, \quad s \in \mathcal{S}. \quad (261)$$

The corresponding component nonlinear Biot coefficient is

$$\boxed{\bar{B}_s^\alpha \equiv 1 - \frac{a_s \eta_s^\alpha}{\bar{v}_{s0}} \frac{\partial \bar{v}_s^\alpha}{\partial J} \Big|_{\{\bar{p}_{E,s}^\beta\}, \theta_S, \{\eta_s^\beta\}, \mathbf{E}}}, \quad s \in \mathcal{S}. \quad (262)$$

Summing the component coefficient complements and using (261) gives

$$\sum_\alpha (1 - \bar{B}_s^\alpha) = \frac{a_s}{\bar{v}_{s0}} \frac{\partial \bar{v}_s}{\partial J} \Big|_{\{\bar{p}_{E,s}^\beta\}, \theta_S, \{\eta_s^\beta\}, \mathbf{E}}, \quad s \in \mathcal{S}. \quad (263)$$

Equation (263) is the phase specific-volume tangent measured while every component equivalent pressure is fixed. It equals $1 - \bar{B}_s$ from (233) when the component equations of state map this experiment to a phase deformation at fixed $\bar{p}_E$. Each $\bar{B}_s^\alpha$ contributes to the intrinsic phase stress; multiplication of the summed intrinsic stress by ϕ_s gives the partial phase stress. Using (262) in (260) gives the component stress split,

$$\bar{\sigma}_s^{\prime\alpha} = \bar{\sigma}_s^{\prime\prime\alpha} + (1 - \bar{B}_s^\alpha) \bar{p}_{E,s}^\alpha \mathbf{I}, \quad s \in \mathcal{S}. \quad (264)$$

Summing the component stresses gives the phase double-prime stress and its pressure correction. Comparison with the phase stress split (237) then gives the pressure-weighted compatibility condition,

$$\bar{\sigma}_s^{\prime\prime} = \sum_\alpha \bar{\sigma}_s^{\prime\prime\alpha}, \quad s \in \mathcal{S}, \quad (265a)$$

$$\bar{\sigma}_s^{\prime} = \bar{\sigma}_s^{\prime\prime} + \sum_\alpha (1 - \bar{B}_s^\alpha) \bar{p}_{E,s}^\alpha \mathbf{I}, \quad s \in \mathcal{S}, \quad (265b)$$

$$(1 - \bar{B}_s) \bar{p}_E = \sum_\alpha (1 - \bar{B}_s^\alpha) \bar{p}_{E,s}^\alpha, \quad s \in \mathcal{S}. \quad (265c)$$

$$\boxed{\bar{B}_s = 1 - \frac{1}{\bar{p}_E} \sum_{\alpha} (1 - \bar{B}_s^{\alpha}) \bar{p}_{E,s}^{\alpha}, \quad \bar{p}_E \neq 0, \quad s \in \mathcal{S}.} \quad (265d)$$

For $\bar{p}_E \neq 0$, the boxed expression solves the pressure-weighted compatibility condition for $\bar{B}_s$. It gives the derivative-defined phase coefficient (233) when the component equations of state produce the fixed- $\bar{p}_E$ tangent described by (263). Thus the component equations of state specify how the component pressure contributions combine to recover the phase coefficient.

5.9 Scalar distension simplifications

For isotropic pore-structure change, each distension factor is spherical. This specialization retains volumetric accommodation but excludes anisotropic pore collapse and fabric evolution,

$$\mathbf{A}_s^e = (a_s^e)^{1/3} \mathbf{I}, \quad \mathbf{A}_s^p = (a_s^p)^{1/3} \mathbf{I}, \quad \mathbf{A}_s^0 = (a_s^0)^{1/3} \mathbf{I}, \quad s \in \mathcal{S}. \quad (266)$$

The factors multiply,

$$a_s = a_s^e a_s^p a_s^0, \quad s \in \mathcal{S}, \quad (267)$$

and the true solid deformation relation becomes

$$\mathbf{F} = a_s^{1/3} \bar{\mathbf{F}}_s, \quad J = a_s \bar{J}_s, \quad s \in \mathcal{S}. \quad (268)$$

The isotropic distension factors cancel from the push-forward in (166), leaving

$$\boldsymbol{\sigma}'_s = \rho_s \left. \frac{\partial \psi_s}{\partial \mathbf{F}_s^e} \right|_{\mathcal{X}_s} (\bar{\mathbf{F}}_s^e)^T, \quad s \in \mathcal{S}. \quad (269)$$

For a generic multicomponent solid, the tensor distension restriction (168) reduces to the trace condition

$$\frac{1}{3} \text{tr}(\boldsymbol{\sigma}'_s) = \rho_s \left. \frac{\partial \psi_s}{\partial a_s^e} \right|_{\mathcal{X}_s} a_s^e, \quad s \in \mathcal{S}. \quad (270)$$

Using the phase-level Biot–Terzaghi effective-stress relation, the same condition can be written as a restriction on the phase double-prime trace,

$$\frac{1}{3} \text{tr}(\boldsymbol{\sigma}''_s) = \rho_s \left. \frac{\partial \psi_s}{\partial a_s^e} \right|_{\mathcal{X}_s} a_s^e - \phi_s (1 - \bar{B}_s) \bar{p}_E, \quad s \in \mathcal{S}. \quad (271)$$

The same specialization reduces the plastic-distension power in (193) to

$$\sum_{s \in \mathcal{S}} \boldsymbol{\sigma}'_s : \mathbf{A}_s^e \dot{\mathbf{A}}_s^p (\mathbf{A}_s^p)^{-1} (\mathbf{A}_s^e)^{-1} = \sum_{s \in \mathcal{S}} \frac{1}{3} \text{tr}(\boldsymbol{\sigma}'_s) \frac{\dot{a}_s^p}{a_s^p}. \quad (272)$$

An associated scalar closure using the nonnegative plastic-distension mobility from (207e) is

$$\frac{\dot{a}_s^p}{a_s^p} = \Lambda_{\mathbf{A}_s}(\mathcal{X}_s, \mathbf{p}_s) \frac{1}{3} \text{tr}(\boldsymbol{\sigma}'_s), \quad s \in \mathcal{S}. \quad (273)$$

Its contribution to the plastic power is $\Lambda_{\mathbf{A}_s}[\text{tr}(\boldsymbol{\sigma}'_s)/3]^2 \geq 0$. Thus scalar plastic distension describes hydrostatic compaction or dilation, with the material mean stress as its conjugate force.

5.10 Distension and crystallization pressure

Crystallization affects momentum only through constitutive ingredients already present in the theory: the solid free energy, the precipitation kinetics, and the reaction affinity. This subsection specializes these ingredients to the scalar setting, in which the volumetric kinematics are

$$\ln J = \ln a_s + \ln \bar{J}_s, \quad s \in \mathcal{S}. \quad (274)$$

The scalar stress restriction depends on this total volumetric strain, so a simple transformed volumetric energy with skeleton bulk modulus $K_s^\star$ is

$$\widetilde{W}_{\text{vol},s} = \frac{K_s^\star}{2} (\ln J)^2, \quad s \in \mathcal{S}. \quad (275)$$

Holding $\bar{J}_s$ and $\bar{p}_E$ fixed,

$$a_s \left. \frac{\partial \widetilde{W}_{\text{vol},s}}{\partial a_s} \right|_{\bar{J}_s, \bar{p}_E} = K_s^\star \ln J, \quad s \in \mathcal{S}. \quad (276)$$

Its derivative gives the fixed-pressure mean stress,

$$\frac{1}{3} \text{tr}(\boldsymbol{\sigma}_s'') = K_s^\star \ln J, \quad s \in \mathcal{S}, \quad (277)$$

and the single-prime trace follows from the Biot–Terzaghi effective-stress relation,

$$\rho_s \left. \frac{\partial \psi_s}{\partial a_s^e} \right|_{\mathcal{X}_s} a_s^e = K_s^\star \ln J + \phi_s (1 - \bar{B}_s) \bar{p}_E, \quad s \in \mathcal{S}. \quad (278)$$

Thus the solid energy supplies a crystallization-induced stress through the same constitutive stress used in the momentum equation.

The precipitation affinity provides the complementary chemical condition. For a mechanism (m) that forms solid phase $s_{(m)}$,

$$\mathcal{A}_{(m)} = - \sum_{\xi} \sum_{\alpha} \mu_{\xi}^{\alpha} \nu_{\xi(m)}^{\alpha}. \quad (279)$$

The kinetic law is driven by the temperature-weighted stoichiometric sum in (199). In the local-thermal-equilibrium limit, its driving coefficient is the traditional affinity minus the explicit phase-transfer work in (186). The dissipation condition reduces to $\mathcal{A}_{(m)} r_{(m)} \geq 0$ when that transfer-work offset vanishes.

If a classical crystallization pressure $\bar{p}_{\text{xtal},s_{(m)}}$ is prescribed, it closes the affinity through the sign convention stated at the beginning of this section: Cauchy stress is tension-positive, so the positive compressive mean pressure acting on the forming solid is $-\text{tr}(\boldsymbol{\sigma}'_{s_{(m)}})/3$. Forming a unit mass of solid against that compression requires mechanical work equal to the specific volume times this compressive mean pressure. The displayed pressure-work term uses a mass-based progress variable whose stoichiometric coefficients are normalized by $\sum_{\alpha} \nu_{s_{(m)}(m)}^{\alpha} = 1$. For a solid mass yield different from unity, the pressure-work term is multiplied by that yield; on a molar progress basis, the specific volume $\bar{v}_{s_{(m)}}$ is replaced by the corresponding molar volume. The net chemical-minus-mechanical driving force is therefore

$$\mathcal{A}_{(m)} = \bar{v}_{s_{(m)}} \left[\bar{p}_{\text{xtal},s_{(m)}} + \frac{1}{3} \text{tr}(\boldsymbol{\sigma}'_{s_{(m)}}) \right], \quad \bar{v}_{s_{(m)}} = \frac{1}{\bar{\rho}_{s_{(m)}}}, \quad s_{(m)} \in \mathcal{S}. \quad (280)$$

For example, the classical supersaturation relation $\bar{p}_{\text{xtal},s(m)} = R\theta_{\mathcal{F}} \ln \Omega_{(m)}/V_{s(m)}$ expresses the crystallization pressure in terms of the gas constant R , the supersaturation ratio $\Omega_{(m)}$, and the molar volume $V_{s(m)}$ of the precipitating solid. The fluid temperature $\theta_{\mathcal{F}}$ is used because supersaturation and the fluid–solid precipitation mechanism are evaluated in the mobile subsystem. Substituting this relation gives

$$\mathcal{A}_{(m)} = \bar{v}_{s(m)} \left[\frac{R\theta_{\mathcal{F}}}{V_{s(m)}} \ln \Omega_{(m)} + \frac{1}{3} \text{tr} \left(\boldsymbol{\sigma}'_{s(m)} \right) \right], \quad s(m) \in \mathcal{S}. \quad (281)$$

At full reversible equilibrium, $\theta_{\mathcal{F}} = \theta_{\mathcal{S}}$ and $\mathcal{A}_{(m)} = 0$, so the chemical crystallization pressure equals the positive compressive phase mean pressure $-\text{tr}(\boldsymbol{\sigma}'_{s(m)})/3$ permitted by the constitutive law. Equivalently, the equilibrium supersaturation is

$$\Omega_{(m)}^{\text{eq}} = \exp \left[-\frac{V_{s(m)} \text{tr} \left(\boldsymbol{\sigma}'_{s(m)} \right)}{3R\theta_{\mathcal{F}}} \right], \quad s(m) \in \mathcal{S}. \quad (282)$$

The stress-free limit gives $\Omega_{(m)}^{\text{eq}} = 1$, whereas compression raises the equilibrium threshold. Under local thermal equilibrium and a vanishing phase-transfer offset, (199) gives $r_{(m)} = K_{(m)}\mathcal{A}_{(m)}/\theta$; therefore $\Omega_{(m)} > \Omega_{(m)}^{\text{eq}}$ drives precipitation and $\Omega_{(m)} < \Omega_{(m)}^{\text{eq}}$ drives dissolution. If stress and affinity are solved simultaneously, $\Omega_{(m)}$ is an output rather than an independently prescribed load.

6 Multicomponent model summary

This section records bulk pointwise unknown and equation counts for a reduced, fully implicit active-phase formulation under the closures stated below. These counts are not a complete boundary-value-problem specification. One mass fraction per phase and one phase volume fraction are reconstructed from (95) and (16). Subtracting the component stationarity equations eliminates the composition-normalization multipliers Π_{ξ} through (97), and the storage multipliers π_{ξ}^{α} then follow from that difference system and the phase-sum relation (83). Phase pressures and electrochemical potentials are likewise evaluated from the constitutive restrictions.

The normalization (180) fixes the reference-solid value of the specific transfer-work potential. One equation (181) evolves the shared transfer potential τ , and the $P - 1$ equations (182) determine the transfer-work potentials L_{ξ}^N of the remaining phases. The component differences (176), equivalently the full recovery (179), reconstruct L_{ξ}^{α} , $\alpha \neq N$, as algebraically recovered variational coefficients rather than primary fields or freely prescribed constitutive functions.

Initial and boundary data, potential gauges, pure-Neumann compatibility conditions, and switching conditions for phase or component appearance are not included in the pointwise counts. A charged reaction that transfers charge between thermal subsystems retains the scalar neutral-force kinetic row. Its reaction-energy transfer may be Onsager-coupled subject to (200); the displayed rate count is unchanged unless a chosen closure introduces additional internal variables. The plastic internal state vector $\mathbf{p}_s$ with evolution (207c) is one such addition, contributing additional components per solid phase to the count.

Both relative-flux families, the phase heat fluxes, the fluid–skeleton interaction forces, and the independent fluid–solid heat-exchange supply are retained as auxiliary fields so that their closures appear explicitly in the count. The closure (212) retains one fluid–skeleton interaction force per fluid phase. The aggregate solid force then follows from (212b). The general pairwise representation (210) remains available for constitutive extensions and is not included in the present count. The total solid scalar distension factors are closed kinematically by (134), while the scalar plastic factors a_s^p follow

(273). The electroquasistatic formulation includes the electric potential and Gauss' law. Mechanical interaction-energy supplies are constitutive outputs associated with the interaction forces and must satisfy (208) and (209); they are therefore not counted as an independent field family. The phase entropies and internal energies and the interfacial quantities $\mathfrak{s}_\gamma$ and u_γ are algebraically evaluated from (141)–(143) and (173). They introduce no additional primary fields or evolution equations. Let $P_{\mathcal{F}} = |\mathcal{F}|$, $P_{\mathcal{S}} = |\mathcal{S}|$, and $P = P_{\mathcal{F}} + P_{\mathcal{S}}$. Let $N^{\mathcal{F}}$ be the number of tracked components in each fluid phase and $N^{\mathcal{S}}$ the number of tracked components in each solid phase. If the component counts vary by phase, the products in the tables are replaced by the corresponding phase sums. Let $N_{(m)}$ be the number of independent conversion mechanisms and d the spatial dimension. The number of continuous capillary-history variables is N_h . The dynamic pressure-lag resistance $\mathcal{T}$ is constitutive, and the saturation rates are obtained from the independent phase volume fractions, so the optional closure introduces no additional pointwise unknown family.

Table 1: Bulk unknown families for a fully implicit active-phase pointwise discretization.

Unknown family	Count
Fluid-phase displacements and the common solid-skeleton displacement	$d(P_{\mathcal{F}} + 1)$
Intrinsic phase densities $\bar{\rho}_\xi$ for $\xi = 1, \dots, P$	P
Independent fluid and solid mass fractions	$P_{\mathcal{F}}(N^{\mathcal{F}} - 1) + P_{\mathcal{S}}(N^{\mathcal{S}} - 1)$
Independent phase volume fractions	$P - 1$
Capillary-history variables $\mathbf{h}$	N_h
Volume-fraction multiplier λ	1
Transfer potential τ	1
Non-reference specific transfer-work potentials L_ξ^N , $\xi \neq s_\star$	$P - 1$
Dispersion and diffusion component-flux vectors	$2d[P_{\mathcal{F}}(N^{\mathcal{F}} - 1) + P_{\mathcal{S}}(N^{\mathcal{S}} - 1)]$
Fluid–skeleton interaction-force vectors $\mathbf{b}_f$, $f \in \mathcal{F}$	$dP_{\mathcal{F}}$
Phase nonadvective energy-flux vectors $\mathbf{q}_\xi$	dP
Independent fluid–solid heat-exchange supply	1
Scalar solid distension factors a_s , for $s = 1, \dots, P_{\mathcal{S}}$	$P_{\mathcal{S}}$
Mechanism process rates $r_{(1)}, \dots, r_{(N_{(m)})}$	$N_{(m)}$
Solid plastic internal variables $\bar{\mathbf{F}}_s^p$ and a_s^p for inelastic response	$(d^2 + 1)P_{\mathcal{S}}$
Fluid and solid temperatures $\theta_{\mathcal{F}}$, $\theta_{\mathcal{S}}$	2
Electric potential φ	1
	$d(P_{\mathcal{F}} + 1) + 2d[P_{\mathcal{F}}(N^{\mathcal{F}} - 1) + P_{\mathcal{S}}(N^{\mathcal{S}} - 1)] + dP$
Total:	$+ dP_{\mathcal{F}} + (d^2 + 1)P_{\mathcal{S}}$
	$+ P_{\mathcal{F}}N^{\mathcal{F}} + P_{\mathcal{S}}N^{\mathcal{S}} + 2P + P_{\mathcal{S}} + N_{(m)} + N_h + 4$

The corresponding equation blocks are listed in Table 2.

Table 2: Bulk equation blocks and closure counts for the active-phase formulation.

Equation block	Count
Fluid-phase momentum balances (103) and overall momentum balance (247)	$d(P_{\mathcal{F}} + 1)$
Component mass balances (29)	$P_{\mathcal{F}}N^{\mathcal{F}} + P_{\mathcal{S}}N^{\mathcal{S}}$
Dispersion and diffusion closures (205)	$2d[P_{\mathcal{F}}(N^{\mathcal{F}} - 1) + P_{\mathcal{S}}(N^{\mathcal{S}} - 1)]$
Fluid–skeleton drag closures (212a); aggregate solid force from (212b) and energy allocation from (213)	$dP_{\mathcal{F}}$
Fourier nonadvective energy-flux closures (219)	dP
Fluid–solid heat-exchange closure (216)	1
Solid-phase and total-fluid pore-volume restrictions (170)	$P_{\mathcal{S}} + 1$
Dynamic pressure-lag relations (118)	$P_{\mathcal{F}} - 1$
Capillary-history evolution laws satisfying (197)	N_h
Reference-component evolution of τ from (181)	1
Non-reference specific transfer-work-potential recovery (182)	$P - 1$
Solid distension evolution laws (134)	$P_{\mathcal{S}}$
Kinetic laws for $r_{(m)}$, for example (199)	$N_{(m)}$
Plastic deformation law (207a) for $\mathbf{F}_s^p$ and scalar plastic-distension law (273) for a_s^p	$(d^2 + 1)P_{\mathcal{S}}$
Fluid and solid energy equations with skeleton-relative internal-energy transport and relative-current electric work (151), supplemented by the field-power identity (150)	2
Gauss’ law (107)	1
	$d(P_{\mathcal{F}} + 1) + 2d[P_{\mathcal{F}}(N^{\mathcal{F}} - 1) + P_{\mathcal{S}}(N^{\mathcal{S}} - 1)] + dP$
Total:	$+ dP_{\mathcal{F}} + (d^2 + 1)P_{\mathcal{S}}$
	$+ P_{\mathcal{F}}N^{\mathcal{F}} + P_{\mathcal{S}}N^{\mathcal{S}} + 2P + P_{\mathcal{S}} + N_{(m)} + N_h + 4$

For a single-component solid phase, the normalization fixes $\eta_s^s = 1$; no solid composition coordinate or composition-normalization multiplier is retained. Equation (262) then gives $\bar{B}_s^s = \bar{B}_s$. The one-component limit removes only the independent composition rate: the phase retains its stress-free thermal maps, plastic and distension variables, and conversion sources. For one solid phase, (242) gives $B = 1 - \phi_s(1 - \bar{B}_s)$, and the common-skeleton momentum equation is (247).

7 Solid-reference form for porous media modeling

This section rewrites the transport and mechanics equations in a form suitable for solution on the trajectory of the solid skeleton. The solid motion χ supplies the map from the solid reference coordinate $\mathbf{X}$ to the current coordinate $\mathbf{x}$, with deformation gradient $\mathbf{F}$ and Jacobian J .

7.1 Relative flux vectors

The phase momentum equation with dynamic pressure lag (103) determines Darcy-scale relative fluxes once interphase drag is written in terms of a velocity relative to the solid skeleton. For each

fluid phase f , define the current relative mass flux by

$$\mathbf{w}_f = \phi_f \bar{\rho}_f (\mathbf{v}_f - \mathbf{v}_S) = \rho_f (\mathbf{v}_f - \mathbf{v}_S), \quad f \in \mathcal{F}. \quad (283)$$

Thus

$$\mathbf{v}_f = \mathbf{v}_S + \frac{\mathbf{w}_f}{\rho_f}, \quad f \in \mathcal{F}. \quad (284)$$

A sufficient fluid–skeleton interaction closure consistent with (212) is

$$\mathbf{b}_f = -\frac{\mu_f^{\text{visc}} \phi_f}{\bar{\rho}_f} \boldsymbol{\kappa}_f^{-1} \mathbf{w}_f, \quad f \in \mathcal{F}. \quad (285)$$

Here μ_f^{visc} is the dynamic viscosity and $\boldsymbol{\kappa}_f$ is the permeability tensor for phase f . Phase relative permeability may be absorbed into $\boldsymbol{\kappa}_f$ and may use the same capillary-history state $\mathbf{h}$ when relative-permeability hysteresis is retained. Equation (285) contains only dissipative drag; all reversible driving forces remain in the phase momentum balance. From (283), the two drag tensors are related by $\mathbf{k}_{fS}^{-1} = \phi_f^2 \mu_f^{\text{visc}} \boldsymbol{\kappa}_f^{-1}$. Thus positive definiteness of $\boldsymbol{\kappa}_f$, together with the interaction-energy allocation (213), makes (209) nonnegative.

Substituting (284) and (285) into the fluid momentum balance (103) gives, for each fluid phase,

$$\begin{aligned} \frac{1}{\rho_f} \left(\phi_f^2 \mu_f^{\text{visc}} \boldsymbol{\kappa}_f^{-1} + \sum_{\alpha} \dot{c}_f^{\alpha} \mathbf{I} \right) \mathbf{w}_f &= \rho_f (\mathbf{g} - \mathbf{a}_f) - \phi_f \nabla_{\mathbf{x}} (\bar{p}_f - \omega_f^+) \\ &+ \nabla_{\mathbf{x}} \cdot (\phi_f \mathbf{E} \otimes \mathbf{d}_f) + \sum_{\alpha} \dot{c}_f^{\alpha} (\nabla_{\mathbf{x}} \tau - \mathbf{v}_S), \quad f \in \mathcal{F}, \end{aligned} \quad (286)$$

By the component mass balance and the separate zero-sum closure for the component-relative fluxes, the scalar $\sum_{\alpha} \dot{c}_f^{\alpha}$ is the net phase-mass source due to conversion. It enters the phase momentum balance as a source coefficient weighting the conversion-driven relative-flow term there. The component-relative transport itself is closed through (205).

To solve the preceding linear system for $\mathbf{w}_f$, invert the coefficient multiplying that flux. Define the resulting conversion-corrected mobility tensor by

$$\tilde{\boldsymbol{\lambda}}_f = \left(\phi_f^2 \mu_f^{\text{visc}} \boldsymbol{\kappa}_f^{-1} + \sum_{\alpha} \dot{c}_f^{\alpha} \mathbf{I} \right)^{-1}, \quad f \in \mathcal{F}. \quad (287)$$

The resistance inside the inverse has units $\text{kg m}^{-3} \text{s}^{-1}$, and $\tilde{\boldsymbol{\lambda}}_f$ therefore has units $\text{m}^3 \text{s kg}^{-1} = \text{m}^2 \text{Pa}^{-1} \text{s}^{-1}$. The underlying drag law is dissipative when the phase permeability $\boldsymbol{\kappa}_f$ is symmetric positive definite, $\mu_f^{\text{visc}} > 0$, and $\phi_f > 0$. These conditions make the drag contribution nonnegative in the entropy inequality. The added scalar term comes from conversion insertion in the momentum balance and supplies no independent quadratic dissipation. Because $\boldsymbol{\kappa}_f$ is symmetric with eigenvalues $\kappa_{f,i}$, the combined resistance $\phi_f^2 \mu_f^{\text{visc}} \boldsymbol{\kappa}_f^{-1} + \sum_{\alpha} \dot{c}_f^{\alpha} \mathbf{I}$ has eigenvalues $\phi_f^2 \mu_f^{\text{visc}} / \kappa_{f,i} + \sum_{\alpha} \dot{c}_f^{\alpha}$, for each $f \in \mathcal{F}$. Algebraic elimination of $\mathbf{w}_f$ requires exactly that none of these shifted eigenvalues vanish,

$$\sum_{\alpha} \dot{c}_f^{\alpha} \neq -\frac{\phi_f^2 \mu_f^{\text{visc}}}{\kappa_{f,i}}, \quad i = 1, \dots, d, \quad f \in \mathcal{F}. \quad (288)$$

This nonsingularity condition defines $\tilde{\boldsymbol{\lambda}}_f$. A stronger positive-resistance regime requires every shifted eigenvalue to be positive. If $\kappa_{f,\max}$ and $\kappa_{f,\min}$ are the largest and smallest eigenvalues of

κ_f , respectively, the binding direction is that of largest permeability, and the positive-resistance condition is

$$\sum_{\alpha} \dot{c}_f^{\alpha} > -\frac{\phi_f^2 \mu_f^{\text{visc}}}{\kappa_{f,\text{max}}}, \quad f \in \mathcal{F}. \quad (289)$$

Within this positive-definite regime, the spectral condition number is

$$\text{cond}_2 \left(\phi_f^2 \mu_f^{\text{visc}} \kappa_f^{-1} + \sum_{\alpha} \dot{c}_f^{\alpha} \mathbf{I} \right) = \frac{\phi_f^2 \mu_f^{\text{visc}} / \kappa_{f,\text{min}} + \sum_{\alpha} \dot{c}_f^{\alpha}}{\phi_f^2 \mu_f^{\text{visc}} / \kappa_{f,\text{max}} + \sum_{\alpha} \dot{c}_f^{\alpha}}, \quad f \in \mathcal{F}. \quad (290)$$

Thus quantitative conditioning within this regime requires the smallest shifted eigenvalue in the denominator to remain bounded away from zero. For an aqueous reaction that removes fluid mass on a time scale t_{rxn} , $\sum_{\alpha} \dot{c}_f^{\alpha} \simeq -\rho_f / t_{\text{rxn}}$. The singular threshold at the first loss of positive definiteness is

$$t_{\text{rxn}} = \frac{\rho_f \kappa_{f,\text{max}}}{\phi_f^2 \mu_f^{\text{visc}}}, \quad f \in \mathcal{F}. \quad (291)$$

For longer time scales the combined resistance remains positive definite. At equality it is singular in the largest-permeability direction. At shorter time scales it leaves the positive-resistance regime, while algebraic inversion remains possible except at the individual eigenvalue-crossing times $t_{\text{rxn}} = \rho_f \kappa_{f,i} / (\phi_f^2 \mu_f^{\text{visc}})$. With representative reservoir values $\rho_f = 10^3 \text{ kg m}^{-3}$, $\mu_f^{\text{visc}} = 10^{-3} \text{ Pa s}$, $\phi_f = 0.3$, and $\kappa_{f,\text{max}} = 10^{-12} \text{ m}^2$, this time is about 10^{-5} s , corresponding to a removal rate of order $10^8 \text{ kg m}^{-3} \text{ s}^{-1}$. For conversion rates whose characteristic time is much longer than this value, the source correction is a small perturbation of the Darcy drag. The estimate supplies a lower reaction-time bound for the positive-resistance form of the algebraic relative-flux closure.

The resulting relative mass flux is

$$\begin{aligned} \mathbf{w}_f = \rho_f \tilde{\lambda}_f \left[\rho_f (\mathbf{g} - \mathbf{a}_f) - \phi_f \nabla_{\mathbf{x}} (\bar{p}_f - \omega_f^+) \right. \\ \left. + \nabla_{\mathbf{x}} \cdot (\phi_f \mathbf{E} \otimes \mathbf{d}_f) + \sum_{\alpha} \dot{c}_f^{\alpha} (\nabla_{\mathbf{x}} \tau - \mathbf{v}_S) \right], \quad f \in \mathcal{F}. \end{aligned} \quad (292)$$

This expression is the multicomponent fluid-phase analogue of a generalized Darcy flux. Its driving force contains body force and inertia, the actual phase-pressure gradient assembled from stored capillarity, electrical corrections, and any dynamic lag, together with Maxwell stress and conversion insertion. The observer-conversion term, the relative-velocity contribution that arises when the phase-following thermodynamic rate is expressed in the skeleton frame, belongs to that single phase-following rate rather than entering the flux as an independent driving force. Equation (162) recombines it with the skeleton-rate free-energy contribution before the collected inequality is separated into reversible and residual parts. Chemical-potential gradients drive component-relative transport through (205), a distinct dissipative mechanism alongside the bulk phase force and the conversion variation of τ . Thermodynamic dissipation resides in the drag and component-transport closures. The nonsingularity condition permits algebraic flux elimination, and the positive-resistance condition selects the stronger regime used for the conditioning estimate. The interaction-energy allocation of (213) is retained.

The neutral, conversion-free, negligible-inertia specialization $\omega_f^+ = 0$, $\mathbf{E} \otimes \mathbf{d}_f = \mathbf{0}$, $\dot{c}_f^{\alpha} = 0$, and $\mathbf{a}_f = \mathbf{0}$ reduces (292) to

$$\phi_f (\mathbf{v}_f - \mathbf{v}_S) = -\frac{\kappa_f}{\mu_f^{\text{visc}}} (\nabla_{\mathbf{x}} \bar{p}_f - \bar{\rho}_f \mathbf{g}), \quad f \in \mathcal{F}. \quad (293)$$

This is Darcy's law for phase f relative to the deforming solid skeleton. Neither isothermality nor a spatially uniform Helmholtz energy is required. Nonisothermal cross effects may modify this law only when they are introduced explicitly through a coupled constitutive closure.

7.2 Solid-reference relative fluxes

The current relative flux in (292) is converted to a flux through surfaces in the solid reference configuration by the Piola transform. Define the reference relative mass flux

$$\mathbf{W}_f = J\mathbf{F}^{-1}\mathbf{w}_f, \quad f \in \mathcal{F}. \quad (294)$$

Define the pulled-back conversion-corrected mobility tensor

$$\tilde{\mathbf{\Lambda}}_f = J\mathbf{F}^{-1}\tilde{\mathbf{\lambda}}_f\mathbf{F}^{-T}, \quad f \in \mathcal{F}. \quad (295)$$

The flux assembled in the reference component balances is then

$$\begin{aligned} \mathbf{W}_f = \rho_f \tilde{\mathbf{\Lambda}}_f \left[\rho_f \mathbf{F}^T (\mathbf{g} - \mathbf{a}_f) - \phi_f \nabla_{\mathbf{X}} (\bar{p}_f - \omega_f^+) \right. \\ \left. + \mathbf{F}^T [\nabla_{\mathbf{x}} \cdot (\phi_f \mathbf{E} \otimes \mathbf{d}_f)] + \sum_{\alpha} \dot{c}_f^{\alpha} (\nabla_{\mathbf{X}} \tau - \mathbf{F}^T \mathbf{v}_S) \right], \quad f \in \mathcal{F}. \end{aligned} \quad (296)$$

Here gradients of scalar fields obey $\nabla_{\mathbf{x}}(\cdot) = \mathbf{F}^{-T} \nabla_{\mathbf{X}}(\cdot)$, while the divergence of a spatial flux obeys

$$J \nabla_{\mathbf{x}} \cdot \mathbf{w}_f = \nabla_{\mathbf{X}} \cdot \mathbf{W}_f, \quad f \in \mathcal{F}. \quad (297)$$

Equations (294)–(296) and (297) give the reference flux used in the multicomponent balances. The expression retains phase labels, component conversion rates, and gradients of τ .

7.3 Component balances on the solid trajectory

For a fluid phase, substituting (284) into (29), using (17b), and writing the storage term on the solid trajectory gives

$$\left. \frac{\partial}{\partial t} (J \phi_f \bar{\rho}_f \eta_f^{\alpha}) \right|_{\mathbf{X}} + \nabla_{\mathbf{X}} \cdot [\eta_f^{\alpha} \mathbf{W}_f + J \mathbf{F}^{-1} (\mathbf{j}_{f,\text{disp}}^{\alpha} + \mathbf{j}_{f,\text{diff}}^{\alpha})] = J \sum_m \nu_{f(m)}^{\alpha} r_{(m)}, \quad f \in \mathcal{F}. \quad (298)$$

For a solid phase s , the phase velocity is the skeleton velocity, so there is no bulk phase flux relative to the solid mesh. Component diffusion and dispersion remain admissible, giving

$$\begin{aligned} \left. \frac{\partial}{\partial t} (J \phi_s \bar{\rho}_s \eta_s^{\alpha}) \right|_{\mathbf{X}} + \nabla_{\mathbf{X}} \cdot [J \mathbf{F}^{-1} (\mathbf{j}_{s,\text{disp}}^{\alpha} + \mathbf{j}_{s,\text{diff}}^{\alpha})] \\ = J \sum_m \nu_{s(m)}^{\alpha} r_{(m)}, \quad s \in \mathcal{S}. \end{aligned} \quad (299)$$

Thus the solid-reference storage variables are the Lagrangian component masses $J \phi_{\xi} \bar{\rho}_{\xi} \eta_{\xi}^{\alpha}$. Transport through the solid mesh contains bulk fluid motion relative to the skeleton and component diffusion or dispersion relative to the fluid or solid phase.

7.4 Overall momentum on the solid trajectory

Define the general solid-reference effective first Piola–Kirchhoff stress by

$$\mathbf{P}'' \equiv J \boldsymbol{\sigma}'' \mathbf{F}^{-T}. \quad (300)$$

The overall momentum balance (247) can be written on the solid trajectory by applying the Piola transform to the stress divergence and multiplying the remaining spatial source terms by J . Using (300), this transformation gives

$$\begin{aligned} J \sum_{\xi} \rho_{\xi} \mathbf{a}_{\xi} = & \nabla_{\mathbf{x}} \cdot \left(\mathbf{P}'' - B \bar{p}_E J \mathbf{F}^{-T} + J (\mathbf{E} \otimes \mathbf{d}) \mathbf{F}^{-T} \right) + J \rho \mathbf{g} \\ & - J \phi \left. \frac{\partial \gamma}{\partial \theta_{\mathcal{F}}} \right|_{\{S_f\}_{f \in \mathcal{F}}, \mathbf{h}} \mathbf{F}^{-T} \nabla_{\mathbf{x}} \theta_{\mathcal{F}} \\ & - J \phi \mathbf{F}^{-T} (\nabla_{\mathbf{x}} \mathbf{h})^T \left. \frac{\partial \gamma}{\partial \mathbf{h}} \right|_{\{S_f\}_{f \in \mathcal{F}}, \theta_{\mathcal{F}}} \\ & + J \phi \mathbf{F}^{-T} \sum_{f \in \mathcal{F}} \left(\bar{p}_f - \bar{p}_E - \gamma_f - \omega_f^+ \right) \nabla_{\mathbf{x}} S_f \\ & + J \sum_{\xi} \sum_{\alpha} \dot{c}_{\xi}^{\alpha} \left(\mathbf{F}^{-T} \nabla_{\mathbf{x}} \tau - \mathbf{v}_{\xi} \right). \end{aligned} \quad (301)$$

Here $\nabla_{\mathbf{x}} \tau = \mathbf{F}^{-T} \nabla_{\mathbf{x}} \tau$, so every gradient in the conversion-insertion force is evaluated from the solid reference configuration. The same pull-back gives $\nabla_{\mathbf{x}} \theta_{\mathcal{F}} = \mathbf{F}^{-T} \nabla_{\mathbf{x}} \theta_{\mathcal{F}}$ in the thermocapillary force and $\nabla_{\mathbf{x}} \mathbf{h} = \nabla_{\mathbf{x}} \mathbf{h} \mathbf{F}^{-1}$ in the capillary-history force. The same scalar-gradient pull-back carries the dynamic pressure-lag term through $\nabla_{\mathbf{x}} S_f = \mathbf{F}^{-T} \nabla_{\mathbf{x}} S_f$.

If a quasi-static solid-skeleton solve is desired, the inertial term on the left is dropped. If the fluid velocities are eliminated with (284), then the same equation is solved with $\mathbf{v}_f = \mathbf{v}_S + \mathbf{w}_f / \rho_f$ for fluid phases and $\mathbf{v}_S$ for the solid skeleton. This leaves the solid displacement, the Lagrangian partial masses, and the fluid relative fluxes as the natural fields for a reference-configuration implementation.

This quasi-static mechanics–fluid block is only part of the coupled model. A complete solve must additionally retain the solid component balances (299), the two subsystem energy balances (151), Gauss’ law (107), mechanism kinetics, capillary-history and solid internal-variable evolution, and the remaining constitutive restrictions appropriate to the selected specialization.

8 Correspondence to other theories

This section shows how the general equations reduce to models used in reservoir simulation and electrochemical transport. Each reduction states its assumptions, identifies the closures that remain, and shows which variables and balances become those of compositional flow, Nernst–Planck–Darcy transport, black-oil flow, or Biot poromechanics.

8.1 Classical compositional-flow limit and interpretation of the potentials

The averaged component balance reduces to the standard compositional-reservoir balance after the fluid pore phases are isolated. Write $\phi_f = \phi S_f$ with $\sum_{f \in \mathcal{F}} S_f = 1$, and use the averaged global component balance (36). The result is

$$\frac{\partial}{\partial t} \left(\phi \sum_{f \in \mathcal{F}} S_f \bar{\rho}_f \eta_f^{\alpha} \right) + \nabla_{\mathbf{x}} \cdot \left(\sum_{f \in \mathcal{F}} \left[\phi S_f \bar{\rho}_f \eta_f^{\alpha} \mathbf{v}_f + \mathbf{j}_{f,\text{disp}}^{\alpha} + \mathbf{j}_{f,\text{diff}}^{\alpha} \right] \right) = \sum_{f \in \mathcal{F}} \sum_m \nu_{f(m)}^{\alpha} r_{(m)}. \quad (302)$$

This is the usual mass-based component balance per unit current mixture volume, with mechanical dispersion and molecular diffusion retained explicitly. Setting both relative fluxes to zero recovers the advective component-balance structure of classical compositional reservoir simulation [1]. To keep the relative fluxes, classical compositional simulation must supply the chemical potentials algebraically; it has no separate transfer-potential field to evolve. The present theory instead evolves a single transfer potential τ through (181) and recovers the remaining phase-reference values of the specific generalized transfer-work potentials through (182). For the stationary skeleton of classical reservoir simulation, that evolution gives $D_S\tau/Dt = 0$, so τ remains at its normalized initial value and introduces no new evolving field in the classical compositional balance. Taking $\mathbf{v}_S = \mathbf{0}$ in (293) and using $\boldsymbol{\kappa}_f = \kappa_{rf}\boldsymbol{\kappa}$ gives the Darcy law in the present notation,

$$\phi S_f \mathbf{v}_f = -\frac{\boldsymbol{\kappa} \kappa_{rf}}{\mu_f^{\text{visc}}} (\nabla_{\mathbf{x}} \bar{p}_f - \bar{\rho}_f \mathbf{g}), \quad f \in \mathcal{F}. \quad (303)$$

The same history state may enter κ_{rf} when relative-permeability hysteresis is retained.

For a neutral specialization, choose a reference phase $f_\star$ and set $\bar{p}_{\text{ref}} = \bar{p}_{f_\star}$. A concrete classical closure set is

$$\begin{aligned} \mathbf{v}_S &= \mathbf{0}, \\ \bar{p}_f &= \bar{p}_{\text{ref}} + p_{c,f} + \sum_{g \neq f_\star} \mathcal{T}_{fg} \dot{S}_g, \quad f \neq f_\star, \\ p_{c,f} &= p_{c,f}(\{S_g\}_{g \in \mathcal{F}}, \mathbf{h}, \theta_{\mathcal{F}}), \quad f \neq f_\star, \\ \bar{\rho}_f &= \bar{\rho}_f(\bar{p}_{\text{ref}}, \theta_{\mathcal{F}}, \{\eta_f^\alpha\}), \quad \mu_f^{\text{visc}} = \mu_f^{\text{visc}}(\bar{p}_{\text{ref}}, \theta_{\mathcal{F}}, \{\eta_f^\alpha\}), \\ \mu_f^\alpha &= \mathcal{G}_f + \frac{\partial \mathcal{G}_f}{\partial \eta_f^\alpha} - \sum_\beta \eta_f^\beta \frac{\partial \mathcal{G}_f}{\partial \eta_f^\beta}, \\ \mathbf{j}_{f,\text{disp}}^\alpha + \mathbf{j}_{f,\text{diff}}^\alpha &= - \sum_{\beta \neq N} (\mathbf{D}_{f,\text{disp}}^{\alpha\beta} + \mathbf{D}_{f,\text{diff}}^{\alpha\beta}) \theta_{\mathcal{F}} \nabla_{\mathbf{x}} \left(\frac{\mu_f^\beta - \mu_f^N}{\theta_{\mathcal{F}}} \right), \quad \alpha \neq N, \\ \mathbf{j}_{f,k}^N &= - \sum_{\alpha \neq N} \mathbf{j}_{f,k}^\alpha, \quad k \in \{\text{disp}, \text{diff}\}, \\ \mu_f^\alpha &= \mu_g^\alpha \quad \text{for equilibrated fluid phases } f, g, \quad f, g \in \mathcal{F}. \end{aligned} \quad (304)$$

Here $\mathcal{G}_f$ is the specific Gibbs energy supplied by the EOS or flash model. The quantity $p_{c,f}$ is the stored, history-dependent capillary offset from the reference phase; in a potential-based model it is the appropriate difference of the γ_f . The separate term containing $\mathcal{T}_{fg} \dot{S}_g$ follows by eliminating the generalized saturation force between (88) and (118). It is the dynamic pressure lag. Setting $\mathcal{T} = \mathbf{0}$ recovers the usual algebraic capillary closure. Although $\mathcal{G}_f$ is physically evaluated for mass fractions whose sum is one, the partial derivatives in (304) may be taken from any differentiable extension to nearby independent compositions. The displayed combination is independent of that choice and gives the absolute chemical potential. The same expression follows by differentiating the total phase Gibbs energy with respect to the mass of component α at fixed pressure, temperature, and masses of the other components. Choose component N as the reference, set $\eta_f^N = 1 - \sum_{\gamma \neq N} \eta_f^\gamma$, and use the $N - 1$ chemical-potential differences. These differences describe every independent composition change that preserves the mass-fraction sum. The final flux row makes each flux family zero-sum, so the reduced mobility matrices act on those $N - 1$ independent changes. The transport row retains the full nonisothermal force from (205). When $\theta_{\mathcal{F}}$ is spatially uniform, it reduces to the chemical-potential-difference gradient used below.

In an isothermal composition-diffusion specialization at fixed phase pressure, eliminate η_f^N and differentiate the $N - 1$ chemical-potential differences with respect to the independent mass fractions:

$$\nabla_{\mathbf{x}} (\mu_f^\beta - \mu_f^N) = \sum_{\gamma \neq N} \frac{\partial (\mu_f^\beta - \mu_f^N)}{\partial \eta_f^\gamma} \nabla_{\mathbf{x}} \eta_f^\gamma, \quad \beta \neq N, \quad f \in \mathcal{F}, \quad (305)$$

where the derivatives are evaluated after setting $\eta_f^N = 1 - \sum_{\gamma \neq N} \eta_f^\gamma$. Substitution converts the admissible potential-gradient flux into the familiar composition-gradient diffusion and dispersion law. For the $N - 1$ independent component balances, define the effective Fickian diffusion–dispersion tensor by

$$\bar{\mathbf{D}}_f^{\alpha\gamma} = \sum_{\beta \neq N} (\mathbf{D}_{f,\text{disp}}^{\alpha\beta} + \mathbf{D}_{f,\text{diff}}^{\alpha\beta}) \frac{\partial (\mu_f^\beta - \mu_f^N)}{\partial \eta_f^\gamma}, \quad \alpha, \gamma \neq N, \quad f \in \mathcal{F}. \quad (306)$$

Substituting these closures into (302) gives

$$\begin{aligned} & \frac{\partial}{\partial t} \left(\phi \sum_{f \in \mathcal{F}} S_f \bar{\rho}_f \eta_f^\alpha \right) \\ & + \nabla_{\mathbf{x}} \cdot \left[\sum_{f \in \mathcal{F}} \left(\bar{\rho}_f \eta_f^\alpha \phi S_f \mathbf{v}_f - \sum_{\gamma \neq N} \bar{\mathbf{D}}_f^{\alpha\gamma} \nabla_{\mathbf{x}} \eta_f^\gamma \right) \right] = \sum_{f \in \mathcal{F}} \sum_m \nu_{f(m)}^\alpha r_{(m)}, \quad \alpha \neq N. \end{aligned} \quad (307)$$

This is the standard reservoir compositional-flow form: storage is written in terms of porosity, saturation, phase density, and phase composition; transport is the phase Darcy flux multiplied by the component mass fraction; and the EOS or flash closure supplies densities, viscosities, equilibrium compositions, and the chemical-potential/composition tangent that converts the entropy-admissible $D\nabla\mu$ flux into the usual Fickian composition-gradient form. The reference-component balance follows from the summed mass balance, the $N - 1$ displayed balances, the zero-sum relative-flux condition, and mechanism mass conservation, so it is not an additional independent equation.

The usual within-phase composition constraint is also recovered:

$$\sum_{\alpha} \eta_{\xi}^{\alpha} = 1. \quad (308)$$

A conventional compositional simulator may supply the equation of state, phase-equilibrium rules, capillary relations, component partitioning, and stress law as separate inputs. Here the phase Helmholtz energies and the interfacial and electrical potentials supply the reversible quantities: pressure, entropy, stress, and the composition and storage potentials. Permeability, diffusivity, mobility, and reaction-rate laws remain constitutive closures. The entropy inequality identifies their thermodynamic forces, while the stored potentials supply the reversible parts of those forces.

Classical flash calculations impose phase-equilibrium closures, commonly written as fugacity equalities. In the present notation, the reversible transfer of component α from phase ξ to phase ζ first gives equality of the generalized transfer potentials,

$$(\psi_{\zeta} + L_{\zeta}^{\alpha} + z_{\zeta}^{\alpha} \varphi) - (\psi_{\xi} + L_{\xi}^{\alpha} + z_{\xi}^{\alpha} \varphi) = 0. \quad (309)$$

At full reversible equilibrium, the active phases participating in the equilibrium calculation have no relative motion, so $\mathbf{v}_{\xi} = \mathbf{v}_{\mathcal{S}}$ and $D_{\xi}\tau/Dt = D_{\mathcal{S}}\tau/Dt$. The reference normalization (180), the Euler identity (175), and the reference evolution (181) give $D_{\mathcal{S}}\tau/Dt = \mathbf{v}_{\mathcal{S}} \cdot \mathbf{v}_{\mathcal{S}}/2$. Hence the right-hand

side of (178) vanishes in every equilibrated phase, and $\psi_\xi + L_\xi^\alpha + z_\xi^\alpha \varphi = \mu_\xi^\alpha$. Equation (309) then becomes the electrochemical-potential equality for a charged component. For a neutral component, or when the same specific charge is transferred between phases at the same electric potential, the electrical contribution cancels and this reduces to the chemical-potential, or fugacity-equality, condition used in isothermal flash calculations. Away from phase equilibrium this identification fails: only the within-phase transfer-potential differences are fixed to electrochemical-potential differences, and the absolute levels are governed by the transfer-work structure of §5.4.1.

The traditional affinity remains the stoichiometric sum of the electrochemical potentials,

$$\mathcal{A}_{(m)} = - \sum_{\xi} \sum_{\alpha} \mu_{\xi}^{\alpha} \nu_{\xi(m)}^{\alpha}. \quad (310)$$

At full thermodynamic equilibrium, the temperatures are equal, the no-relative-motion argument above identifies every generalized transfer potential with its electrochemical potential, and imposing $\mathcal{A}_{(m)} = 0$ gives

$$\sum_{\xi} \sum_{\alpha} \mu_{\xi}^{\alpha} \nu_{\xi(m)}^{\alpha} = 0, \quad (311)$$

which is the classical statement that the stoichiometric sum of chemical potentials vanishes. Away from equilibrium, the generalized conversion power differs from this traditional affinity by the explicit phase-transfer work in (186). That contribution vanishes for chemistry that conserves mass separately in every phase and remains for phase change, precipitation, dissolution, and pore filling. Away from local thermal equilibrium, every uncoupled fluid–solid mechanism is driven by the gauge-invariant neutral temperature-weighted stoichiometric sum in (199). Charged transfer between thermal subsystems may couple that reaction rate to reaction-energy transfer subject to (200). When $\theta_{\mathcal{F}} = \theta_S = \theta$ and the transfer-work contribution vanishes, the uncoupled law reduces to

$$r_{(m)} = \frac{K_{(m)}}{\theta} \mathcal{A}_{(m)}, \quad \mathcal{A}_{(m)} r_{(m)} \geq 0. \quad (312)$$

Here $K_{(m)}/\theta$ is the conventional linear affinity mobility. The temperature-weighted law therefore recovers the classical isothermal sign convention for phasewise mass-conserving chemistry without assigning a separate temperature to a cross-subsystem mechanism. General phase-changing mechanisms retain the additional term shown in (186).

8.2 Black-oil limit

The black-oil model is obtained by further specializing (302). Take the fluid phases to be water, oil, and gas, $\mathcal{F} = \{w, o, g\}$, neglect mechanical dispersion and molecular diffusion by setting $\mathbf{j}_{f,\text{disp}}^\alpha = \mathbf{j}_{f,\text{diff}}^\alpha = \mathbf{0}$, use a fixed solid frame, and impose the neutral nonelectrical specialization $\omega_\xi^+ = 0$, $z_\xi^\alpha = 0$, and $\mathbf{E} = \mathbf{d} = \mathbf{0}$. Replace the full component EOS by black-oil formation-volume factors and solution-gas data. In stock-tank units the phase/component storage factors are identified as

$$\bar{\rho}_w \eta_w^W = \frac{\rho_{w,\text{sc}}}{B_w}, \quad \bar{\rho}_o \eta_o^O = \frac{\rho_{o,\text{sc}}}{B_o}, \quad \bar{\rho}_g \eta_g^G = \frac{\rho_{g,\text{sc}}}{B_g}, \quad \bar{\rho}_o \eta_o^G = \frac{\rho_{g,\text{sc}} R_s}{B_o}. \quad (313)$$

Here W , O , and G label stock-tank water, oil, and gas components; B_w , B_o , and B_g are formation-volume factors; R_s is the dissolved gas-oil ratio, and the subscript sc denotes surface conditions. Let $\mathbf{q}_f = \phi S_f \mathbf{v}_f$ be the phase volumetric flux and divide the water, oil-component, and gas-component

balances by their corresponding surface densities to obtain

$$\frac{\partial}{\partial t} \left(\phi \frac{S_w}{B_w} \right) + \nabla_{\mathbf{x}} \cdot \left(\frac{\mathbf{q}_w}{B_w} \right) = 0, \quad (314)$$

$$\frac{\partial}{\partial t} \left(\phi \frac{S_o}{B_o} \right) + \nabla_{\mathbf{x}} \cdot \left(\frac{\mathbf{q}_o}{B_o} \right) = 0, \quad (315)$$

$$\frac{\partial}{\partial t} \left[\phi \left(\frac{S_g}{B_g} + R_s \frac{S_o}{B_o} \right) \right] + \nabla_{\mathbf{x}} \cdot \left[\frac{\mathbf{q}_g}{B_g} + R_s \frac{\mathbf{q}_o}{B_o} \right] = 0. \quad (316)$$

These are the standard black-oil conservation laws: water occupies the water phase, the stock-tank oil component occupies the oil phase, and the stock-tank gas component is present in the gas phase and dissolved in the oil phase through R_s . Black-oil PVT closures B_f and R_s determine the phase/component storage factors.

The phase fluxes follow from the neutral, conversion-free, negligible-inertia reduction (293). With $\boldsymbol{\kappa}_f = k_{rf} \boldsymbol{\kappa}$, where k_{rf} is the relative permeability and may depend on $\mathbf{h}$, the fixed-frame flux closure is

$$\mathbf{q}_f = - \frac{k_{rf}}{\mu_f^{\text{visc}}} \boldsymbol{\kappa} (\nabla_{\mathbf{x}} \bar{p}_f - \bar{\rho}_f \mathbf{g}), \quad f \in \{w, o, g\}. \quad (317)$$

If oil pressure is chosen as the black-oil reference pressure, a diagonal pairwise specialization of (118) gives the water–oil and gas–oil relations

$$\bar{p}_w = \bar{p}_o - p_{cow}(S_w, \mathbf{h}) + \mathcal{T}_{ow} \dot{S}_w, \quad \bar{p}_g = \bar{p}_o + p_{cgo}(S_g, \mathbf{h}) + \mathcal{T}_{go} \dot{S}_g, \quad \mathcal{T}_{ow}, \mathcal{T}_{go} \geq 0. \quad (318)$$

These closures are used with one pressure, for example $\bar{p}_o$, and two independent saturations because $S_w + S_o + S_g = 1$. The functions p_{cow} and p_{cgo} are the stored capillary offsets, while the terms containing $\mathcal{T}_{ow}$ and $\mathcal{T}_{go}$ are the dynamic pressure lags. The remaining phase pressures are reconstructed from (318) before evaluating (317). Pair-specific entries of $\mathbf{h}$ store reversal and trapping data for the water–oil and gas–oil paths. Holding $\mathbf{h}$ fixed recovers single-valued saturation functions; updating it with an admissible loading–unloading rule gives drainage, imbibition, and scanning curves for the stored capillary offsets and, when selected, relative permeability. Setting $\mathcal{T}_{ow} = \mathcal{T}_{go} = 0$ recovers the standard algebraic black-oil closures. In a potential-based three-phase specialization, both stored pairwise pressure laws must be derivatives of the common γ , and the dynamic coefficients are entries of the positive-semidefinite resistance that closes the generalized saturation-force differences. Independently fitted pairwise laws are an empirical reservoir closure when those compatibility conditions are not imposed.

8.3 Nernst–Planck–Darcy limit

The electrostatic single-fluid specialization recovers the Nernst–Planck–Darcy system. Take one isothermal fluid phase in a fixed solid frame with two ionic components $i \in \{1, 2\}$ and a neutral solvent reference component N . Set the reaction and phase-transformation rates and mechanical-dispersion fluxes to zero, and neglect inertia, gravity, and capillarity. Let ϕ_f be constant, take a linear isotropic dielectric response $\mathbf{d}_f = \epsilon_f \mathbf{E}$ with constant ϵ_f , set fixed solid charge and the solid electrical displacement to zero, and assign all free charge to the ionic components. A background solid dielectric contribution may be included in a specified effective ϵ_f . Gauss’ law then gives $\nabla_{\mathbf{x}} \cdot (\phi_f \mathbf{d}_f) = \sum_{i=1}^2 z_f^i \rho_f^i$. Because $\nabla_{\mathbf{x}} \times \mathbf{E} = \mathbf{0}$, the electrical and pressure forces in (292) reduce

according to

$$\begin{aligned} & -\phi_f \nabla_{\mathbf{x}} (\bar{p}_f - \omega_f^+) + \nabla_{\mathbf{x}} \cdot (\phi_f \mathbf{E} \otimes \mathbf{d}_f) \\ & = -\phi_f \nabla_{\mathbf{x}} \bar{p}_f + \left(\sum_{\alpha} z_f^{\alpha} \rho_f^{\alpha} \right) \mathbf{E}, \quad f \in \mathcal{F}. \end{aligned} \quad (319)$$

Here the linear dielectric relation $\omega_f^+ = -\frac{1}{2} \mathbf{E} \cdot \mathbf{d}_f$, absorbs the isotropic part of the Maxwell stress. Thus the tensor-divergence term in the general flux law becomes the familiar electric body force exerted on the mobile charge.

With $\mathbf{v}_S = \mathbf{0}$, the reaction-free form of (287), the component balances, (205), and Gauss' law give

$$\phi_f \mathbf{v}_f = -\frac{\kappa_f}{\mu_f^{\text{visc}}} \left[\nabla_{\mathbf{x}} \bar{p}_f - \frac{1}{\phi_f} \left(\sum_{\alpha} z_f^{\alpha} \rho_f^{\alpha} \right) \mathbf{E} \right], \quad f \in \mathcal{F}, \quad (320a)$$

$$\frac{\partial \rho_f^{\alpha}}{\partial t} + \nabla_{\mathbf{x}} \cdot \left[\rho_f^{\alpha} \mathbf{v}_f - \sum_{\beta \neq N} \mathbf{D}_{f,\text{diff}}^{\alpha\beta} \nabla_{\mathbf{x}} \left(\hat{\mu}_f^{\beta} - \hat{\mu}_f^N + (z_f^{\beta} - z_f^N) \varphi \right) \right] = 0, \quad \alpha \neq N, \quad f \in \mathcal{F}, \quad (320b)$$

$$\nabla_{\mathbf{x}} \cdot (\phi_f \mathbf{d}_f) = \sum_{\alpha} z_f^{\alpha} \rho_f^{\alpha}, \quad \mathbf{E} = -\nabla_{\mathbf{x}} \varphi, \quad f \in \mathcal{F}. \quad (320c)$$

For the neutral solvent reference, set $z_f^N = 0$. After nondimensionalization, adopt constant solvent activity and the ideal-dilute component-potential differences and reduced mobility

$$\begin{aligned} \hat{\mu}_f^i - \hat{\mu}_f^N &= \hat{\mu}_f^{\circ i} + \ln \rho_f^i, \quad i \in \{1, 2\}, \\ \mathbf{D}_{f,\text{diff}}^{ij} &= D_i \rho_f^i \delta^{ij}, \quad i, j \in \{1, 2\}. \end{aligned} \quad (321)$$

The two independent diffusion closures then give

$$\begin{aligned} \mathbf{j}_{f,\text{diff}}^i &= -D_i \rho_f^i \left(\nabla_{\mathbf{x}} \ln \rho_f^i + z_f^i \nabla_{\mathbf{x}} \varphi \right) \\ &= -D_i \nabla_{\mathbf{x}} \rho_f^i - z_f^i D_i \rho_f^i \nabla_{\mathbf{x}} \varphi, \quad i \in \{1, 2\}, \end{aligned} \quad (322)$$

$$\mathbf{j}_{f,\text{diff}}^N = -\sum_{i=1}^2 \mathbf{j}_{f,\text{diff}}^i. \quad (323)$$

Thus the two ionic fluxes have the standard Nernst–Planck form while the solvent flux enforces the zero-sum mass-averaged convention. Set $\phi_f = 1$, set the isotropic Darcy mobility to unity, and identify $u = \mathbf{v}_f$, $p = \bar{p}_f$, $\Phi = \varphi$, $c_i = \rho_f^i$, $z_i = z_f^i$, and $\varepsilon = \epsilon_f$. Equations (320a), (320c), and (322) substituted into (320b) then give equations (1.4), (1.2)–(1.3), and (1.1), respectively, of Ignatova and Shu [37]. Summing the two ionic balances and the solvent balance gives the total phase mass balance; constant total density therefore gives $\nabla_{\mathbf{x}} \cdot u = 0$, their equation (1.5). Their analysis further specializes to opposite ionic valences and $D_1 = D_2$. Ion exchange extends this fluid-only limit by retaining the charged solid-site components described in §3. Their fixed charge then contributes to the mixture Gauss law, while the mobile fluid charge in (320a) supplies the electrical fluid-driving force; exchange kinetics or equilibrium relations close the solid–fluid component transfer.

8.4 Single-solid, single-fluid Biot limit

The classical Biot poromechanics specialization has one solid skeleton phase and one fluid pore phase, $\mathcal{S} = \{s\}$ and $\mathcal{F} = \{f\}$, with $r_{(m)} = 0$, $\omega_{\xi}^+ = 0$, $\mathbf{d} = \mathbf{0}$, and $\gamma = 0$ because no fluid–fluid interface

remains. The equivalent pressure relation (93) then gives the unique fluid pressure, $\bar{p}_E = \bar{p}_f$. The solid pressure relation (238) also gives $\bar{p}_s = \bar{p}_E$. In this limit, (242) reduces to $B = 1 - \phi_s(1 - \bar{B}_s)$, the volume-fraction-weighted combination of the intrinsic coefficient in (233). With $r_{(m)} = 0$ the accumulated solid mass vanishes, $C_s = 0$, so the distension–mass relation (133) gives $a_s \phi_s = \phi_{s0}$; combining this with $v_{s0} = \bar{v}_{s0}/\phi_{s0}$ from (226) resolves the aggregate coefficient to the reference specific-volume form,

$$B = 1 - \frac{1}{v_{s0}} \left. \frac{\partial \bar{v}_s}{\partial J} \right|_{\bar{p}_f, \theta_S}, \quad (324)$$

the single-solid reduction of the intrinsic coefficient in (233). In this single-solid, single-fluid specialization, (324) is equivalent to the fixed-pressure nonlinear Biot coefficient that Foster and Xu derive directly for a binary solid–fluid mixture [25].

Under $r_{(m)} = 0$, the overall momentum balance (247) becomes

$$\sum_{\xi \in \{s, f\}} \rho_\xi \mathbf{a}_\xi = \nabla_{\mathbf{x}} \cdot (\boldsymbol{\sigma}'' - B \bar{p}_f \mathbf{I}) + \rho \mathbf{g}, \quad f \in \mathcal{F}. \quad (325)$$

Thus the total Cauchy stress is the fixed-pressure skeleton stress minus the Biot pressure correction. For a quasi-static skeleton solve the inertial term is dropped, giving the usual equilibrium equation

$$\nabla_{\mathbf{x}} \cdot (\boldsymbol{\sigma}'' - B \bar{p}_f \mathbf{I}) + \rho \mathbf{g} = \mathbf{0}, \quad f \in \mathcal{F}. \quad (326)$$

The corresponding fixed-pressure effective first Piola–Kirchhoff stress is the single-solid specialization of the general definition (300). Multiplying (326) by J and applying the Piola identity gives the solid-reference equilibrium equation

$$\nabla_{\mathbf{X}} \cdot (\mathbf{P}'' - B \bar{p}_f J \mathbf{F}^{-T}) + J \rho \mathbf{g} = \mathbf{0}, \quad f \in \mathcal{F}. \quad (327)$$

The fluid transport equation is the single-fluid specialization of the solid-reference component balance. Let $\mathbf{w}_f = \phi_f \bar{\rho}_f (\mathbf{v}_f - \mathbf{v}_S)$ be the current relative mass flux and let $\mathbf{W}_f$ be its Piola transform defined in (294). In (298), take the single component in the single fluid phase to be the fluid itself. Then $\eta_f^f = 1$, and the conversion source vanishes. The zero-sum condition (34) also makes the single component’s diffusion and dispersion fluxes vanish, and the component storage $J \phi_f \bar{\rho}_f \eta_f^f$ reduces to the Lagrangian fluid mass $J \phi_f \bar{\rho}_f$. The corresponding current-balance form is obtained from (29) by the same specialization and by splitting the fluid velocity into solid motion plus relative flux,

$$\frac{\partial}{\partial t} (\phi_f \bar{\rho}_f) + \nabla_{\mathbf{x}} \cdot (\phi_f \bar{\rho}_f \mathbf{v}_S) + \nabla_{\mathbf{x}} \cdot \mathbf{w}_f = 0, \quad f \in \mathcal{F}. \quad (328)$$

Using the material derivative following the solid skeleton, $D_S/Dt = \partial/\partial t + \mathbf{v}_S \cdot \nabla_{\mathbf{x}}$, this becomes

$$\frac{D_S}{Dt} (\phi_f \bar{\rho}_f) + \phi_f \bar{\rho}_f \nabla_{\mathbf{x}} \cdot \mathbf{v}_S + \nabla_{\mathbf{x}} \cdot \mathbf{w}_f = 0, \quad f \in \mathcal{F}. \quad (329)$$

Since $D_S J/Dt = J \nabla_{\mathbf{x}} \cdot \mathbf{v}_S$, the first two terms combine into the derivative of $J \phi_f \bar{\rho}_f$,

$$\frac{1}{J} \frac{D_S}{Dt} (J \phi_f \bar{\rho}_f) + \nabla_{\mathbf{x}} \cdot \mathbf{w}_f = 0, \quad f \in \mathcal{F}. \quad (330)$$

Multiplying by J , using the divergence transform (297), and observing that $D_S/Dt = \partial/\partial t$ at fixed $\mathbf{X}$ gives (331),

$$\frac{\partial}{\partial t} (J \phi_f \bar{\rho}_f) + \nabla_{\mathbf{X}} \cdot \mathbf{W}_f = 0, \quad f \in \mathcal{F}. \quad (331)$$

Thus the finite-deformation storage variable is the Lagrangian fluid mass $J\phi_f\bar{\rho}_f$. Equivalently, with $\Phi_f = J\phi_f$,

$$\frac{\partial}{\partial t}(\Phi_f\bar{\rho}_f) + \nabla_{\mathbf{x}} \cdot \mathbf{W}_f = 0, \quad f \in \mathcal{F}. \quad (332)$$

If the fluid is barotropic, $\bar{\rho}_f = \bar{\rho}_f(\bar{p}_f)$, and $d\bar{\rho}_f/d\bar{p}_f = \bar{\rho}_f/K_f$, where K_f is the fluid bulk modulus, then (331) can be written as

$$\bar{\rho}_f \left[\frac{\partial \Phi_f}{\partial t} + \frac{\Phi_f}{K_f} \frac{\partial \bar{p}_f}{\partial t} \right] + \nabla_{\mathbf{x}} \cdot \mathbf{W}_f = 0, \quad f \in \mathcal{F}. \quad (333)$$

For comparison with the classical Biot storage equation, we supplement the phase energy with a finite-deformation extension of the standard small-strain porosity tangent summarized by [16, 17]. We also assume homogeneous solid grains, so theunjacketed moduli coincide and uniform unjacketed loading does not change porosity. Using the same B in the stress and pore-volume tangents is an additional reciprocity and storage assumption. Over a finite loading history, this tangent must come from an integrable storage law or serve as the evolution law for Φ_f ; an arbitrary state-dependent B need not produce a path-independent $\Phi_f(J, \bar{p}_f)$. With B fixed over the increment, K_s denoting the solid-grain bulk modulus, and M denoting the Biot storage modulus,

$$\frac{\partial \Phi_f}{\partial t} = B \frac{\partial J}{\partial t} + \frac{B - \Phi_f}{K_s} \frac{\partial \bar{p}_f}{\partial t}, \quad \frac{1}{M} = \frac{B - \Phi_f}{K_s} + \frac{\Phi_f}{K_f}, \quad f \in \mathcal{F}. \quad (334)$$

Stable pressure storage additionally requires $1/M > 0$. Substitution gives the finite-deformation pressure-storage balance

$$B \frac{\partial J}{\partial t} + \frac{1}{M} \frac{\partial \bar{p}_f}{\partial t} + \frac{1}{\bar{\rho}_f} \nabla_{\mathbf{x}} \cdot \mathbf{W}_f = 0, \quad f \in \mathcal{F}. \quad (335)$$

Finally, take $J \simeq 1 + \nabla_{\mathbf{x}} \cdot \mathbf{u}$ and $\mathbf{F} \simeq \mathbf{I}$, and neglect spatial density gradients in the mass-to-volume flux conversion while retaining temporal barotropic compressibility in $1/M$. With the current volumetric relative flux $\mathbf{q}_f = \mathbf{w}_f/\bar{\rho}_f$, the exact Piola identity and this small-strain, small-compressibility transport approximation give

$$\frac{1}{\bar{\rho}_f} \nabla_{\mathbf{x}} \cdot \mathbf{W}_f = J \nabla_{\mathbf{x}} \cdot \mathbf{q}_f + J \mathbf{q}_f \cdot \nabla_{\mathbf{x}} \ln \bar{\rho}_f \simeq \nabla_{\mathbf{x}} \cdot \mathbf{q}_f, \quad f \in \mathcal{F}. \quad (336)$$

The fluid–skeleton interaction closure gives, in the current configuration,

$$\phi_f(\mathbf{v}_f - \mathbf{v}_S) = -\frac{\kappa_f}{\mu_f^{\text{visc}}} (\nabla_{\mathbf{x}} \bar{p}_f - \bar{\rho}_f \mathbf{g}), \quad f \in \mathcal{F}. \quad (337)$$

The familiar small-strain Biot equations follow by linearizing these solid-reference equations about $\mathbf{F} = \mathbf{I}$ and $J = 1$, using a linear elastic law for $\boldsymbol{\sigma}''$, and substituting the Darcy flux directly into the fluid balance. In this linearization, B , M , κ_f , μ_f^{visc} , and $\bar{\rho}_f$ are frozen at the reference state, and $\Phi_{f0} = \phi_{f0}$ when $J_0 = 1$. The source-free reduced system is

$$\nabla_{\mathbf{x}} \cdot (\boldsymbol{\sigma}'' - B\bar{p}_f \mathbf{I}) + \rho \mathbf{g} = \mathbf{0}, \quad f \in \mathcal{F}, \quad (338a)$$

$$\frac{1}{M} \frac{\partial \bar{p}_f}{\partial t} + B \frac{\partial}{\partial t} (\nabla_{\mathbf{x}} \cdot \mathbf{u}) - \nabla_{\mathbf{x}} \cdot \left[\frac{\kappa_f}{\mu_f^{\text{visc}}} (\nabla_{\mathbf{x}} \bar{p}_f - \bar{\rho}_f \mathbf{g}) \right] = 0, \quad f \in \mathcal{F}. \quad (338b)$$

Here $\mathbf{u}$ is the small displacement of the skeleton. The pressure coupling in (338a) comes from the same fixed-pressure Legendre stress split that produced (237); the fluid-content coupling in (338b)

is the small-strain form of the finite-deformation storage $J\phi_f\bar{\rho}_f$. The coefficient limits are explicit in this frozen linear system: $K_s \rightarrow \infty$ removes solid-grain compressibility from $1/M$, $K_f \rightarrow \infty$ removes fluid compressibility, and taking both moduli to infinity makes pressure a constraint with $1/M \rightarrow 0$. A rigid skeleton removes the $B\partial_t(\nabla_{\mathbf{x}} \cdot \mathbf{u})$ term and leaves the pressure-diffusion equation, whereas zero relative flux gives the undrained storage relation $(1/M)\partial_t\bar{p}_f + B\partial_t(\nabla_{\mathbf{x}} \cdot \mathbf{u}) = 0$. The classical Biot system is therefore the single-solid, single-fluid, no-conversion, linearized limit of the variational mixture model.

Equations (327) and (335) are the finite-deformation momentum and fluid-storage equations of the single-fluid Biot specialization, with the fluid-storage balance written in the neutral, no-capillary form of the reference relative mass flux $\mathbf{W}_f$ defined in (294). Sun, Ostien, and Salinger present this pair of equations in final form in their stabilized assumed-deformation-gradient poromechanical formulation [55]; the linearized system (338) is the small-strain reduction of the same pair, in the classical consolidation form of Biot [7, 8].

9 Conclusions and outlook

We developed a nonequilibrium, finite-deformation theory for multicomponent, multiphase porous media with reactions, phase transformations, two thermal subsystems, and electrostatics. The central contribution is a traceable division of the model into conservation laws, reversible constraints, thermodynamic restrictions, and dissipative closures. The constrained Hamilton–d’Alembert statement produces the phase-coordinate, momentum, storage, composition, transfer-potential, and electrostatic relations, including the d’Alembert work of the saturation resistance when that branch is active. The Coleman–Noll procedure identifies the material stresses, phase pressures, entropies, generalized component-transfer forces, electrochemical affinities, gauge-invariant nonisothermal transport forces, capillary-history dissipation, and residual dissipation. The entropy inequality supplies the admissibility and nonnegative-dissipation restrictions. Onsager stationarity selects near-equilibrium rates for dynamic saturation redistribution, reaction, diffusion, and dispersion. The independently derived reversible relations agree, which supplies an internal check on the construction.

Converted mass enters the phase momentum production and the generalized Darcy law. The resulting source-shifted resistance distinguishes dissipation of the underlying drag from algebraic nonsingularity and the stronger positive-resistance regime. For the solids, the fixed-pressure Legendre construction gives nonlinear Biot coefficients at the current reacted state, while the phase/component kinematics connect pore-filling conversion to distension, stress-free deformation, elasticity, and plastic flow. The true-plastic and distension powers identify two conjugate stress–rate pairs and provide the basis for a coupled generalized-plasticity specialization.

The thermal, chemical, and electrical results use the same component-transfer and electric-enthalpy structure. Composition stationarity recovers electrochemical equilibrium and supplies the transfer-work correction away from equilibrium. Separating the nonisothermal component-potential force from the electric field preserves gauge invariance. The constrained interfacial energy gives the stored capillary pressure and capillary-history dissipation; the optional saturation resistance adds a dynamic pressure lag without changing the stored energy. Separate interfacial entropy and internal-energy densities retain this storage on the skeleton trajectory, while the moving fluid phases transport only their phase caloric quantities.

The construction is internally consistent. The common charge-rate and electrostatic-power identities couple electrical body force and source power without double counting. The same phase electric-enthalpy family supplies the electrocapillary and momentum relations, and the component material measures control both conversion momentum and solid compositional evolution. Writing

the energy and entropy balances in a skeleton observer retains bulk phase transport relative to the solid and exposes its joint admissibility condition with mechanical interaction-energy exchange.

The specialized reductions check the general equations. Under their stated assumptions, the theory recovers the standard mass-based compositional balance, Fick–Onsager transport in $N - 1$ independent composition directions, black-oil conservation equations and Darcy fluxes, a Nernst–Planck–Darcy system, and the finite-deformation and linearized single-solid/single-fluid Biot equations. The neutral one-fluid limit removes the electrocapillary and interfacial terms, and the local-thermal-equilibrium limit recovers the usual affinity power for phasewise mass-conserving chemistry or vanishing transfer-work offsets. These recoveries identify the thermodynamic structure retained when the full model is specialized.

Several limitations delimit the present result. The theory applies while the participating phases and components remain present; phase appearance and disappearance require separate switching conditions. Capillary hysteresis is represented by continuous internal variables and material-specific loading–unloading rules. The dynamic pressure lag is an optional near-equilibrium saturation-rate resistance whose calibration determines whether the branch is active for a given reservoir transient. Independent interfacial-area evolution requires a further state variable and kinetic equation. The electrical state is electroquasistatic and isotropic and excludes permanent polarization, directional dielectric structure, relaxation, and wave dynamics. Inserted mass carries recipient-phase energy and entropy under a local-equilibrium source convention. Reactions spanning the two thermal subsystems use the gauge-invariant neutral temperature-weighted reaction force; their physical reaction-energy transfer may be Onsager-coupled under the stated mechanismwise dissipation condition. The quadratic closures shown here are limited to near-equilibrium response. The finite-deformation Biot storage tangent used in the classical comparison is an additional integrable storage assumption introduced independently of the general phase energy. Constitutive calibration, well-posedness, discretization, and benchmark validation remain outside the present derivation.

Implementation should proceed with equation-level traceability. A solid-reference discretization can first verify neutral-isothermal component balances, relative-flux reconstruction, and coupled momentum before adding reaction-induced solid-volume change, two-temperature exchange, and electrochemical transport. Manufactured solutions and the derived limits then provide regression targets for pore-filling, crystallization, and electrocapillary benchmarks. A cyclic two-fluid drainage–imbibition test can verify reversal continuity, scanning paths, trapping, and nonnegative capillary-history dissipation before the closure is extended to three phases. A rate sweep for fracture–matrix imbibition and flowback in a tight or shale sample can then compare $\mathcal{T} = \mathbf{0}$ with the dynamic closure using uptake, pressure lag, and saturation profiles as observables.

A Observer transformations, gauges, and admissible data

This appendix records the technical setting assumed throughout the main derivation: the superposed-observer transformation rules and the frame-indifference restrictions they impose on the constitutive potentials, the gauge conditions for the electrostatic and transfer potentials, and the admissible initial and boundary data for a boundary-value problem.

A.1 Frame indifference, material symmetry, and angular momentum

Let a superposed rigid change of spatial observer be described by a translation $\mathbf{c}(t)$ and a proper-orthogonal tensor $\mathbf{Q}(t)$. Scalars are observer invariant, apart from the gauges of the electrostatic and Bedford–Drumheller transfer potentials specified below. The kinematic, electrical, flux, and

stress variables used below transform as

$$\mathbf{x}^* = \mathbf{c}(t) + \mathbf{Q}(t)\mathbf{x}, \quad \mathbf{Q}^T \mathbf{Q} = \mathbf{I}, \quad \det \mathbf{Q} = 1, \quad (\text{A.1a})$$

$$\mathbf{v}_\xi^* = \dot{\mathbf{c}} + \dot{\mathbf{Q}}\mathbf{x} + \mathbf{Q}\mathbf{v}_\xi, \quad (\mathbf{v}_\xi - \mathbf{v}_\zeta)^* = \mathbf{Q}(\mathbf{v}_\xi - \mathbf{v}_\zeta), \quad (\text{A.1b})$$

$$\mathbf{F}_\xi^* = \mathbf{Q}\mathbf{F}_\xi, \quad \mathbf{F}^* = \mathbf{Q}\mathbf{F}, \quad \bar{\mathbf{F}}_s^* = \mathbf{Q}\bar{\mathbf{F}}_s, \quad \mathbf{A}_s^* = \mathbf{Q}\mathbf{A}_s\mathbf{Q}^T, \quad s \in \mathcal{S}, \quad (\text{A.1c})$$

$$\mathbf{h}^*(\mathbf{x}^*, t) = \mathbf{h}(\mathbf{x}, t), \quad (\text{A.1d})$$

$$\varphi^*(\mathbf{x}^*, t) = \varphi(\mathbf{x}, t) + c_\varphi(t), \quad \mathbf{E}^* = \mathbf{Q}\mathbf{E}, \quad \mathbf{d}_\xi^* = \mathbf{Q}\mathbf{d}_\xi, \quad (\text{A.1e})$$

$$(\mathbf{j}_{\xi,k}^\alpha)^* = \mathbf{Q}\mathbf{j}_{\xi,k}^\alpha, \quad \mathbf{q}_\xi^* = \mathbf{Q}\mathbf{q}_\xi, \quad (\boldsymbol{\sigma}_\xi'^+)^* = \mathbf{Q}\boldsymbol{\sigma}_\xi'^+\mathbf{Q}^T. \quad (\text{A.1f})$$

Here $k \in \{\text{disp}, \text{diff}\}$. The entries of $\mathbf{h}$ are internal scalar variables, so the bold notation collects them but does not make $\mathbf{h}$ a spatial vector. Consequently, the capillary-history-gradient force in (247) transforms as a spatial vector. The transfer potential is a kinematic potential rather than an objective thermodynamic scalar. Between inertial observers, take $\mathbf{Q}(t) = \mathbf{Q}_0$ and $\mathbf{c}(t) = \mathbf{c}_0 + t\mathbf{u}_{\text{obs}}$, where $\mathbf{u}_{\text{obs}}$ is constant in the starred frame. Its Galilean transformation is

$$\tau^*(\mathbf{x}^*, t) = \tau(\mathbf{x}, t) + \mathbf{u}_{\text{obs}} \cdot \mathbf{x}^* - \frac{1}{2}\mathbf{u}_{\text{obs}} \cdot \mathbf{u}_{\text{obs}} t + c_\tau, \quad (\text{A.2})$$

where c_τ is a time-independent gauge constant. Consequently,

$$\nabla_{\mathbf{x}^*}\tau^* - \mathbf{v}_\xi^* = \mathbf{Q}_0(\nabla_{\mathbf{x}}\tau - \mathbf{v}_\xi), \quad \frac{D_\xi^*\tau^*}{Dt} - \frac{1}{2}\mathbf{v}_\xi^* \cdot \mathbf{v}_\xi^* = \frac{D_\xi\tau}{Dt} - \frac{1}{2}\mathbf{v}_\xi \cdot \mathbf{v}_\xi. \quad (\text{A.3})$$

These are the two combinations that enter the insertion-momentum and component-transfer equations. A time-dependent rotation produces an observer velocity that cannot be written as the gradient of a scalar, so this transfer-potential form is restricted to inertial observers. Noninertial balance laws must include the corresponding fictitious forces. Spatial gradients of objective scalars transform by left multiplication with $\mathbf{Q}$. The velocity gradient transforms as $\mathbf{L}_\xi^* = \dot{\mathbf{Q}}\mathbf{Q}^T + \mathbf{Q}\mathbf{L}_\xi\mathbf{Q}^T$, while its symmetric part transforms covariantly. Constitutive objectivity concerns arbitrary time-dependent $\mathbf{Q}$; the balance laws themselves are written for inertial observers, with fictitious accelerations included in the body force if a noninertial frame is used.

The elastic factors are assigned consistently with (A.1c), so that $\bar{\mathbf{F}}_s^{e*} = \mathbf{Q}\bar{\mathbf{F}}_s^e$ and $\mathbf{A}_s^{e*} = \mathbf{Q}\mathbf{A}_s^e\mathbf{Q}^T$. Frame indifference of the stored potentials therefore requires

$$\psi_s(\mathbf{Q}\bar{\mathbf{F}}_s^e, \mathbf{Q}\mathbf{A}_s^e\mathbf{Q}^T, \bar{\rho}_s, \{\eta_s^\alpha\}, \theta_s) = \psi_s(\bar{\mathbf{F}}_s^e, \mathbf{A}_s^e, \bar{\rho}_s, \{\eta_s^\alpha\}, \theta_s), \quad s \in \mathcal{S}, \quad (\text{A.4a})$$

$$\omega_\xi^+(\mathbf{Q}\mathbf{E}, \bar{\rho}_\xi, \{\eta_\xi^\alpha\}, \theta_\xi) = \omega_\xi^+(\mathbf{E}, \bar{\rho}_\xi, \{\eta_\xi^\alpha\}, \theta_\xi). \quad (\text{A.4b})$$

The plastic and stress-free factors are intermediate-configuration variables; their constitutive laws are understood to be invariant under a change of intermediate basis. Likewise, every tensor mobility, permeability, and thermal conductivity used below must transform by $\mathbf{Q}(\cdot)\mathbf{Q}^T$, every vector-valued closure must be equivariant, and the scalar reaction and plastic mobilities must be invariant. If such a transport tensor depends only on the scalar state variables displayed in this manuscript, material isotropy reduces it to a scalar multiple of $\mathbf{I}$; anisotropic transport requires an objective structural or resolved-flow argument.

Because ω_ξ^+ in (A.4b) has only one spatial-vector argument, its derived electric displacement is parallel to the electric field. Hence

$$\mathbf{d}_\xi(\mathbf{Q}\mathbf{E}, \dots) = \mathbf{Q}\mathbf{d}_\xi(\mathbf{E}, \dots), \quad \mathbf{E} \times \mathbf{d}_\xi = \mathbf{0}, \quad \boldsymbol{\sigma}_\xi^+ = (\boldsymbol{\sigma}_\xi^+)^T. \quad (\text{A.5})$$

Thus the present electrical state set describes an isotropic, possibly density-, composition-, and temperature-dependent dielectric response. A permanent polarization or bedding-directed dielectric response would require an additional objective structural argument and the associated stress and torque terms; those extensions are outside the present model.

The continuum is nonpolar and has no body couples, constituent couple stresses, or interphase interaction couples. Local angular-momentum balance therefore imposes

$$\boldsymbol{\sigma}'_{\xi^+} = (\boldsymbol{\sigma}'_{\xi^+})^T, \quad \xi \in \mathcal{F} \cup \mathcal{S}. \quad (\text{A.6})$$

Equation (A.6) is a constitutive restriction on the solid energy derivatives as well as on the electrical stress. Mechanical anisotropy remains admissible through the solid elastic arguments and the assigned material-symmetry group. An isotropic mechanical specialization requires invariance under every proper material rotation and therefore representation by objective scalar invariants and isotropic tensor functions; no such specialization is assumed unless stated locally.

A.2 Electrical ensemble and gauge

The electrical specialization is electroquasistatic: $\mathbf{E} = -\nabla_{\mathbf{x}}\varphi$, with no electromagnetic-wave dynamics. The phase electric enthalpies take $\mathbf{E}$ as their electrical argument, and $\mathbf{d}_{\xi} = -\partial\omega_{\xi}^+/\partial\mathbf{E}$. Free bulk charge ϱ and prescribed outward surface charge $\bar{q}$ are source-work coefficients rather than additional stored energies. Material-carried charge is obtained by weighting each component mass by z_{ξ}^{α} .

The boundary is partitioned into Γ_{φ} , where φ is prescribed, and $\Gamma_{\bar{q}}$, where $\mathbf{d} \cdot \mathbf{n} = \bar{q}$. This electric-displacement datum is distinct from normal material-current data. For a pure electric-displacement boundary problem, $\Gamma_{\bar{q}} = \partial\mathcal{B}$, solvability and its fixed-domain rate require

$$\int_{\mathcal{B}} \varrho \, dv = \int_{\partial\mathcal{B}} \bar{q} \, da, \quad (\text{A.7a})$$

$$\int_{\partial\mathcal{B}} \left[\frac{\partial\bar{q}}{\partial t} + \mathbf{i} \cdot \mathbf{n} \right] da = 0. \quad (\text{A.7b})$$

If a nonempty potential boundary is present, its normal displacement adjusts instead of being prescribed by these global equalities. If no potential value is prescribed, the additive gauge of φ must also be fixed, for example by prescribing its mean. Reaction sums conserve charge, and transport keeps the chemical driving force separate from the electric field; neither result changes when a constant is added to φ . At nonuniform temperature, differentiating an electrochemical potential divided by temperature would introduce that arbitrary constant. The neutral thermal and electric forces are therefore kept separate. The reservoir specialization takes ω_{ξ}^+ to have the objective single-vector dependence in (A.4b), thereby excluding permanent polarization at zero field, directional dielectric structure, and independent dielectric relaxation.

A.3 Initial and boundary data

The local theory does not prescribe a single boundary-value problem. An application must supply a compatible independent set of initial phase/component masses, active phase fractions, fluid and solid temperatures, capillary-history variables, solid kinematic and internal variables, and, when inertia is retained, phase velocities. These data must satisfy the mass-fraction, volume-fraction, mass, and charge restrictions, together with the constitutive bounds on the capillary-history state. The local evolution law for $\mathbf{h}$ requires initial data but no boundary data; a nonlocal regularization would add the corresponding boundary conditions. Here $s_{\star} \in \mathcal{S}$ denotes the selected solid-phase

transfer reference. The transfer potential requires one initial datum for the skeleton-trajectory evolution (181). The specific generalized transfer-work potentials L_ξ^N of the non-reference phases are then recovered from (182), rather than prescribing additional initial data for τ along every phase trajectory. The reference state used here takes the transfer potential to be initially uniform. Its time-independent additive constant is fixed by choosing

$$\tau(\mathbf{x}, 0) = 0, \quad \mathbf{x} \in \mathcal{B}. \quad (\text{A.8})$$

The electrostatic potential has no independent evolution datum; it is obtained at each time from Gauss' law, the current charge state, and its boundary data.

Mechanical data use the complementary motion/traction partition defined with (51). The solid and fluid natural phase tractions are (100) and (104), respectively. When the phase virtual motions coincide on the mixture boundary, their boundary powers give the overall traction (248). For every independent component $\alpha \neq N$ in phase $\xi \in \mathcal{G}$, transport data use complementary normal-flux and component-potential portions. The electric-potential or electric-displacement datum is supplied independently on Γ_φ or $\Gamma_{\bar{q}}$:

$$\partial\mathcal{B} = \overline{\Gamma_{m,\xi}^\alpha} \cup \overline{\Gamma_{\mathcal{M}_\xi}^\alpha}, \quad \Gamma_{m,\xi}^\alpha \cap \Gamma_{\mathcal{M}_\xi}^\alpha = \emptyset, \quad (\text{A.9a})$$

$$\left(\rho_\xi^\alpha \mathbf{v}_\xi + \mathbf{j}_{\xi,\text{disp}}^\alpha + \mathbf{j}_{\xi,\text{diff}}^\alpha \right) \cdot \mathbf{n} = \bar{m}_\xi^{\alpha,\text{out}} \quad \text{on } \Gamma_{m,\xi}^\alpha, \quad (\text{A.9b})$$

$$\frac{\hat{\mu}_\xi^\alpha - \hat{\mu}_\xi^N}{\theta_\mathcal{G}} = \overline{(\hat{\mu}_\xi^\alpha - \hat{\mu}_\xi^N) / \theta_\mathcal{G}} \quad \text{on } \Gamma_{\mathcal{M}_\xi}^\alpha. \quad (\text{A.9c})$$

Impermeability sets $\bar{m}_\xi^{\alpha,\text{out}} = 0$. The reference-component flux is reconstructed rather than prescribed independently, and the relative parts of the boundary fluxes must satisfy the zero-sum conditions in (34).

Each thermal subsystem uses a complementary temperature/heat-flux partition, with the sign convention that positive prescribed flux leaves $\mathcal{B}$. Here $\mathbf{q}_\xi$ is the gauge-invariant nonadvective material-energy flux in (151); its Fourier closure is (219). Electrical work on component transport relative to a phase is a gauge-invariant volume power in (151), not an additional potential-dependent boundary flux:

$$\partial\mathcal{B} = \overline{\Gamma_{\theta,\mathcal{G}}} \cup \overline{\Gamma_{q,\mathcal{G}}}, \quad \Gamma_{\theta,\mathcal{G}} \cap \Gamma_{q,\mathcal{G}} = \emptyset, \quad (\text{A.10a})$$

$$\theta_\mathcal{G} = \bar{\theta}_\mathcal{G} \quad \text{on } \Gamma_{\theta,\mathcal{G}}, \quad (\text{A.10b})$$

$$\sum_{\xi \in \mathcal{G}} \mathbf{q}_\xi \cdot \mathbf{n} = \bar{q}_\mathcal{G}^{\text{out}} \quad \text{on } \Gamma_{q,\mathcal{G}}, \quad \mathcal{G} \in \{\mathcal{F}, \mathcal{S}\}. \quad (\text{A.10c})$$

The corresponding entropy flux also contains the component-potential-weighted component-relative contribution stated in (157). Its normal value is fixed by the component flux and potential data in (A.9), and it vanishes on an impermeable boundary. It is therefore not an additional independent thermal boundary datum. The unresolved interfacial entropy follows the skeleton trajectory and has no separate boundary flux, so it introduces no additional thermal boundary datum.

Insulation sets $\bar{q}_\mathcal{G}^{\text{out}} = 0$. For a steady pure-heat-flux problem, integrating (151) shows that the prescribed outward heat flux must equal the net nonconductive volume production minus the nonconductive steady storage and transport terms. This is the thermal pure-Neumann compatibility condition, with its sign fixed by the $-\nabla_{\mathbf{x}} \cdot \mathbf{q}_\xi$ term in that balance. Similarly, a quasi-static pure-traction problem must satisfy the integrated overall momentum balance (247); with inertia retained, the same integral determines the rate of total momentum.

Electrostatic data use the potential/displacement partition and compatibility conditions (A.7). Normal component mass fluxes determine the material-carried current $\mathbf{i} \cdot \mathbf{n}$. Pure-flux component data must also satisfy the component mass balances integrated over $\mathcal{B}$, so that initial mass plus integrated mechanism supply minus outward boundary flux equals current component mass.

B Derivation of the component Euler identity

This appendix derives (175) from the constituent-mass definition (139). At fixed ϕ_ξ , variation of one partial density gives

$$\frac{\partial \rho_\xi}{\partial \rho_\xi^\alpha} = 1, \quad \frac{\partial \bar{\rho}_\xi}{\partial \rho_\xi^\alpha} = \frac{1}{\phi_\xi}, \quad (\text{B.1a})$$

$$\frac{\partial \eta_\xi^\beta}{\partial \rho_\xi^\alpha} = \frac{\delta_{\alpha\beta} - \eta_\xi^\beta}{\rho_\xi}. \quad (\text{B.1b})$$

For a fluid phase, substitution into (139) gives

$$\begin{aligned} \hat{\mu}_f^\alpha = & \psi_f + \bar{\rho}_f \left. \frac{\partial \psi_f}{\partial \bar{\rho}_f} \right|_{\mathcal{X}_f} + \left. \frac{\partial \omega_f^+}{\partial \bar{\rho}_f} \right|_{\mathcal{X}_f, \mathbf{E}} \\ & + \frac{1}{\rho_f} \left[\rho_f \left. \frac{\partial \psi_f}{\partial \eta_f^\alpha} \right|_{\mathcal{X}_f} + \phi_f \left. \frac{\partial \omega_f^+}{\partial \eta_f^\alpha} \right|_{\mathcal{X}_f, \mathbf{E}} \right. \\ & \left. - \sum_\beta \eta_f^\beta \left(\rho_f \left. \frac{\partial \psi_f}{\partial \eta_f^\beta} \right|_{\mathcal{X}_f} + \phi_f \left. \frac{\partial \omega_f^+}{\partial \eta_f^\beta} \right|_{\mathcal{X}_f, \mathbf{E}} \right) \right], \quad f \in \mathcal{F}. \end{aligned} \quad (\text{B.2})$$

The differentiated variable is omitted from the held-fixed state set. Dividing (83) by $\bar{\rho}_f$, and using (96), gives

$$\bar{\rho}_f \left. \frac{\partial \psi_f}{\partial \bar{\rho}_f} \right|_{\mathcal{X}_f} + \left. \frac{\partial \omega_f^+}{\partial \bar{\rho}_f} \right|_{\mathcal{X}_f, \mathbf{E}} = \frac{1}{\rho_f} \sum_\beta \pi_f^\beta, \quad f \in \mathcal{F}, \quad (\text{B.3a})$$

$$\rho_f \left. \frac{\partial \psi_f}{\partial \eta_f^\beta} \right|_{\mathcal{X}_f} + \phi_f \left. \frac{\partial \omega_f^+}{\partial \eta_f^\beta} \right|_{\mathcal{X}_f, \mathbf{E}} = \Pi_f + \frac{\pi_f^\beta}{\eta_f^\beta}, \quad f \in \mathcal{F}. \quad (\text{B.3b})$$

Because $\sum_\beta \eta_f^\beta = 1$, the weighted sum of (B.3b) is

$$\sum_\beta \eta_f^\beta \left(\rho_f \left. \frac{\partial \psi_f}{\partial \eta_f^\beta} \right|_{\mathcal{X}_f} + \phi_f \left. \frac{\partial \omega_f^+}{\partial \eta_f^\beta} \right|_{\mathcal{X}_f, \mathbf{E}} \right) = \Pi_f + \sum_\beta \pi_f^\beta, \quad f \in \mathcal{F}. \quad (\text{B.4})$$

Substitution of (B.3) and (B.4) into (B.2) cancels both Π_f and $\sum_\beta \pi_f^\beta$, leaving

$$\begin{aligned} \hat{\mu}_f^\alpha &= \psi_f + \frac{\pi_f^\alpha}{\rho_f \eta_f^\alpha} \\ &= \psi_f + \frac{\pi_f^\alpha}{\phi_f \bar{\rho}_f \eta_f^\alpha}, \quad f \in \mathcal{F}. \end{aligned} \quad (\text{B.5})$$

which is the fluid form of (175).

For a solid phase, the constituent-mass derivative is instead taken at fixed $\mathbf{A}_s$, $\bar{\mathbf{F}}_s$, $\mathbf{A}_s^p$, and $\bar{\mathbf{F}}_s^p$. Applying (174) and the material-stress relations gives the total composition derivative

$$\begin{aligned} \rho_s \left. \frac{\partial \psi_s}{\partial \eta_s^\beta} \right|_{\bar{\rho}_s, \theta_s, \mathbf{A}_s, \bar{\mathbf{F}}_s, \mathbf{A}_s^p, \bar{\mathbf{F}}_s^p} &= \rho_s \left. \frac{\partial \psi_s}{\partial \eta_s^\beta} \right|_{\mathcal{X}_s} \\ &- \text{tr} \left[(\mathbf{A}_s^p)^{-1} (\mathbf{A}_s^e)^{-1} (\boldsymbol{\sigma}'_s)^T \mathbf{A}_s^e \mathbf{A}_s^p \left. \frac{\partial \mathbf{A}_s^0}{\partial \eta_s^\beta} \right|_{\mathcal{X}_s} (\mathbf{A}_s^0)^{-1} \right] \\ &- \text{tr} \left[(\bar{\mathbf{F}}_s^p)^{-1} (\bar{\mathbf{F}}_s^e)^{-1} \mathbf{A}_s^{-1} (\boldsymbol{\sigma}'_s)^T \mathbf{A}_s \bar{\mathbf{F}}_s^e \bar{\mathbf{F}}_s^p \left. \frac{\partial \bar{\mathbf{F}}_s^0}{\partial \eta_s^\beta} \right|_{\mathcal{X}_s} (\bar{\mathbf{F}}_s^0)^{-1} \right], \quad s \in \mathcal{S}. \end{aligned} \quad (\text{B.6})$$

Adding the explicit electric-enthalpy composition derivative and subtracting the component- N equation from the component- β equation reproduces (172). Thus the complete solid composition coefficient has component-dependent part $\pi_s^\beta / \eta_s^\beta$; its remaining part is common to every component. Because $\sum_\beta \eta_s^\beta = 1$, that common part cancels between the component- α coefficient and its mass-fraction-weighted sum in the constituent-mass chain rule. Combining this cancellation with the density contribution gives

$$\begin{aligned} \hat{\mu}_s^\alpha &= \psi_s + \frac{1}{\rho_s} \sum_\beta \pi_s^\beta + \frac{1}{\rho_s} \left(\frac{\pi_s^\alpha}{\eta_s^\alpha} - \sum_\beta \pi_s^\beta \right) \\ &= \psi_s + \frac{\pi_s^\alpha}{\rho_s \eta_s^\alpha} = \psi_s + \frac{\pi_s^\alpha}{\phi_s \bar{\rho}_s \eta_s^\alpha}, \quad s \in \mathcal{S}. \end{aligned} \quad (\text{B.7})$$

This is the solid form of (175).

C Term-by-term correspondence of the single-phase energy balances

This appendix verifies the correspondence between (153) and (154). Take the nonporous, single-phase specialization used to obtain (153), write $\mathbf{E}^M = \mathbf{E}$, and identify the phase material derivative with the single-phase material derivative. The field kinematics stated before (153) give

$$\mathbf{d} \cdot \nabla_{\mathbf{x}} \dot{\boldsymbol{\varphi}} = -\mathbf{d} \cdot \dot{\mathbf{E}} - (\mathbf{E} \otimes \mathbf{d}) : \mathbf{L}. \quad (\text{C.1})$$

The electrical boundary and free-charge terms in (153) satisfy (150); hence

$$\nabla_{\mathbf{x}} \cdot (\dot{\boldsymbol{\varphi}} \mathbf{d}) - \varrho \dot{\boldsymbol{\varphi}} = \mathbf{d} \cdot \nabla_{\mathbf{x}} \dot{\boldsymbol{\varphi}}. \quad (\text{C.2})$$

Substitution of (C.1) and (C.2) into (153), followed by $\boldsymbol{\sigma}_\xi^+ = \omega_\xi^+ \mathbf{I} + \mathbf{E} \otimes \mathbf{d}$ from (75), gives

$$\rho_\xi \dot{\mathbf{e}}_\xi + \dot{\omega}_\xi^+ = (\boldsymbol{\sigma}'_\xi - \bar{p}_\xi \mathbf{I}) : \mathbf{L}_\xi - \nabla_{\mathbf{x}} \cdot \mathbf{q}_\xi - \mathbf{d} \cdot \dot{\mathbf{E}} + \rho_\xi r_\xi. \quad (\text{C.3})$$

Here the two $\omega_\xi^+ \text{tr} \mathbf{L}_\xi$ terms cancel: one is part of the material-volume rate on the left of (153), and the other is the isotropic part of $\boldsymbol{\sigma}_\xi^+$. The dyadic Maxwell term cancels the second term on the right of (C.1). Thus the mechanical, electrical, heat-flux, and heat-supply terms have each been accounted for once.

To compare with the polarization convention of [45], separate the vacuum displacement from the material polarization according to

$$\begin{aligned} \mathbf{d} &= \varepsilon_0 \mathbf{E} + \mathbf{P}, & \boldsymbol{\pi} &= \frac{\mathbf{P}}{\rho_\xi}, \\ \rho_\xi \left(\varepsilon - \mathbf{E}^M \cdot \boldsymbol{\pi} \right) &= \rho_\xi e_\xi + \omega_\xi^+ + \frac{\varepsilon_0}{2} \mathbf{E} \cdot \mathbf{E}, \\ \boldsymbol{\tau} &= \boldsymbol{\sigma}'_\xi - \bar{p}_\xi \mathbf{I} + \left(\omega_\xi^+ + \frac{\varepsilon_0}{2} \mathbf{E} \cdot \mathbf{E} \right) \mathbf{I}. \end{aligned} \quad (\text{C.4})$$

The last two equalities specify the energy and stress identifications between the two conventions. The current electric enthalpy contains the vacuum-field contribution $-\varepsilon_0 \mathbf{E} \cdot \mathbf{E}/2$; adding the vacuum-field energy converts it to the polarization-based specific energy. Because ω_ξ^+ and the vacuum-field energy are densities per current volume, material differentiation of the energy identification gives

$$\begin{aligned} \rho_\xi \frac{D_\xi}{Dt} \left(\varepsilon - \mathbf{E}^M \cdot \boldsymbol{\pi} \right) &= \rho_\xi \dot{e}_\xi + \dot{\omega}_\xi^+ + \left(\omega_\xi^+ + \frac{\varepsilon_0}{2} \mathbf{E} \cdot \mathbf{E} \right) \text{tr} \mathbf{L}_\xi \\ &+ \varepsilon_0 \mathbf{E} \cdot \dot{\mathbf{E}}. \end{aligned} \quad (\text{C.5})$$

Substitution of (C.3) into (C.5), followed by $\mathbf{d} = \varepsilon_0 \mathbf{E} + \mathbf{P}$ and the stress identification in (C.4), yields

$$\rho_\xi \frac{D_\xi}{Dt} \left(\varepsilon - \mathbf{E}^M \cdot \boldsymbol{\pi} \right) = \boldsymbol{\tau} : \mathbf{L}_\xi - \nabla_{\mathbf{x}} \cdot \mathbf{q}_\xi - \mathbf{P} \cdot \dot{\mathbf{E}}^M + \rho_\xi r_\xi. \quad (\text{C.6})$$

Equation (C.6) is the electric-enthalpy form obtained from equations (10), (12), and (16) of [45]. It is (154) after the notational identifications $\rho = \rho_\xi$, $\mathbf{L} = \mathbf{L}_\xi$, $\mathbf{q} = \mathbf{q}_\xi$, and $r = r_\xi$, together with the energy and stress identifications in (C.4). The current formulation keeps the free-charge bulk power and electrical boundary flux visible until (150) is applied; the polarization form instead combines them into the field-rate work. The two balances are therefore equivalent under the stated single-phase specialization, vacuum-field energy partition, and stress identification.

Acknowledgements

The author thanks Professors David DiCarlo, Mojdeh Delshad, D. Nicolas Espinoza, and Marc Hesse for useful conversations. This work was funded by the U.S. Department of Energy under awards DE-FE0032349 “Hydrogen Storage in Salt Caverns in the Permian Basin: Seal Integrity Evaluation and Field Test” and DE-AR0001864283, assigned control number 2784-1755, “Cyclic Injection for Commercial Seismic-Safe Geologic H2 Production.”

Declaration of generative AI and AI-assisted technologies

From 8 May 2026 through the latest covered commit on 21 September 2026, the author used OpenAI Codex (model versions were not consistently recorded) and GitHub Copilot (model versions were not consistently recorded) within an author-directed, version-controlled manuscript-development workflow. AI assistance was used for proposing and critiquing prose; examining notation and equation references; auditing derivational consistency; identifying candidate literature and bibliographic issues; supporting LaTeX quality assurance; assisting with reproducibility and scientific-software development. The author determined the scientific questions, theoretical structure, assumptions,

mathematical arguments, physical interpretations, and final wording. Every accepted change was reviewed by the author; equations and citations were checked against manuscript source and primary literature as applicable, and computational changes were subjected to the repository’s applicable validation procedures. AI output was not treated as a scholarly source or credited with authorship. The author takes full responsibility for the accuracy, originality, and integrity of the work.

References

- [1] Matthew Balhoff. *An Introduction to Multiphase, Multicomponent Reservoir Simulation*, volume 75 of *Developments in Petroleum Science*. Elsevier, 2022. doi:10.1016/C2021-0-01590-X.
- [2] A Bedford and DS Drumheller. A variational theory of porous media. *International Journal of Solids and Structures*, 15(12):967–980, 1979. doi:10.1016/0020-7683(79)90025-8.
- [3] A. Bedford and D.S. Drumheller. Theories of immiscible and structured mixtures. *International Journal of Engineering Science*, 21(8):863–960, 1983. doi:10.1016/0020-7225(83)90071-X.
- [4] Roman Beloborodov, Marina Pervukhina, Tongcheng Han, and Matthew Josh. Experimental characterization of dielectric properties in fluid saturated artificial shales. *Geofluids*, 2017:1019461, 2017. doi:10.1155/2017/1019461.
- [5] Lynn Schreyer Bennethum and John H. Cushman. Multicomponent, multiphase thermodynamics of swelling porous media with electroquasistatics: I. macroscale field equations. *Transport in Porous Media*, 47(3):309–336, 2002. doi:10.1023/A:1015558130315.
- [6] Lynn Schreyer Bennethum and John H. Cushman. Multicomponent, multiphase thermodynamics of swelling porous media with electroquasistatics: II. constitutive theory. *Transport in Porous Media*, 47(3):337–362, 2002. doi:10.1023/A:1015562614386.
- [7] M.A. Biot. General theory of three-dimensional consolidation. *Journal of applied physics*, 12(2):155–164, 1941.
- [8] Maurice A. Biot and David G. Willis. The elastic coefficients of the theory of consolidation. *Journal of Applied Mechanics*, 24:594–601, 1957.
- [9] Dieter Bothe. Sharp-interface continuum thermodynamics of multicomponent fluid systems with interfacial mass. *International Journal of Engineering Science*, 179:103731, 2022. doi:10.1016/j.ijengsci.2022.103731.
- [10] Dieter Bothe and Wolfgang Dreyer. Continuum thermodynamics of chemically reacting fluid mixtures. *Acta Mechanica*, 226(6):1757–1805, 2015. doi:10.1007/s00707-014-1275-1.
- [11] Dieter Bothe and Pierre-Étienne Druet. On the structure of continuum thermodynamical diffusion fluxes—a novel closure scheme and its relation to the Maxwell–Stefan and the Fick–Onsager approach. *International Journal of Engineering Science*, 184:103818, 2023. doi:10.1016/j.ijengsci.2023.103818.
- [12] Herbert B. Callen. *Thermodynamics and an Introduction to Thermostatistics*. John Wiley and Sons, 2 edition, 1985.

- [13] Jeremy Camps-Roach, Denis M. O’Carroll, Timothy A. Newson, Toshihiro Sakaki, and Tissa H. Illangasekare. Experimental investigation of dynamic effects in capillary pressure: Grain size dependency and upscaling. *Water Resources Research*, 46(8):W08544, 2010. doi:10.1029/2009WR008881.
- [14] B.D. Coleman and W. Noll. The thermodynamics of elastic materials with heat conduction and viscosity. In *The Foundations of Mechanics and Thermodynamics*, pages 145–156. Springer, 1974. doi:10.1007/978-3-642-65817-4_9.
- [15] I. F. Collins and G. T. Houlsby. Application of thermomechanical principles to the modelling of geotechnical materials. *Proceedings of the Royal Society of London. Series A: Mathematical, Physical and Engineering Sciences*, 453(1964):1975–2001, 1997. doi:10.1098/rspa.1997.0107.
- [16] O. Coussy. *Poromechanics*. John Wiley & Sons, 2004. doi:10.1002/0470092718.
- [17] Emmanuel Detournay and Alexander H.-D. Cheng. Fundamentals of poroelasticity. In C. Fairhurst, editor, *Comprehensive Rock Engineering: Principles, Practice and Projects*, volume 2, pages 113–171. Pergamon Press, 1993. doi:10.1016/B978-0-08-040615-2.50011-3.
- [18] Masao Doi. Onsager’s variational principle in soft matter. *Journal of Physics: Condensed Matter*, 23(28):284118, 2011. doi:10.1088/0953-8984/23/28/284118.
- [19] Luis Dorfmann and Ray W. Ogden. Nonlinear electroelasticity: Material properties, continuum theory and applications. *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences*, 473(2204):20170311, 2017. doi:10.1098/rspa.2017.0311.
- [20] Wolfgang Dreyer, Clemens Gohlke, and Rüdiger Müller. Bulk-surface electrothermodynamics and applications to electrochemistry. *Entropy*, 20(12):939, 2018. doi:10.3390/e20120939.
- [21] D.S. Drumheller. On theories for reacting immiscible mixtures. *International Journal of Engineering Science*, 38(3):347–382, 2000. doi:10.1016/S0020-7225(99)00047-6.
- [22] D.S. Drumheller and A. Bedford. A thermomechanical theory for reacting immiscible mixtures. *Archive for Rational Mechanics and Analysis*, 73(3):257–284, 1980. doi:10.1007/BF00282206.
- [23] Nasser Faraz, Ehsan Khamenechi, and Hamid Naderan Tahan. Impact of boiling heat transfer on geothermal reservoir simulation using local thermal non-equilibrium model. *Geothermics*, 90:102016, 2021. doi:10.1016/j.geothermics.2020.102016.
- [24] John T. Foster, Syed Talha Tirmizi, Emmanuel Ikpesu, and Marc Hesse. A finite deformation formulation for reacting porous media with volume change. *Journal of the Mechanics and Physics of Solids*, 217:106811, December 2026. doi:10.1016/j.jmps.2026.106811.
- [25] John T. Foster and Xiao Xu. Revisiting finite deformation poromechanics: Deriving a nonlinear Biot coefficient from first principles. *Journal of the Mechanics and Physics of Solids*, 204:106263, 2025. doi:10.1016/j.jmps.2025.106263.
- [26] Paul Germain. The method of virtual power in continuum mechanics. part 2: Microstructure. *SIAM Journal on Applied Mathematics*, 25(3):556–575, 1973. doi:10.1137/0125053.
- [27] S. Ghabezloo. Micromechanics analysis of thermal expansion and thermal pressurization of a hardened cement paste. *Cement and Concrete Research*, 41(5):520–532, 2011. doi:10.1016/j.cemconres.2011.01.023.

- [28] S. Ghabezloo and J. Sulem. Stress dependent thermal pressurization of a fluid-saturated rock. *Rock Mechanics and Rock Engineering*, 42(1):1–24, 2009. doi:10.1007/s00603-008-0165-z.
- [29] Denis S. Goldobin. On thermal diffusion and gauge transformations for thermodynamic fluxes and forces. *Computational Continuum Mechanics*, 9(1):52–58, 2016. doi:10.7242/1999-6691/2016.9.1.5.
- [30] William G. Gray. Thermodynamics and constitutive theory for multiphase porous-media flow considering internal geometric constraints. *Advances in Water Resources*, 22(5):521–547, 1999. doi:10.1016/S0309-1708(98)00021-9.
- [31] William G. Gray and Cass T. Miller. Thermodynamically constrained averaging theory approach for modeling flow and transport phenomena in porous medium systems: 5. single-fluid-phase transport. *Advances in Water Resources*, 32(5):681–711, 2009. doi:10.1016/j.advwatres.2008.10.013.
- [32] Zhenlin Guo and Ping Lin. A thermodynamically consistent phase-field model for two-phase flows with thermocapillary effects. *Journal of Fluid Mechanics*, 766:226–271, 2015. doi:10.1017/jfm.2014.696.
- [33] Morton E. Gurtin, Eliot Fried, and Lallit Anand. *The Mechanics and Thermodynamics of Continua*. Cambridge University Press, 2010. doi:10.1017/CB09780511762956.
- [34] Andrzej Hanyga and Jianfei Lu. Thermal effects in immiscible two-fluid porous flow. *International Journal of Engineering Science*, 42(3–4):291–301, 2004. doi:10.1016/j.ijengsci.2003.07.003.
- [35] S. Majid Hassanizadeh, Michael A. Celia, and Helge K. Dahle. Dynamic effect in the capillary pressure–saturation relationship and its impacts on unsaturated flow. *Vadose Zone Journal*, 1(1):38–57, 2002. doi:10.2136/vzj2002.3800.
- [36] S. Majid Hassanizadeh and William G. Gray. Thermodynamic basis of capillary pressure in porous media. *Water Resources Research*, 29(10):3389–3405, 1993. doi:10.1029/93WR01495.
- [37] Mihaela Ignatova and Jingyang Shu. Global smooth solutions of the Nernst–Planck–Darcy system. *Journal of Mathematical Fluid Mechanics*, 24:Article 26, 2022. doi:10.1007/s00021-022-00666-7.
- [38] David Jasnow and Jorge Viñals. Coarse-grained description of thermo-capillary flow. *Physics of Fluids*, 8(3):660–669, 1996. doi:10.1063/1.868851.
- [39] Jihoon Kim, Hamdi A. Tchelepi, and Ruben Juanes. Rigorous coupling of geomechanics and multiphase flow with strong capillarity. *SPE Journal*, 18(6):1123–1139, 2013. doi:10.2118/141268-PA.
- [40] Alex Kirichek, Claire Chassagne, and Ranajit Ghose. Predicting the dielectric response of saturated sandstones using a 2-electrode measuring system. *Frontiers in Physics*, 6:148, 2019. doi:10.3389/fphy.2018.00148.
- [41] Philippe Leroy and André Revil. A triple-layer model of the surface electrochemical properties of clay minerals. *Journal of Colloid and Interface Science*, 270(2):371–380, 2004. doi:10.1016/j.jcis.2003.08.007.

- [42] Robert M. McMeeking, Chad M. Landis, and Salomon M. A. Jimenez. A principle of virtual work for combined electrostatic and mechanical loading of materials. *International Journal of Non-Linear Mechanics*, 42(6):831–838, 2007. doi:10.1016/j.ijnonlinmec.2007.03.008.
- [43] J. R. Melcher and G. I. Taylor. Electrohydrodynamics: A review of the role of interfacial shear stresses. *Annual Review of Fluid Mechanics*, 1:111–146, 1969.
- [44] Mahsanam Mirzaei and Diganta Bhusan Das. Experimental investigation of hysteretic dynamic effect in capillary pressure–saturation relationship for two-phase flow in porous media. *AIChE Journal*, 59(10):3958–3974, 2013. doi:10.1002/aic.14121.
- [45] Adriano Montanaro. On the constitutive relations in thermo-electroelasticity. *arXiv preprint arXiv:0910.1344*, 2009. Version 3, revised 21 April 2015. URL: <https://arxiv.org/abs/0910.1344>, doi:10.48550/arXiv.0910.1344.
- [46] Jeffrey R. Moore and Steven D. Glaser. Self-potential observations during hydraulic fracturing. *Journal of Geophysical Research: Solid Earth*, 112(B2):B02204, 2007. doi:10.1029/2006JB004373.
- [47] John Newman and Karen E. Thomas-Alyea. *Electrochemical Systems*. John Wiley and Sons, 3 edition, 2004.
- [48] Grigor Nika. Thermodynamic modelling and derivation of effective properties for heterogeneous dielectrics. *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences*, 481(2315):20241001, 2025. doi:10.1098/rspa.2024.1001.
- [49] V.V. Palciauskas and P.A. Domenico. Characterization of drained and undrained response of thermally loaded repository rocks. *Water Resources Research*, 18(2):281–290, 1982. doi:10.1029/WR018i002p00281.
- [50] Demetrios T. Papageorgiou. Film flows in the presence of electric fields. *Annual Review of Fluid Mechanics*, 51:155–187, 2019. doi:10.1146/annurev-fluid-122316-044531.
- [51] O. A. Plumb and Stephen Whitaker. Dispersion in heterogeneous porous media: 1. local volume averaging and large-scale averaging. *Water Resources Research*, 24(7):913–926, 1988. doi:10.1029/WR024i007p00913.
- [52] Brian Seguin and Noel J. Walkington. Multi-component multiphase flow through a poroelastic medium. *Journal of Elasticity*, 135(1–2):485–507, 2019. doi:10.1007/s10659-018-09721-9.
- [53] J.C. Simo and T.J. Hughes. *Computational Inelasticity*. Springer, New York, 1998. doi:10.1007/b98904.
- [54] Juan C Simo. A framework for finite strain elastoplasticity based on maximum plastic dissipation and the multiplicative decomposition: Part i. continuum formulation. *Computer methods in applied mechanics and engineering*, 66(2):199–219, 1988. doi:10.1016/0045-7825(88)90076-X.
- [55] WaiChing Sun, Jakob T Ostien, and Andrew G Salinger. A stabilized assumed deformation gradient finite element formulation for strongly coupled poromechanical simulations at finite strain. *International Journal for Numerical and Analytical Methods in Geomechanics*, 37(16):2755–2788, 2013. doi:10.1002/nag.2161.

- [56] Haiqin Wang, Tiezheng Qian, and Xinpeng Xu. Onsager’s variational principle in active soft matter. *Soft Matter*, 17:3634–3653, 2021. doi:10.1039/D0SM02076A.
- [57] Changfu Wei and Mandar M. Dewoolkar. Formulation of capillary hysteresis with internal state variables. *Water Resources Research*, 42(7):W07405, 2006. doi:10.1029/2005WR004594.
- [58] Tetsuya Yamamoto, Masao Doi, and David Andelman. Contact angle saturation in electrowetting: Injection of ions into the surrounding media. *arXiv preprint arXiv:1510.00613*, 2015. URL: <https://arxiv.org/abs/1510.00613>.