Modeling Two-Fluid-Phase Flow and Species Transport in Porous Media

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Abstract

The thermodynamically constrained averaging theory (TCAT) is used to formulate a modeling framework for mechanistic models of species transport in multiphase porous medium systems containing two fluid phases and a solid phase. Primary restrictions guide the selection of entities and the set of conservation and balance equations needed to formulate an augmented entropy inequality (EI). Classical irreversible thermodynamics is upscaled from the microscale to the macroscale and used to provide a connection among material derivatives that arise from the conservation and balance equations under near-equilibrium conditions. An essentially exact constrained EI (CEI) is derived to approach the force-flux form of the EI that is desired. A set of approximations is applied to the CEI to produce a non-unique simplified EI (SEI), which is in the strict force-flux form needed to guide the formulation of closure relations.

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22 Sets of secondary restrictions are applied to the general SEI to form sim-
 23 pler subsets of the general SEI that apply for the local thermal equilibrium
 24 and isothermal cases. The SEI is then used to constrain the permissible form
 25 of the closure relations and to formulate a set of low-order closure relations.
 26 A specific model instance is formulated in closed form by specifying a com-
 27 plete set of conservation equations and closure relations. Many other model
 28 instances can be derived from the general modeling framework presented,
 29 and these potential extensions are discussed.

30 *Keywords:* TCAT, Porous medium, Multiphase flow, Species transport,
 31 Model formulation

32 **Nomenclature**

33 *Roman letters*

34 $\hat{A}^\alpha$	interfacial velocity coefficient related to velocity of fluid phase α
35 $\hat{B}^\alpha$	common curve velocity coefficient related to velocity of fluid phase α
36 b	entropy body source density
37 $\mathbf{C}$	Green's deformation tensor
38 $\hat{c}$	closure coefficient
39 $\hat{\mathbf{D}}$	dispersion tensor
40 $\mathbf{d}$	rate of strain tensor, $\mathbf{d} = [\nabla \mathbf{v} + (\nabla \mathbf{v})^\top] / 2$
41 E	internal energy density
42 $\bar{E}$	partial mass energy
43 $\mathcal{E}_{**}^{\bar{\alpha}}$	macroscale entity-based total energy conservation equation, Eq. (3)

44	f	general scalar function
45	$\mathbf{G}$	geometric orientation tensor, $\mathbf{G}_\alpha = \mathbf{I} - \mathbf{l}'_\alpha$ for $\alpha \in \mathcal{I}_I$, $\mathbf{G}_{wns} = \mathbf{I} - \mathbf{l}''_{wns}$
46	$\overset{\kappa \rightarrow \alpha}{G}_0$	macroscale transfer rate of potential energy due to variability of
47		mass exchange per volume
48	$\mathcal{G}_{**}^{\bar{\alpha}}$	macroscale entity-based body force potential balance equation, Eq. (5)
49	$\mathbf{g}$	body force per unit mass, gravity
50	$\overline{H}$	partial mass enthalpy
51	h	energy source density
52	$h_0^{\bar{\alpha}}$	macroscale energy source density for entity α due to body force
53		and velocity fluctuations
54	$\mathbf{I}$	identity tensor
55	$\mathbf{l}'$	unit tensor in a surface, $\mathbf{l}'_\alpha = \mathbf{I} - \mathbf{n}_\beta \mathbf{n}_\beta$ for $\alpha \in \mathcal{I}_I$, $\beta \in \mathcal{I}_{c\alpha}^+$
56	$\mathbf{l}''$	unit tensor in a common curve, $\mathbf{l}''_{wns} = \mathbf{l}_{wns} \mathbf{l}_{wns}$
57	$\mathbf{l}^{(n)}$	unit tensor associated with 3 - n -dimensional entity where (n) is
58		the number of primes used
59	$\mathcal{I}$	set of entity indices
60	$\mathcal{I}_C$	set of common curve entities
61	$\mathcal{I}_{c\alpha}$	connected set of indices for entity α , $\mathcal{I}_{c\alpha} = \mathcal{I}_{c\alpha}^+ \cup \mathcal{I}_{c\alpha}^-$
62	$\mathcal{I}_{c\alpha}^+$	connected set of indices of one dimension higher than entity α
63	$\mathcal{I}_{c\alpha}^-$	connected set of indices of one dimension lower than entity α
64	$\mathcal{I}_f$	set of fluid-phase indices

65	$\mathcal{J}_I$	set of interface indices
66	$\mathcal{J}_P$	set of phase indices
67	$\mathcal{J}_s$	set of species indices
68	$\mathcal{J}_{s \setminus N}$	set of species indices except species N
69	$\mathcal{J}_{\setminus S}$	set of entity indices except the solid phase
70	$J_\alpha^{\alpha\beta}$	macroscale surface curvature, $J_\alpha^{\alpha\beta} = \langle \nabla' \cdot \mathbf{n}_\alpha \rangle_{\Omega_{\alpha\beta}, \Omega_{\alpha\beta}}$ for $\alpha, \beta \in \mathcal{J}_f$
71	j	Jacobian
72	K_E	kinetic energy per mass due to velocity fluctuations
73	$\hat{K}_M$	mass transfer coefficient
74	$\hat{\mathbf{K}}_\theta$	heat conductivity tensor
75	$\hat{k}^{wn}$	parameter for rate of relaxation of interfacial area
76	$\hat{k}_1^{wn}$	parameter for rate of relaxation of interfacial area
77	$\hat{k}^{wns}$	parameter for rate of relaxation of common curve length
78	$\mathbf{l}$	unit vector tangent to a common curve
79	$\overset{i\kappa \rightarrow i\alpha}{M}$	macroscale transfer rate of mass of species i in entity κ to species
80		i in entity α per volume
81	$\mathcal{M}_{**}^{\overline{i\alpha}}$	macroscale species mass conservation equation, Eq. (1)
82	N	number of chemical species
83	$\mathbf{n}$	unit normal vector
84	$\mathcal{P}_{**}^{\overline{\alpha}}$	macroscale entity-based momentum conservation equation, Eq. (2)
85	p	pressure

86	$Q_1^{\kappa \rightarrow \alpha}$	macroscale transfer rate of internal energy from entity κ to entity α per volume
87		
88	$Q_0^{*\kappa \rightarrow \alpha}$	macroscale energy exchange between entities which dimensionalities differ by two
89		
90	$\mathbf{q}$	non-advective energy flux
91	$\mathbf{q}_{g0}$	non-advective energy flux associated with mechanical processes
92	$\hat{\mathbf{R}}$	resistance tensor
93	r	mass production rate density
94	$\mathcal{S}_{**}^{\bar{\alpha}}$	macroscale entity-based entropy balance equation, Eq. (4)
95	s	saturation
96	$\mathbf{T}_0^{\kappa \rightarrow \alpha}$	macroscale transfer rate of momentum from entity κ to entity α per volume
97		
98	$\mathbf{T}^{*\kappa \rightarrow \alpha}$	macroscale momentum exchange between entities which dimensionalities differ by two
99		
100	$\mathcal{T}_*^{\bar{\alpha}}$	ial derivative form of a macroscale Euler equation, Eq. (6), for all entities except solid, and Eq. (7) for solid phase
101		
102	$\mathcal{T}_{\mathcal{G}*}^{\bar{\alpha}}$	macroscale body source potential balance equation, Eq. (8)
103	$\mathbf{t}$	stress tensor
104	t	time
105	$\mathcal{U}_{**}^{\bar{\alpha}}$	macroscale entity-based internal energy equation, Eq. (64)
106	$\mathbf{u}$	diffusion/dispersion velocity, $\mathbf{u}_{i\alpha} = \mathbf{v}_{i\alpha} - \mathbf{v}_\alpha$, $\mathbf{u}^{\bar{i}\bar{\alpha}} = \mathbf{v}^{\bar{i}\bar{\alpha}} - \mathbf{v}^{\bar{\alpha}}$
107	$\mathcal{V}$	set of variables

108	$\mathbf{v}$	velocity
109	W	weighting function for averaging
110	$\mathbf{w}$	velocity of a domain boundary
111	<i>Greek letters</i>	
112	γ	interfacial or common curve lineal tension
113	ϵ	porosity
114	$\epsilon^{\bar{\alpha}}$	specific entity measure
115	η	entropy density
116	$\bar{\eta}$	partial mass entropy
117	θ	temperature
118	κ_G	geodesic curvature, $\kappa_{Gws} = \mathbf{l}_{ws} \cdot \nabla'' \mathbf{l}_{ws} \cdot \mathbf{n}_{ws}$
119	κ_N	normal curvature, $\kappa_{Nws} = \mathbf{l}_{ws} \cdot \nabla'' \mathbf{l}_{ws} \cdot \mathbf{n}_s$
120	Λ	entropy production rate
121	$\boldsymbol{\lambda}$	vector Lagrange multiplier
122	λ	scalar Lagrange multiplier
123	μ	chemical potential
124	ρ	mass density
125	$\boldsymbol{\sigma}$	Lagrangian solid-phase stress tensor
126	$\overset{\kappa \rightarrow \alpha}{\Phi}_0$	macroscale transfer rate of entropy from entity κ to entity α per
127		volume

44	f	general scalar function
45	$\mathbf{G}$	geometric orientation tensor, $\mathbf{G}_\alpha = \mathbf{I} - \mathbf{l}'_\alpha$ for $\alpha \in \mathcal{I}_I$, $\mathbf{G}_{wns} = \mathbf{I} - \mathbf{l}''_{wns}$
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56	$\mathbf{l}''$	unit tensor in a common curve, $\mathbf{l}''_{wns} = \mathbf{l}_{wns} \mathbf{l}_{wns}$
57	$\mathbf{l}^{(n)}$	unit tensor associated with 3 - n -dimensional entity where (n) is
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62	$\mathcal{I}_{c\alpha}^+$	connected set of indices of one dimension higher than entity α
63	$\mathcal{I}_{c\alpha}^-$	connected set of indices of one dimension lower than entity α
64	$\mathcal{I}_f$	set of fluid-phase indices

146	w	wetting-phase qualifier
147	wn	qualifier for interface between wetting and non-wetting phases
148	wns	qualifier for common curve where wn , ws and ns interfaces meet
149	ws	qualifier for interface between wetting and solid phases
150	α	entity qualifier
151	β	entity qualifier
152	γ	entity qualifier
153	κ	entity qualifier
154	$\bar{\alpha}$	superscript indicating mass average over entity α
155	$\overline{\bar{\alpha}}$	superscript indicating uniquely defined average over entity α
156	$*$	indicates a concentrated force in an exchange between entities with
157		a difference in dimensionality equal two
158	$—$	above a superscript refers to a density weighted macroscale average
159	$=$	above a superscript refers to a uniquely defined macroscale average
160	T	transpose
161	eq	subscript indicating the property is at equilibrium
162	$\mathcal{E}$	total energy conservation equation qualifier
163	$\mathcal{G}$	potential energy equation qualifier
164	$\mathcal{M}$	mass conservation equation qualifier
165	$\mathcal{P}$	momentum conservation equation qualifier
166	$\mathcal{T}$	thermodynamic equation qualifier

167	$\mathcal{T}_{\mathcal{G}}$	derivative of potential energy equation qualifier	
168	<i>Other mathematical symbols</i>		
169	$D^{\bar{\alpha}}/Dt$	material derivative of entity α , D	$^{\alpha}\cdot\nabla$
170	$D'^{\bar{s}}/Dt$	material derivative on a surface where the macroscale solid is em-	
171		ployed, D'	$^s\cdot\nabla'$
172	$D''^{\bar{s}}/Dt$	material derivative on a curve where the macroscale solid is em-	
173		ployed, D''	$^s\cdot\nabla''$
174	$D^{(n)\bar{s}}/Dt$	material derivative on a 3 – n -dimensional entity where the mac-	
175		roscale solid is employed, $D^{(n)}$	$^s\cdot\nabla^{(n)}$, (n) is
176		replaced by n primes	
177	$\partial'/\partial t$	partial time derivative at a point fixed on a surface,	
178		$\partial'/\partial t = d/dt - \mathbf{w}_{\alpha}\cdot\nabla'$, $\alpha \in \mathcal{I}_{\text{I}}$	
179	$\partial''/\partial t$	partial time derivative at a point fixed on a common curve,	
180		$\partial''/\partial t = d/dt - \mathbf{w}_{\alpha}\cdot\nabla''$, $\alpha \in \mathcal{I}_{\text{C}}$	
181	$\partial^{(n)}/\partial t$	partial time derivative at a point fixed on 3 – n -dimensional entity,	
182		(n) is replaced by n primes	
183	∇'	microscale surficial del operator, $\nabla' = \mathbf{l}'_{\alpha}\cdot\nabla$	
184	∇''	microscale curvilinear del operator, $\nabla'' = \mathbf{l}''_{\alpha}\cdot\nabla$	
185	$\nabla^{(n)}$	microscale 3 – n -dimensional del operator, $\nabla^{(n)} = \mathbf{l}_{\alpha}^{(n)}\cdot\nabla$, (n) is	
186		replaced by n primes	
187	$\langle f_{\alpha} \rangle_{\Omega_{\beta}, \Omega_{\gamma}, W} = \int_{\Omega_{\beta}} W f_{\alpha} d\mathbf{r} / \int_{\Omega_{\gamma}} W d\mathbf{r}$	general average of microscale property f_{α}	
188	$\langle f_{\alpha} \rangle_{\Omega_{\beta}, \Omega_{\gamma}} = \langle f_{\alpha} \rangle_{\Omega_{\beta}, \Omega_{\gamma}, 1}$		

189	f_α^β	$= \langle f_\alpha \rangle_{\Omega_\beta, \Omega_\beta},$	general average
190	f_α^α	$= \langle f_\alpha \rangle_{\Omega_\alpha, \Omega_\alpha},$	intrinsic average
191	$f_\alpha^{\bar{\beta}}$	$= \langle f_\alpha \rangle_{\Omega_\beta, \Omega_\beta, \rho_\alpha},$	general density-weighted average
192	$f_\alpha^{\bar{\alpha}}$	$= \langle f_\alpha \rangle_{\Omega_\alpha, \Omega_\alpha, \rho_\alpha},$	intrinsic density-weighted average
193	$f_\alpha^{i\bar{\alpha}}$	$= \langle f_{i\alpha} \rangle_{\Omega_\alpha, \Omega_\alpha, \rho_\alpha},$	intrinsic density-weighted average
194	$f_{i\alpha}^{\bar{\beta}}$	$= \langle f_{i\alpha} \rangle_{\Omega_\beta, \Omega_\beta, \rho_\alpha \omega_{i\alpha}},$	general species mass density weighted average
195	$f_{i\alpha}^{i\bar{\alpha}}$	$= \langle f_{i\alpha} \rangle_{\Omega_\alpha, \Omega_\alpha, \rho_\alpha \omega_{i\alpha}},$	intrinsic species mass density weighted average

196 *Abbreviations*

197	CEI	constrained entropy inequality
198	CIT	classical irreversible thermodynamics
199	EI	entropy inequality
200	SEI	simplified entropy inequality
201	TCAT	thermodynamically constrained averaging theory

202 **1. Introduction**

203 Multiphase flow and transport processes in porous medium systems are
204 important for a wide range of environmental, industrial, and biological appli-
205 cations, such as groundwater contamination, carbon storage and sequestra-
206 tion, design of filters and insulators, enhanced gas and oil recovery, transport
207 of nutrients in natural tissues, and biofilm growth [2, 27, 30, 33, 34, 36].

208 Processes important in these applications evolve on multiple length and
209 time scales, contributing to the complexity of these systems. One contribut-
210 ing factor to this complexity is the existence of multiple classes of entities,

211 which include phases, interfaces between phases, and common curves that
 212 form at the boundary between three phases. Accounting for interfaces and
 213 common curves in the model formulation provides a higher fidelity represen-
 214 tation of the underlying system compared to formulations based upon con-
 215 servation equations for phases alone. This is so because many processes hap-
 216 pen across interfaces and along common curves, e.g., transport of chemical
 217 species, momentum, and energy. Surfactants are known to accumulate at in-
 218 terfaces, altering the interfacial tension and the morphology of the boundary
 219 between phases. Although these facts are widely acknowledged, traditional
 220 approaches [3, 10, 27] do not account for these lower dimensional entities
 221 explicitly in the formulation. Instead, traditional models of two-fluid-phase
 222 porous medium systems are closed using *ad hoc* closure relations that must
 223 implicitly be dependent on the unresolved entities through parametric de-
 224 pendence of constitutive relations. However, these extensions do not have a
 225 rigorous basis and as a consequence often lead to a non-physical behaviour
 226 of the system, such as apparent hysteretic behavior.

227 The classical approach to apply Fick’s law for modeling species transport
 228 in porous medium systems [6, 27], according to which the dispersive mass
 229 flux is proportional to the concentration gradient and independent of the con-
 230 centration itself, is successful for dilute solutions and homogeneous porous
 231 media. For some applications the concentration of dissolved substances is
 232 indeed low. However, many porous medium systems are non-dilute and not
 233 sufficiently homogeneous for a Fickian approximation to be accurate, e.g.,
 234 brines in aquifers above salt formations, radioactive waste disposal in salt
 235 domes, evaporative salt precipitation, and transport in fractured porous me-

236 dia [5, 7, 8, 25, 35]. Several alternative approaches have been proposed
237 to treat diffusion processes in such systems [13, 21, 24], however some issues
238 still require particular consideration, e.g., species transport in two-fluid-phase
239 porous media. Therefore, the goal of the current work is to extend the de-
240 velopments and fill that gap.

241 The traditional approach to modeling multiphase flows through porous
242 media assumes that the macroscale capillary pressure is defined as a difference
243 between the fluid pressures and it is a unique function of the wetting-phase
244 saturation [3, 27]. This functional dependency is however inadequate for
245 modeling dynamical flow systems, because the capillary pressure is equal to
246 the difference between the fluid-phase pressures only at equilibrium and in
247 addition at the same saturation the capillary pressure is different for drainage
248 and imbibition processes. Therefore, the capillary pressure can also be a
249 function of other variables, e.g., fluid-fluid interfacial area [17, 22, 26]. The
250 interface between the gas and liquid phases in the porous medium is of special
251 importance since water vaporization depends on the extent of the interfacial
252 surfaces, and capillary forces related to these interfaces strongly impact the
253 flow behavior. These issues have been resolved through recent advances
254 [17, 18, 28]. However, high fidelity modeling of species and energy transport
255 in multiphase porous medium systems for non-dilute systems that explicitly
256 resolve interfacial and common curve properties remains an open issue.

257 For many applications, such as design of oxygen sensors and batteries or
258 water-gas management in PEM fuel cells [1, 4, 37], chemical reactions take
259 place along the common curve. Therefore, modeling of this entity can be
260 important for the accurate representation of some systems.

261 Mechanistic models of porous medium systems are often developed at the
 262 macroscale where the value of a property at a point represents an average
 263 about some finite-sized region that includes multiple entities. It is desirable
 264 to produce such mechanistic macroscale models where these averages are
 265 precisely defined in terms of microscale variables, which is the smallest scale
 266 above which the laws of continuum mechanics are applicable and a microscale
 267 point lies entirely within a single entity. Systems that are well characterized
 268 at the microscale provide a means to evaluate and validate macroscale models
 269 intended to describe transport phenomena in an averaged sense.

270 Traditional approaches to simulate both multiple fluid flows and species
 271 and energy transport at the macroscale in porous medium systems suffer
 272 from inconsistencies and therefore an advanced approach is required. The
 273 thermodynamically constrained averaging theory (TCAT) provides a means
 274 to formulate macroscale models that have the desired properties of being pre-
 275 cisely defined and consistent across scales, while also being consistent with
 276 the second law of thermodynamics [11, 31]. TCAT has been employed to ob-
 277 tain modeling frameworks for single-fluid-phase flow in porous media [12],
 278 non-dilute species transport in single-fluid-phase porous medium systems
 279 [13, 32], multiple fluid-phase flow [28], heat transport in single-fluid-phase
 280 porous medium systems [14], single-fluid phase flow in megascale systems in
 281 which spatial variability is not resolved [15], and transition regions between
 282 domains that contain different sets of entities [29]. Evolution equations de-
 283 scribing dynamic changes in entity measures, such as specific interfacial areas
 284 and specific common curve lengths, have been considered [16] as have the
 285 dynamic aspects of the rate of relaxation to an equilibrium state for fluid

286 pressures, specific interfacial extent measures, and entity curvatures in a
287 two-fluid-phase porous medium system [17].

288 Models based upon TCAT have resolved some critical open issues associ-
289 ated with our fundamental understanding of transport phenomena in porous
290 medium systems [19, 20], but the final word has not been written. For exam-
291 ple, specific forms of closure relations are needed to produce solvable models
292 in some cases, implementation of approximate solutions of TCAT models are
293 needed since the models deviate from well-studied traditional formulations
294 and require new approximations. Detailed evaluation of TCAT model as-
295 sumptions, model validation, and extensions to new classes of problems are
296 all worthy areas for additional TCAT research.

297 A class of models not yet formulated using the TCAT approach is com-
298 positional modeling of species transport in a two-fluid-phase porous medium
299 system. Compositional two-fluid-phase modeling is of importance for three
300 reasons. First, this class of models is of intrinsic interest for a wide variety
301 of applications. Second, modeling the interaction of the subsurface envi-
302 ronment and the atmosphere requires such a model for applications such
303 as multi-domain species transport and evaporation of water from a porous
304 medium and transport to the atmosphere. The multi-domain application can
305 be formulated using the previously developed TCAT transition region model
306 [29], but the transition region model must be coupled to a compositional two-
307 fluid-phase porous medium model, which has not yet been formulated using
308 TCAT. A TCAT formulation is attractive because it includes specific, precise
309 links between microscale and macroscale variables and would include natural
310 quantities such as contact angles, interfacial tensions, and interfacial areas

311 that are not explicitly a part of traditional models. Third, traditional mod-
 312 els for compositional two-phase flows in porous media contain inconsistencies
 313 and require an improvement [11, 23]. Therefore, a generalized compositional
 314 two-fluid-phase porous medium model, which can be approached through
 315 TCAT, is desired.

316 The overall goal of this work is to advance a TCAT modeling framework to
 317 describe species transport in a two-fluid-phase porous medium system. The
 318 specific objectives of this work are: (1) to formulate a general, essentially ex-
 319 act constrained entropy inequality for a compositional two-fluid-phase porous
 320 medium system; (2) to reduce the constrained entropy inequality to pure
 321 force-flux form; (3) to advance an allowable set of closure relations from the
 322 hierarchy of permissible relations; and (4) to formulate an example closed
 323 model for the case of species transport in a porous medium system.

324 2. Primary Restrictions

325 The development of TCAT models requires certain restrictions and ap-
 326 proximations, which are divided into the categories primary restrictions, SEI
 327 approximations, and secondary restrictions. These restrictions and approx-
 328 imations will be introduced in the order in which they are needed for the
 329 model formulation, and they will be stated formally and discussed. If a
 330 TCAT model must be revised to describe a physical system, formulation en-
 331 try points affected by these restrictions and approximations are logical places
 332 to start. Primary restrictions are introduced to define the fundamental as-
 333 pects of how the system is modeled, including aspects such as the length
 334 scale characteristics of the system, the entities involved, the form of the con-

335 servation equations, and the microscale thermodynamic theory relied upon.
336 These primary restrictions are specified in turn below.

337 **Primary Restriction 1 (Flow System Description and Scale).**

338 *The flow system of interest contains the following entities: two fluid phases,*
339 *wetting phase w and non-wetting phase n , a relatively immobile solid phase*
340 *s , fluid-fluid interface wn , two fluid-solid interfaces, ws and ns , and a com-*
341 *mon curve wns where three phases meet. All the entities are composed of N*
342 *chemical species, which can react and transfer between the entities. The mod-*
343 *els will be formulated at the macroscale, and separation of scales is assumed.*

344
345 This restriction states that the system entities are restricted to two fluid
346 phases, a solid phase, three interfaces between phases, and a common curve,
347 and a hierarchy of models will be developed for such systems only. The
348 restriction on relatively immobile solid means that the fluid flow through
349 porous medium will be modeled, and the velocities of the solid and fluid
350 phases are not of the same order of magnitude. Due to the presence of
351 chemical species, compositional effects will be modeled. The stipulation on
352 the system scale implies that a fully macroscale model will be derived where
353 the macroscale is a length scale above the pore scale such that the value of
354 a property at a point represents an average of this property over a region
355 containing multiple entities. A clear separation of length scales means that
356 the values of all averaged quantities are not sensitive to small changes of the
357 averaging volume.

358 **Primary Restriction 2 (Phenomena Modeled).**

359 *The phenomena to be modeled consist of the conservation of mass for each*
 360 *chemical species in each of the entities, and conservation of momentum and*
 361 *energy for each entity as a whole.*

362 This restriction specifies that compositional effects are considered only
 363 with respect to the conservation of mass.

364 **Primary Restriction 3 (Thermodynamic Theory).**

365 *Classical irreversible thermodynamics (CIT) is used to describe the thermo-*
 366 *dynamic behaviour of the system at the microscale.*

367 This restriction specifies the thermodynamic theory that is employed to
 368 connect variables in the entropy inequality to variables that appear in the
 369 conservation equations. CIT is averaged from the microscale to the macro-
 370 scale to ensure that the variables retain their physical meaning across scales.

371 **Primary Restriction 4 (Smooth Solid Surface).**

372 *From a microscale perspective, the outward unit normal vector at each point*
 373 *on the solid surface, $\mathbf{n}_s$, is unique.*

374 Primary Restriction 4 states that the surface of the solid material at the
 375 microscale has a unique normal vector at every point, which is appropriate
 376 for modeling a smooth solid phase that deforms negligibly at the microscale.

377 **3. Conservation, Balance, and Thermodynamic Equations**

378 The TCAT models of focus in this work require conservation of mass
 379 equations for each species, conservation of momentum equations, and con-
 380 servation of energy equations for each entity in the system. Additionally,

an aggregate equation of entropy balance accounting for all entities within an averaged region and balance equations for body force potential are required. Lastly, macroscale thermodynamic equations relating the material derivatives of thermodynamic quantities under near-equilibrium conditions are needed. These basic building blocks have been previously derived [18], and the results will be relied upon in this work.

The macroscale conservation of mass equation for species i in entity α can be written as

$$\begin{aligned} \mathcal{M}_{**}^{\bar{\bar{i}\alpha}} = & \frac{D^{\bar{\alpha}} \left(\epsilon^{\bar{\alpha}} \rho^{\alpha} \omega^{i\bar{\alpha}} \right)}{Dt} + \epsilon^{\bar{\alpha}} \rho^{\alpha} \omega^{i\bar{\alpha}} \mathbf{l} : \mathbf{d}^{\bar{\alpha}} + \nabla \cdot \left(\epsilon^{\bar{\alpha}} \rho^{\alpha} \omega^{i\bar{\alpha}} \mathbf{u}^{\bar{\bar{i}\alpha}} \right) \\ & - \epsilon^{\bar{\alpha}} r^{i\alpha} - \sum_{\kappa \in \mathcal{J}_{c\alpha}} \overset{i\kappa \rightarrow i\alpha}{M} = 0 \quad \text{for } i \in \mathcal{J}_s, \alpha \in \mathcal{J}, \end{aligned} \quad (1)$$

where $\epsilon^{\bar{\alpha}}$ is the entity extent measure (volume fraction, specific interfacial area, specific common curve length), ρ^{α} is the mass density of entity α , $\omega^{i\bar{\alpha}}$ is the mass fraction of species i in entity α , $\mathbf{l}$ is the identity tensor, $\mathbf{d}^{\bar{\alpha}}$ is the rate of strain tensor, $\mathbf{u}^{\bar{\bar{i}\alpha}}$ is the diffusion/dispersion velocity, $r^{i\alpha}$ is the rate of mass production of species i resulting from all reactions in entity α , $\overset{i\kappa \rightarrow i\alpha}{M}$ represents the transfer of mass of species i from connected entity κ to entity α per unit volume per unit time, $\mathcal{J}_s$ is the index set of chemical species, $\mathcal{J}_{c\alpha}$ is the index set of entities connected to entity α , and $\mathcal{J}$ is the index set of all entities in the system. Superscripted entity and species qualifiers refer to macroscale quantities.

The entity-based conservation of momentum equation is

$$\mathcal{P}_{**}^{\bar{\alpha}} = \frac{D^{\bar{\alpha}} \left(\epsilon^{\bar{\alpha}} \rho^{\alpha} \mathbf{v}^{\bar{\alpha}} \right)}{Dt} + \epsilon^{\bar{\alpha}} \rho^{\alpha} \mathbf{v}^{\bar{\alpha}} \mathbf{l} : \mathbf{d}^{\bar{\alpha}} - \sum_{i \in \mathcal{J}_s} \epsilon^{\bar{\alpha}} \rho^{\alpha} \omega^{i\bar{\alpha}} \mathbf{g}^{\bar{i}\alpha}$$

$$\begin{aligned}
& - \sum_{\kappa \in \mathcal{J}_{c\alpha}} \sum_{i \in \mathcal{J}_s} M^{i\kappa \rightarrow i\alpha} \left(\mathbf{v}^{\overline{\alpha}, \overline{\kappa}} + \mathbf{u}_i^{\overline{\alpha}, \overline{\kappa}} \right) - \sum_{\kappa \in \mathcal{J}_{c\alpha}} \mathbf{T}_0^{\kappa \rightarrow \alpha} - \frac{1}{2} \sum_{\beta \in \mathcal{J}_{c\alpha}^-} \sum_{\kappa \in \mathcal{J}_{c\beta}^-} \mathbf{T}^{\kappa \rightarrow \alpha} \\
& - \frac{1}{2} \sum_{\beta \in \mathcal{J}_{c\alpha}^+} \sum_{\kappa \in \mathcal{J}_{c\beta}^+} \mathbf{T}^{\kappa \rightarrow \alpha} - \nabla \cdot \left(\epsilon^{\overline{\alpha}} \mathbf{t}^{\overline{\alpha}} \right) = 0 \quad \text{for } \alpha \in \mathcal{J},
\end{aligned} \tag{2}$$

400 where $\mathbf{v}^{\overline{\alpha}}$ is the macroscale velocity of entity α , $\mathbf{g}^{\overline{i\alpha}}$ is the body force acceler-
 401 ation vector for species i in entity α , $\mathbf{v}^{\overline{\alpha}, \overline{\kappa}}$ is the velocity of flow in an entity
 402 averaged over the boundary of the entity, $\mathbf{u}_i^{\overline{\alpha}, \overline{\kappa}}$ is the diffusion/dispersion ve-
 403 locity in an entity averaged over the boundary of the entity, $\mathbf{t}^{\overline{\alpha}}$ is the stress
 404 tensor, $\mathbf{T}_0^{\kappa \rightarrow \alpha}$ represents the transfer of momentum from entity κ to entity α
 405 per unit volume per unit time, $\mathbf{T}^{\kappa \rightarrow \alpha}$ is the transfer of momentum from entity
 406 κ to entity α where the dimensionality of the entities differs by two, $\mathcal{J}_{c\alpha}^+$ is
 407 the set of connected entities of one dimension higher than entity α , and $\mathcal{J}_{c\alpha}^-$
 408 is the set of connected entities of one dimension lower than entity α . The
 409 inclusion of the $\mathbf{T}^{\kappa \rightarrow \alpha}$ term accounts for the concentrated force that a common
 410 curve can exert on a solid phase [18].

411 The entity-based conservation of total energy equation can be written as

$$\begin{aligned}
\mathcal{E}_{**}^{\overline{\alpha}} &= \frac{D^{\overline{\alpha}} E^{\overline{\alpha}}}{Dt} + \mathbf{v}^{\overline{\alpha}} \cdot \frac{D^{\overline{\alpha}} \left(\epsilon^{\overline{\alpha}} \rho^{\alpha} \mathbf{v}^{\overline{\alpha}} \right)}{Dt} + \sum_{i \in \mathcal{J}_s} \left(K_E^{\overline{i\alpha}} + \frac{\mathbf{u}^{\overline{i\alpha}} \cdot \mathbf{u}^{\overline{i\alpha}}}{2} \right) \frac{D^{\overline{\alpha}} \left(\epsilon^{\overline{\alpha}} \rho^{\alpha} \omega^{i\overline{\alpha}} \right)}{Dt} \\
& - \frac{\mathbf{v}^{\overline{\alpha}} \cdot \mathbf{v}^{\overline{\alpha}}}{2} \sum_{i \in \mathcal{J}_s} \frac{D^{\overline{\alpha}} \left(\epsilon^{\overline{\alpha}} \rho^{\alpha} \omega^{i\overline{\alpha}} \right)}{Dt} + \sum_{i \in \mathcal{J}_s} \epsilon^{\overline{\alpha}} \rho^{\alpha} \omega^{i\overline{\alpha}} \frac{D^{\overline{\alpha}}}{Dt} \left(K_E^{\overline{i\alpha}} + \frac{\mathbf{u}^{\overline{i\alpha}} \cdot \mathbf{u}^{\overline{i\alpha}}}{2} \right) \\
& + \left[E^{\overline{\alpha}} + \epsilon^{\overline{\alpha}} \rho^{\alpha} \frac{\mathbf{v}^{\overline{\alpha}} \cdot \mathbf{v}^{\overline{\alpha}}}{2} + \sum_{i \in \mathcal{J}_s} \epsilon^{\overline{\alpha}} \rho^{\alpha} \omega^{i\overline{\alpha}} \left(K_E^{\overline{i\alpha}} + \frac{\mathbf{u}^{\overline{i\alpha}} \cdot \mathbf{u}^{\overline{i\alpha}}}{2} \right) \right] \mathbf{l} : \mathbf{d}^{\overline{\alpha}} \\
& - \sum_{i \in \mathcal{J}_s} \epsilon^{\overline{\alpha}} \rho^{\alpha} \omega^{i\overline{\alpha}} \mathbf{g}^{\overline{i\alpha}} \cdot \left(\mathbf{v}^{\overline{\alpha}} + \mathbf{u}^{\overline{i\alpha}} \right) - \epsilon^{\overline{\alpha}} h_0^{\overline{\alpha}} - \epsilon^{\overline{\alpha}} h^{\alpha}
\end{aligned}$$

$$\begin{aligned}
& - \sum_{\kappa \in \mathcal{I}_{c\alpha}} \sum_{i \in \mathcal{I}_s} i\kappa \rightarrow i\alpha \left[\overline{E}_i^{\overline{\alpha}, \overline{\kappa}} + \frac{(\mathbf{v}_{\alpha, \overline{\kappa}} + \mathbf{u}_i^{\overline{\alpha}, \overline{\kappa}}) \cdot (\mathbf{v}_{\alpha, \overline{\kappa}} + \mathbf{u}_i^{\overline{\alpha}, \overline{\kappa}})}{2} + K_{Ei}^{\overline{\alpha}, \overline{\kappa}} \right] \\
& - \sum_{\kappa \in \mathcal{I}_{c\alpha}} \mathbf{T}_0^{\kappa \rightarrow \alpha} \cdot \mathbf{v}_{\alpha, \overline{\kappa}} - \sum_{\kappa \in \mathcal{I}_{c\alpha}} Q_1^{\kappa \rightarrow \alpha} \\
& - \frac{1}{2} \sum_{\beta \in \mathcal{I}_{c\alpha}^-} \sum_{\kappa \in \mathcal{I}_{c\beta}^-} \mathbf{T}^{\kappa \rightarrow \alpha} \cdot \mathbf{v}_{\alpha}^{\overline{\kappa}} - \frac{1}{2} \sum_{\beta \in \mathcal{I}_{c\alpha}^-} \sum_{\kappa \in \mathcal{I}_{c\beta}^-} Q_1^{\kappa \rightarrow \alpha} \\
& - \frac{1}{2} \sum_{\beta \in \mathcal{I}_{c\alpha}^+} \sum_{\kappa \in \mathcal{I}_{c\beta}^+} \mathbf{T}^{\kappa \rightarrow \alpha} \cdot \mathbf{v}_{\kappa}^{\overline{\alpha}} - \frac{1}{2} \sum_{\beta \in \mathcal{I}_{c\alpha}^+} \sum_{\kappa \in \mathcal{I}_{c\beta}^+} Q_1^{\kappa \rightarrow \alpha} \\
& - \nabla \cdot (\epsilon^{\overline{\alpha}} \mathbf{t}^{\overline{\alpha}} \cdot \mathbf{v}^{\overline{\alpha}} + \epsilon^{\overline{\alpha}} \mathbf{q}^{\overline{\alpha}}) = 0 \quad \text{for } \alpha \in \mathcal{I},
\end{aligned} \tag{3}$$

412 where $E^{\overline{\alpha}}$ is the macroscale internal energy density of entity α , $K_E^{\overline{\alpha}}$ is the
 413 kinetic energy per unit mass of species i in entity α due to velocity fluctua-
 414 tions, $\overline{E}_i^{\overline{\alpha}, \overline{\kappa}}$ is the partial mass energy of species i in an entity averaged over
 415 the boundary of the entity, $K_{Ei}^{\overline{\alpha}, \overline{\kappa}}$ is the average of a species deviation kinetic
 416 energy over the boundary of the entity, $\mathbf{q}^{\overline{\alpha}}$ is the non-advective energy flux,
 417 h^{α} is the energy source density, $h_0^{\overline{\alpha}}$ is the energy source density due to body-
 418 force and velocity fluctuations, $Q_1^{\kappa \rightarrow \alpha}$ is the transfer of internal energy from
 419 entity κ to entity α per unit volume per unit time, and $Q^{\kappa \rightarrow \alpha}$ represents the
 420 energy exchange between entities for which dimensionalities differ by two. If
 421 both subscript and superscript entity qualifiers are present, the quantity is
 422 averaged over the lower dimensional entity.

423 The entity-based balance of entropy equation reads

$$\mathcal{S}_{**}^{\overline{\alpha}} = \frac{D^{\overline{\alpha}} \eta^{\overline{\alpha}}}{Dt} + \eta^{\overline{\alpha}} \mathbf{l} : \mathbf{d}^{\overline{\alpha}} - \epsilon^{\overline{\alpha}} b^{\alpha} - \sum_{\kappa \in \mathcal{I}_{c\alpha}} \sum_{i \in \mathcal{I}_s} i\kappa \rightarrow i\alpha \overline{\eta}_i^{\overline{\alpha}, \overline{\kappa}} - \sum_{\kappa \in \mathcal{I}_{c\alpha}} \Phi_0^{\kappa \rightarrow \alpha}$$

$$-\frac{1}{2} \sum_{\beta \in \mathcal{J}_{c\alpha}^-} \sum_{\kappa \in \mathcal{J}_{c\beta}^-} \overset{\kappa \rightarrow \alpha}{\Phi^*} - \frac{1}{2} \sum_{\beta \in \mathcal{J}_{c\alpha}^+} \sum_{\kappa \in \mathcal{J}_{c\beta}^+} \overset{\kappa \rightarrow \alpha}{\Phi^*} - \nabla \cdot (\epsilon^{\bar{\alpha}} \boldsymbol{\varphi}^{\bar{\alpha}}) = \Lambda^{\bar{\alpha}} \text{ for } \alpha \in \mathcal{J}, \quad (4)$$

where $\eta^{\bar{\alpha}}$ is the macroscale entropy density, $\bar{\eta}_i^{\bar{\alpha}, \bar{\kappa}}$ is the partial mass entropy of species i per volume in an entity averaged over the boundary of the entity, b^α is the entropy source density, $\boldsymbol{\varphi}^{\bar{\alpha}}$ is the non-advective entropy flux, $\overset{\kappa \rightarrow \alpha}{\Phi}_0$ is the transfer of entropy from entity κ to entity α per unit volume per unit time, $\overset{\kappa \rightarrow \alpha}{\Phi^*}$ represents the entropy exchange between entities for which dimensionalities differ by two, and $\Lambda^{\bar{\alpha}}$ is the entropy production rate associated with entity α .

The entity-based body force potential balance equation can be written as

$$\begin{aligned} \mathcal{G}_{**}^{\bar{\alpha}} &= \frac{D^{\bar{\alpha}} \Psi^{\bar{\alpha}}}{Dt} + \Psi^{\bar{\alpha}} \mathbf{l} : \mathbf{d}^{\bar{\alpha}} + \sum_{i \in \mathcal{J}_s} \epsilon^{\bar{\alpha}} \rho^\alpha \omega^{i\bar{\alpha}} \mathbf{g}^{i\bar{\alpha}} \cdot (\mathbf{v}^{\bar{\alpha}} + \mathbf{u}^{i\bar{\alpha}}) + \epsilon^{\bar{\alpha}} h_0^{\bar{\alpha}} \\ &\quad - \sum_{\kappa \in \mathcal{J}_{c\alpha}} \sum_{i \in \mathcal{J}_s} \overset{i\kappa \rightarrow i\alpha}{M} \psi_i^{\bar{\alpha}, \bar{\kappa}} - \sum_{\kappa \in \mathcal{J}_{c\alpha}} \overset{\kappa \rightarrow \alpha}{G}_0 - \nabla \cdot \left(\epsilon^{\bar{\alpha}} \mathbf{q}_{\mathbf{g}0}^{\bar{\alpha}} - \sum_{i \in \mathcal{J}_s} \epsilon^{\bar{\alpha}} \rho^\alpha \omega^{i\bar{\alpha}} \psi^{i\bar{\alpha}} \mathbf{u}^{i\bar{\alpha}} \right) \\ &\quad - \sum_{i \in \mathcal{J}_s} \left\langle \rho_\alpha \omega_{i\alpha} \left[\frac{\partial^{(n)} \psi_{i\alpha}}{\partial t} + \mathbf{v}_{i\alpha} \cdot (\mathbf{l} - \mathbf{l}_\alpha^{(n)}) \cdot \mathbf{g}_{i\alpha} \right] \right\rangle_{\Omega_\alpha, \Omega} \\ &\quad - \sum_{i \in \mathcal{J}_s} \langle r_{i\alpha} \psi_{i\alpha} \rangle_{\Omega_\alpha, \Omega} = 0 \quad \text{for } \alpha \in \mathcal{J}, \end{aligned} \quad (5)$$

where $\Psi^{\bar{\alpha}}$ is the macroscale body force potential density, $\psi_i^{\bar{\alpha}, \bar{\kappa}}$ is the body force potential for species i in an entity averaged over the boundary of the entity, $\overset{\kappa \rightarrow \alpha}{G}_0$ is the transfer of potential energy due to variability of species mass exchange per unit volume per unit time, $\mathbf{q}_{\mathbf{g}0}^{\bar{\alpha}}$ is non-advective energy flux associated with mechanical processes, $\partial^{(n)}/\partial t$ is the partial time derivative at a point fixed on 3- n -dimensional entity, and $\mathbf{l}_\alpha^{(n)}$ is the unit tensor associated with 3- n -dimensional entity, (n) is the number of primes used. Entity and

species qualifiers are superscripted for macroscale quantities and subscripted for microscale quantities. If both subscript and superscript are present, the quantity is averaged over the entity boundary.

The desired form of the EI is a sum of products of forces and fluxes. It is precisely these expressions for which closure relations are needed to form closed models. While material derivatives of entropy density and the conserved quantities vanish at equilibrium, we wish to examine conditions slightly away from equilibrium, where the relationship among these material derivatives is not clear from the conservation and balance equations alone. To deduce these changes in material derivatives and combine the conservation and balance equations such that they are eliminated from the EI, material derivative expressions based upon CIT are developed. While CIT is well established at the microscale [9], TCAT relies upon upscaling of microscale CIT to the macroscale. In accordance with [18, Chap. 7], the resultant macroscale CIT expression for all entities except the solid phase can be written as

$$\begin{aligned}
\mathcal{T}_*^{\bar{\alpha}} = & \frac{D^{\bar{\alpha}} E^{\bar{\alpha}}}{Dt} - \theta^{\bar{\alpha}} \frac{D^{\bar{\alpha}} \eta^{\bar{\alpha}}}{Dt} - \sum_{i \in \mathcal{I}_s} \mu^{\bar{i}\alpha} \frac{D^{\bar{\alpha}} \left(\epsilon^{\bar{\alpha}} \rho^{\alpha} \omega^{i\bar{\alpha}} \right)}{Dt} \\
& + \sum_{\kappa \in \mathcal{I}_{c\alpha}^-} \langle \mathbf{n}_{\alpha} \cdot (\mathbf{v}_{\kappa} - \mathbf{v}^{\bar{s}}) f_{\alpha} \rangle_{\Omega_{\kappa}, \Omega} \\
& + \left\langle \eta_{\alpha} \frac{D^{(n)\bar{s}} (\theta_{\alpha} - \theta^{\bar{\alpha}})}{Dt} \right\rangle_{\Omega_{\alpha}, \Omega} + \sum_{i \in \mathcal{I}_s} \left\langle \rho_{\alpha} \omega_{i\alpha} \frac{D^{(n)\bar{s}} (\mu_{i\alpha} - \mu^{\bar{i}\alpha})}{Dt} \right\rangle_{\Omega_{\alpha}, \Omega} \\
& - \left[\eta^{\bar{\alpha}} \nabla \theta^{\bar{\alpha}} - \nabla \cdot \langle \mathbf{l}_{\alpha}^{(n)} f_{\alpha} \rangle_{\Omega_{\alpha}, \Omega} + \sum_{i \in \mathcal{I}_s} \epsilon^{\bar{\alpha}} \rho^{\alpha} \omega^{i\bar{\alpha}} \nabla \mu^{\bar{i}\alpha} \right] \cdot (\mathbf{v}^{\bar{\alpha}} - \mathbf{v}^{\bar{s}}) \\
& - \nabla \cdot \left\langle \left(\mathbf{I} - \mathbf{l}_{\alpha}^{(n)} \right) \cdot (\mathbf{v}_{\alpha} - \mathbf{v}^{\bar{\alpha}}) f_{\alpha} \right\rangle_{\Omega_{\alpha}, \Omega} - \left\langle \left(\mathbf{I} - \mathbf{l}_{\alpha}^{(n)} \right) f_{\alpha} \right\rangle_{\Omega_{\alpha}, \Omega} : \mathbf{d}^{\bar{\alpha}}
\end{aligned}$$

$$\begin{aligned}
& - \left\langle \nabla^{(n)} \cdot \mathbf{l}_\alpha^{(n)} \cdot (\mathbf{v}_\alpha - \mathbf{v}^{\bar{s}}) f_\alpha \right\rangle_{\Omega_\alpha, \Omega} + \left\langle \eta_\alpha (\mathbf{v}_\alpha - \mathbf{v}^{\bar{s}}) \cdot (\mathbf{l} - \mathbf{l}_\alpha^{(n)}) \right\rangle_{\Omega_\alpha, \Omega} \cdot \nabla \theta^{\bar{\alpha}} \\
& + \sum_{i \in \mathcal{J}_s} \left\langle \rho_\alpha \omega_{i\alpha} (\mathbf{v}_\alpha - \mathbf{v}^{\bar{s}}) \cdot (\mathbf{l} - \mathbf{l}_\alpha^{(n)}) \right\rangle_{\Omega_\alpha, \Omega} \cdot \nabla \mu^{\bar{i}\bar{\alpha}} = 0 \quad \text{for } \alpha \in \mathcal{J}_{\setminus S}, \quad (6)
\end{aligned}$$

455 where $f_\alpha = p_\alpha$ when $\alpha \in \mathcal{J}_f$, $f_\alpha = -\gamma_\alpha$ when $\alpha \in \mathcal{J}_I$, $f_\alpha = \gamma_\alpha$ when $\alpha \in \mathcal{J}_C$,
 456 p_α is the fluid phase pressure, γ_α is the interfacial or curvilinear tension
 457 depending on the entity, θ is the temperature, μ is the chemical potential,
 458 $\mathbf{v}_\kappa$ is the velocity of a lower dimensional entity κ , $\mathcal{J}_f$ is the index set of fluid
 459 phases, $\mathcal{J}_I$ is the index set of interfaces, $\mathcal{J}_C$ is the index set of common curves,
 460 and $\mathcal{J}_{\setminus S}$ is the index set of all entities except the solid phase. Vector $\mathbf{n}_\alpha$ is a
 461 microscale unit outward normal vector from entity α on its boundary when
 462 $\alpha \in \mathcal{J}_P$, tangent vector to the surface and outward normal from the bounding
 463 common curve when $\alpha \in \mathcal{J}_I$, and tangent to the common curve and pointing
 464 outward from the curve at its ends such that $\mathbf{n}_\alpha \cdot \mathbf{l}_\alpha = \pm 1$ when $\alpha \in \mathcal{J}_C$. The
 465 system under consideration contains only one common curve, so $\alpha = wns$
 466 for this case. $D^{(n)\bar{s}}/Dt = \partial^{(n)}/\partial t + \mathbf{v}^{\bar{s}} \cdot \nabla^{(n)}$ is the material derivative for a
 467 $3 - n$ -dimensional entity. Phase and species qualifiers are superscripted for
 468 macroscale quantities and subscripted for microscale quantities.

469 The corresponding macroscale dynamic energy equation for the solid
 470 phase [18, Chap. 7] is

$$\begin{aligned}
\mathcal{T}_*^{\bar{s}} &= \frac{D^{\bar{s}} E^{\bar{s}}}{Dt} - \theta^{\bar{s}} \frac{D^{\bar{s}} \eta^{\bar{s}}}{Dt} - \sum_{i \in \mathcal{J}_s} \mu^{\bar{i}s} \frac{D^{\bar{s}} (\epsilon^{\bar{s}} \rho^s \omega^{\bar{i}\bar{s}})}{Dt} \\
& - \sum_{\kappa \in \mathcal{J}_{cs}} \left\langle \mathbf{n}_s \cdot (\mathbf{v}_\kappa - \mathbf{v}_s) \boldsymbol{\sigma}_s : \frac{\mathbf{C}_s}{\dot{\mathbf{j}}_s} \right\rangle_{\Omega_\kappa, \Omega} - \sum_{\kappa \in \mathcal{J}_{cs}} \langle \mathbf{n}_s \cdot \mathbf{t}_s \cdot (\mathbf{v}_s - \mathbf{v}^{\bar{s}}) \rangle_{\Omega_\kappa, \Omega} \\
& - \frac{1}{2} \sum_{\beta \in \mathcal{J}_{cs}^-} \sum_{\kappa \in \mathcal{J}_{c\beta}^-} \left\langle \mathbf{n}_s \cdot (\mathbf{v}_\kappa - \mathbf{v}_s) \boldsymbol{\sigma}_s^* : \frac{\mathbf{C}_s}{\dot{\mathbf{j}}_s} \right\rangle_{\Omega_\kappa, \Omega}
\end{aligned}$$

$$\begin{aligned}
& -\frac{1}{2} \sum_{\beta \in \mathcal{I}_{cs}^-} \sum_{\kappa \in \mathcal{I}_{c\beta}^-} \langle \mathbf{n}_s \cdot \mathbf{t}_s^* \cdot (\mathbf{v}_s - \mathbf{v}^{\bar{s}}) \rangle_{\Omega_{\kappa}, \Omega} + \left\langle \eta_s \frac{D^{\bar{s}} (\theta_s - \theta^{\bar{s}})}{Dt} \right\rangle_{\Omega_s, \Omega} \\
& + \sum_{i \in \mathcal{I}_s} \left\langle \rho_s \omega_{is} \frac{D^{\bar{s}} (\mu_{is} - \mu^{\bar{is}})}{Dt} \right\rangle_{\Omega_s, \Omega} - \nabla \cdot \left\langle \left(\mathbf{t}_s - \boldsymbol{\sigma}_s : \frac{\mathbf{C}_s}{j_s} \mathbf{I} \right) \cdot (\mathbf{v}_s - \mathbf{v}^{\bar{s}}) \right\rangle_{\Omega_s, \Omega} \\
& - \epsilon^{\bar{s}} \mathbf{t}^s : \mathbf{d}^{\bar{s}} + \epsilon^{\bar{s}} \boldsymbol{\sigma}^{\bar{s}} : \frac{\mathbf{C}^s}{j^s} \mathbf{l} : \mathbf{d}^{\bar{s}} + \left\langle \left(\nabla \cdot \mathbf{t}_s - \nabla \boldsymbol{\sigma}_s : \frac{\mathbf{C}_s}{j_s} \right) \cdot (\mathbf{v}_s - \mathbf{v}^{\bar{s}}) \right\rangle_{\Omega_s, \Omega} = 0, \quad (7)
\end{aligned}$$

471 where $\boldsymbol{\sigma}$ is the Lagrangian stress tensor, $\mathbf{C}$ is the Green's deformation tensor,
472 and j_s is the solid-phase Jacobian.

473 Following [18, Chap. 7], the macroscale dynamic equation for the entity
474 potential energy reads

$$\begin{aligned}
\mathcal{T}_{\mathcal{G}^*}^{\bar{\alpha}} &= \frac{D^{\bar{\alpha}} \Psi^{\bar{\alpha}}}{Dt} - \sum_{i \in \mathcal{I}_s} \psi^{\bar{i}\alpha} \frac{D^{\bar{\alpha}} (\epsilon^{\bar{\alpha}} \rho^\alpha \omega^{i\bar{\alpha}})}{Dt} - \sum_{i \in \mathcal{I}_s} \left\langle \rho_\alpha \omega_{i\alpha} \frac{D^{(n)\bar{s}} \psi^{i\bar{\alpha}}}{Dt} \right\rangle_{\Omega_\alpha, \Omega} \\
& - \sum_{i \in \mathcal{I}_s} \epsilon^{\bar{\alpha}} \rho^\alpha \omega^{i\bar{\alpha}} (\mathbf{v}^{\bar{\alpha}} - \mathbf{v}^{\bar{s}}) \cdot \nabla \psi^{i\bar{\alpha}} \\
& + \sum_{i \in \mathcal{I}_s} \left\langle \rho_\alpha \omega_{i\alpha} (\mathbf{v}_\alpha - \mathbf{v}^{\bar{s}}) \cdot \left(\mathbf{I} - \mathbf{l}_\alpha^{(n)} \right) \right\rangle_{\Omega_\alpha, \Omega} \cdot \nabla \psi^{i\bar{\alpha}} = 0 \quad \text{for } \alpha \in \mathcal{I}. \quad (8)
\end{aligned}$$

475 4. Entropy Inequality

476 The goal of TCAT analysis is to construct a framework for formulating
477 closed, solvable models. This goal requires a set of closure relations, which
478 TCAT analysis assures are consistent with the second law of thermodynam-
479 ics. The closure relations are based upon an EI written in strict force-flux
480 form, where the fluxes correspond to dissipative processes that produce en-
481 tropy away from equilibrium. The purpose of this section is to formulate such
482 an EI for the case of species transport in a two-fluid-phase porous medium
483 system.

As is typically the case, substantial effort is needed to derive the desired form of the EI. This work can be divided into two component parts: the first part that can be done exactly given the primary restrictions, which is called the constrained EI (CEI); and the second part that requires additional approximations and potentially restrictions to arrive at the desired force-flux form, which is called the simplified EI (SEI). The CEI and SEI are chief archival equations resulting from a TCAT analysis and provide logical entry points for researchers wishing to extend the foundational formulation presented in this work. The subsections that follow will detail these results.

4.1. Constrained Entropy Inequality

The CEI is derived by augmenting a system balance of entropy equation with a set of conservation and thermodynamic equations that are chosen to include the desired physics. The desired physics for the class of model considered herein requires species mass conservation for each entity and overall conservation of momentum and total energy for each entity. The augmented EI is formed by adding the product of Lagrange multipliers and conservation and thermodynamic equations giving

$$\sum_{\alpha \in \mathcal{J}} \left[\mathcal{S}_{**}^{\bar{\alpha}} + \lambda_{\mathcal{E}}^{\alpha} \mathcal{E}_{**}^{\bar{\alpha}} + \boldsymbol{\lambda}_{\mathcal{P}}^{\alpha} \cdot \mathcal{P}_{**}^{\bar{\alpha}} + \sum_{i \in \mathcal{J}_s} \lambda_{\mathcal{M}}^{i\alpha} \mathcal{M}_{**}^{\bar{i}\bar{\alpha}} + \lambda_{\mathcal{G}}^{\alpha} \mathcal{G}_{**}^{\bar{\alpha}} + \lambda_{\mathcal{T}}^{\alpha} \mathcal{T}_{*}^{\bar{\alpha}} + \lambda_{\mathcal{T}\mathcal{G}}^{\alpha} \mathcal{T}_{\mathcal{G}*}^{\bar{\alpha}} \right] = \sum_{\alpha \in \mathcal{J}} \Lambda^{\bar{\alpha}} \geq 0, \quad (9)$$

where λ denotes a scalar Lagrange multiplier, $\boldsymbol{\lambda}$ is a vector Lagrange multiplier, the subscripts on the Lagrange multipliers are equation qualifiers, and the superscripts are entity or species-entity qualifiers. The specific forms of the equations given by $\mathcal{S}_{**}^{\bar{\alpha}}$, $\mathcal{E}_{**}^{\bar{\alpha}}$, $\mathcal{P}_{**}^{\bar{\alpha}}$, $\mathcal{M}_{**}^{\bar{i}\bar{\alpha}}$, $\mathcal{G}_{**}^{\bar{\alpha}}$, $\mathcal{T}_{*}^{\bar{\alpha}}$, and $\mathcal{T}_{\mathcal{G}*}^{\bar{\alpha}}$ are given by

505 Eqs. (1)–(8). Each of these equations is a conservation, balance, thermody-
 506 namic near-equilibrium dynamic, or dynamic potential energy equation with
 507 units of some extensive quantity per averaging volume, which is termed a
 508 density form.

509 Our objective is to derive an SEI in strict force-flux form, which requires
 510 independence of all members of the set of forces and independence of all
 511 members of the set of fluxes. Because the material derivatives are not in
 512 general independent of each other, due to the inter-relationships among entity
 513 measures, we wish to eliminate as many of the material derivatives as possible
 514 from the CEI; conditions of solvability do not allow for all material derivatives
 515 to be eliminated. The mechanism for removing these material derivatives is
 516 through proper selection of the Lagrange multipliers in Eq. (9). Therefore,
 517 the material derivatives from the corresponding conservation, balance and
 518 thermodynamic equations (1)–(8) are substituted into Eq. (9), the product
 519 rule is applied when necessary, and the multipliers of the material derivatives
 520 are collected. These multipliers contain the Lagrange parameters, and the
 521 values given can be derived based upon solvability of a linear algebra problem.
 522 The Lagrange multipliers for the system under consideration are

$$\left\{ \begin{array}{c} \lambda_{\mathcal{M}}^{i\alpha} \\ \lambda_{\mathcal{P}}^{\alpha} \\ \lambda_{\mathcal{E}}^{\alpha} \\ \lambda_{\mathcal{G}}^{\alpha} \\ \lambda_{\mathcal{T}}^{\alpha} \\ \lambda_{\mathcal{TG}}^{\alpha} \end{array} \right\} = \frac{1}{\theta^{\bar{\alpha}}} \left\{ \begin{array}{c} K_{\bar{E}}^{\bar{i}\alpha} + \frac{\mathbf{u}^{\bar{i}\alpha} \cdot \mathbf{u}^{\bar{i}\alpha}}{2} + \mu^{\bar{i}\alpha} + \psi^{\bar{i}\alpha} - \frac{\mathbf{v}^{\bar{\alpha}} \cdot \mathbf{v}^{\bar{\alpha}}}{2} \\ \mathbf{v}^{\bar{\alpha}} \\ -1 \\ -1 \\ 1 \\ 1 \end{array} \right\} \quad \text{for } \alpha \in \mathcal{J}, i \in \mathcal{J}_s. \quad (10)$$

523 Substitution of Eq. (10) into Eq. (9), replacing the equation variables with
 524 the corresponding conservation, balance, and thermodynamic equations, and
 525 simplifying to a force-flux form to the extent possible without approximation
 526 yields

$$\begin{aligned}
 & - \sum_{\alpha \in \mathcal{I}_P} \left\{ \epsilon^{\bar{\alpha}} b^\alpha - \frac{1}{\theta^{\bar{\alpha}}} \left[\epsilon^{\bar{\alpha}} h^\alpha + \left\langle \eta_\alpha \frac{D^{\bar{s}} (\theta_\alpha - \theta^{\bar{\alpha}})}{Dt} \right\rangle_{\Omega_\alpha, \Omega} \right. \right. \\
 & \quad \left. \left. + \sum_{i \in \mathcal{I}_s} \left\langle \rho_\alpha \omega_{i\alpha} \frac{D^{\bar{s}}}{Dt} \left(\mu_{i\alpha} + \psi_{i\alpha} - \mu^{\bar{i}\bar{\alpha}} - K_E^{\bar{i}\bar{\alpha}} - \frac{\mathbf{u}^{\bar{i}\bar{\alpha}} \cdot \mathbf{u}^{\bar{i}\bar{\alpha}}}{2} - \psi^{\bar{i}\bar{\alpha}} \right) \right\rangle_{\Omega_\alpha, \Omega} \right] \right\} \\
 & - \sum_{\alpha \in \mathcal{I}_I} \left\{ \epsilon^{\bar{\alpha}} b^\alpha - \frac{1}{\theta^{\bar{\alpha}}} \left[\epsilon^{\bar{\alpha}} h^\alpha + \left\langle \eta_\alpha \frac{D^{\bar{s}} (\theta_\alpha - \theta^{\bar{\alpha}})}{Dt} \right\rangle_{\Omega_\alpha, \Omega} \right. \right. \\
 & \quad \left. \left. + \sum_{i \in \mathcal{I}_s} \left\langle \rho_\alpha \omega_{i\alpha} \frac{D^{\bar{s}}}{Dt} \left(\mu_{i\alpha} + \psi_{i\alpha} - \mu^{\bar{i}\bar{\alpha}} - K_E^{\bar{i}\bar{\alpha}} - \frac{\mathbf{u}^{\bar{i}\bar{\alpha}} \cdot \mathbf{u}^{\bar{i}\bar{\alpha}}}{2} - \psi^{\bar{i}\bar{\alpha}} \right) \right\rangle_{\Omega_\alpha, \Omega} \right] \right\} \\
 & - \left\{ \epsilon^{\bar{w}\bar{n}\bar{s}} b^{wns} - \frac{1}{\theta^{\bar{w}\bar{n}\bar{s}}} \left[\epsilon^{\bar{w}\bar{n}\bar{s}} h^{wns} + \left\langle \eta_{wns} \frac{D^{\bar{w}\bar{n}\bar{s}} (\theta_{wns} - \theta^{\bar{w}\bar{n}\bar{s}})}{Dt} \right\rangle_{\Omega_{wns}, \Omega} \right. \right. \\
 & \quad \left. \left. + \sum_{i \in \mathcal{I}_s} \left\langle \rho_{wns} \omega_{iwns} \frac{D^{\bar{w}\bar{n}\bar{s}}}{Dt} \left(\mu_{iwns} + \psi_{iwns} - \mu^{\bar{i}\bar{w}\bar{n}\bar{s}} - K_E^{\bar{i}\bar{w}\bar{n}\bar{s}} \right. \right. \right. \\
 & \quad \left. \left. \left. - \frac{\mathbf{u}^{\bar{i}\bar{w}\bar{n}\bar{s}} \cdot \mathbf{u}^{\bar{i}\bar{w}\bar{n}\bar{s}}}{2} - \psi^{\bar{i}\bar{w}\bar{n}\bar{s}} \right) \right\rangle_{\Omega_{wns}, \Omega} \right] \right\} \\
 & - \sum_{\alpha \in \mathcal{I}_{\setminus S}} \nabla \cdot \left\{ \epsilon^{\bar{\alpha}} \boldsymbol{\varphi}^{\bar{\alpha}} - \frac{1}{\theta^{\bar{\alpha}}} \left[\epsilon^{\bar{\alpha}} \mathbf{q}^{\bar{\alpha}} + \epsilon^{\bar{\alpha}} \mathbf{q}_{\mathbf{g}0}^{\bar{\alpha}} \right. \right. \\
 & \quad \left. \left. + \sum_{i \in \mathcal{I}_s} \epsilon^{\bar{\alpha}} \rho^\alpha \omega^{i\bar{\alpha}} \left(\mu^{i\bar{\alpha}} + K_E^{i\bar{\alpha}} + \frac{\mathbf{u}^{i\bar{\alpha}} \cdot \mathbf{u}^{i\bar{\alpha}}}{2} \right) \mathbf{u}^{i\bar{\alpha}} \right] \right\} \\
 & - \nabla \cdot \left\{ \epsilon^{\bar{s}} \boldsymbol{\varphi}^{\bar{s}} - \frac{1}{\theta^{\bar{s}}} \left[\epsilon^{\bar{s}} \mathbf{q}^{\bar{s}} + \epsilon^{\bar{s}} \mathbf{q}_{\mathbf{g}0}^{\bar{s}} + \sum_{i \in \mathcal{I}_s} \epsilon^{\bar{s}} \rho^s \omega^{i\bar{s}} \left(\mu^{i\bar{s}} + K_E^{i\bar{s}} + \frac{\mathbf{u}^{i\bar{s}} \cdot \mathbf{u}^{i\bar{s}}}{2} \right) \mathbf{u}^{i\bar{s}} \right. \right. \\
 & \quad \left. \left. \right] \right\}
 \end{aligned}$$

$$\begin{aligned}
& - \left\langle \left(\mathbf{t}_s - \frac{\boldsymbol{\sigma}_s : \mathbf{C}_s}{j_s} \mathbf{I} \right) \cdot (\mathbf{v}_s - \mathbf{v}^{\bar{s}}) \right\rangle_{\Omega_s, \Omega} \Bigg] \Bigg\} \tag{11} \\
& + \sum_{\alpha \in \mathcal{J}_f} \frac{1}{\theta^{\bar{\alpha}}} \left(\epsilon^{\bar{\alpha}} \mathbf{t}^{\bar{\alpha}} + \epsilon^{\bar{\alpha}} p^{\alpha} \mathbf{I} \right) : \mathbf{d}^{\bar{\alpha}} + \frac{1}{\theta^{\bar{s}}} \left(\epsilon^{\bar{s}} \mathbf{t}^{\bar{s}} - \epsilon^{\bar{s}} \mathbf{t}^s \right) : \mathbf{d}^{\bar{s}} \tag{12} \\
& + \sum_{\alpha \in \mathcal{J}_I} \frac{1}{\theta^{\bar{\alpha}}} \left[\epsilon^{\bar{\alpha}} \mathbf{t}^{\bar{\alpha}} - \langle \mathbf{l}'_{\alpha} \gamma_{\alpha} \rangle_{\Omega_{\alpha}, \Omega} \right] : \mathbf{d}^{\bar{\alpha}} \tag{13} \\
& + \frac{1}{\theta^{\overline{wns}}} \left[\epsilon^{\overline{wns}} \mathbf{t}^{\overline{wns}} + \langle \mathbf{l}''_{wns} \gamma_{wns} \rangle_{\Omega_{wns}, \Omega} \right] : \mathbf{d}^{\overline{wns}} \tag{14} \\
& - \sum_{\alpha \in \mathcal{J}_{\setminus s}} \left[\epsilon^{\bar{\alpha}} \mathbf{q}^{\bar{\alpha}} + \epsilon^{\bar{\alpha}} \mathbf{q}_{\mathbf{g}0}^{\bar{\alpha}} + \sum_{i \in \mathcal{J}_s} \epsilon^{\bar{\alpha}} \rho^{\alpha} \omega^{i\bar{\alpha}} \left(\mu^{\bar{i}\bar{\alpha}} + K_E^{\bar{i}\bar{\alpha}} + \frac{\mathbf{u}^{\bar{i}\bar{\alpha}} \cdot \mathbf{u}^{\bar{i}\bar{\alpha}}}{2} \right) \mathbf{u}^{\bar{i}\bar{\alpha}} \right] \cdot \nabla \left(\frac{1}{\theta^{\bar{\alpha}}} \right) \tag{15} \\
& - \left[\epsilon^{\bar{s}} \mathbf{q}^{\bar{s}} + \epsilon^{\bar{s}} \mathbf{q}_{\mathbf{g}0}^{\bar{s}} + \sum_{i \in \mathcal{J}_s} \epsilon^{\bar{s}} \rho^s \omega^{i\bar{s}} \left(\mu^{\bar{i}\bar{s}} + K_E^{\bar{i}\bar{s}} + \frac{\mathbf{u}^{\bar{i}\bar{s}} \cdot \mathbf{u}^{\bar{i}\bar{s}}}{2} \right) \mathbf{u}^{\bar{i}\bar{s}} \right. \tag{16} \\
& \quad \left. - \left\langle \left(\mathbf{t}_s - \frac{\boldsymbol{\sigma}_s : \mathbf{C}_s}{j_s} \mathbf{I} \right) \cdot (\mathbf{v}_s - \mathbf{v}^{\bar{s}}) \right\rangle_{\Omega_s, \Omega} \right] \cdot \nabla \left(\frac{1}{\theta^{\bar{s}}} \right) \tag{17} \\
& - \sum_{\alpha \in \mathcal{J}} \sum_{i \in \mathcal{J}_{s \setminus N}} \frac{1}{\theta^{\bar{\alpha}}} \epsilon^{\bar{\alpha}} \rho^{\alpha} \omega^{i\bar{\alpha}} \mathbf{u}^{\bar{i}\bar{\alpha}} \cdot \nabla \left[\mu^{\bar{i}\bar{\alpha}} + K_E^{\bar{i}\bar{\alpha}} + \frac{\mathbf{u}^{\bar{i}\bar{\alpha}} \cdot \mathbf{u}^{\bar{i}\bar{\alpha}}}{2} + \psi^{\bar{i}\bar{\alpha}} \right. \tag{18} \\
& \quad \left. - \left(\mu^{\bar{N}\bar{\alpha}} + K_E^{\bar{N}\bar{\alpha}} + \frac{\mathbf{u}^{\bar{N}\bar{\alpha}} \cdot \mathbf{u}^{\bar{N}\bar{\alpha}}}{2} + \psi^{\bar{N}\bar{\alpha}} \right) \right] \tag{19} \\
& - \sum_{\alpha \in \mathcal{J}} \sum_{i \in \mathcal{J}_s} \frac{1}{\theta^{\bar{\alpha}}} \left(\mu^{\bar{i}\bar{\alpha}} + K_E^{\bar{i}\bar{\alpha}} + \frac{\mathbf{u}^{\bar{i}\bar{\alpha}} \cdot \mathbf{u}^{\bar{i}\bar{\alpha}}}{2} + \psi^{\bar{i}\bar{\alpha}} \right) \epsilon^{\bar{\alpha}} r^{i\alpha} \tag{20} \\
& + \sum_{\alpha \in \mathcal{J}} \sum_{i \in \mathcal{J}_s} \frac{1}{\theta^{\bar{\alpha}}} \langle r_{i\alpha} \psi_{i\alpha} \rangle_{\Omega_{\alpha}, \Omega} \tag{21} \\
& + \sum_{\alpha \in \mathcal{J}_f} \sum_{\kappa \in \mathcal{J}_{c\alpha}} \sum_{i \in \mathcal{J}_s} M^{i\alpha \rightarrow i\kappa} \left[\frac{1}{\theta^{\bar{\alpha}}} \left(\mu^{\bar{i}\bar{\alpha}} + K_E^{\bar{i}\bar{\alpha}} + \frac{\mathbf{u}^{\bar{i}\bar{\alpha}} \cdot \mathbf{u}^{\bar{i}\bar{\alpha}}}{2} + \psi^{\bar{i}\bar{\alpha}} \right) \right. \tag{22} \\
& \quad \left. - \frac{1}{\theta^{\bar{\kappa}}} \left(\mu^{\bar{i}\bar{\kappa}} + K_E^{\bar{i}\bar{\kappa}} + \frac{\mathbf{u}^{\bar{i}\bar{\kappa}} \cdot \mathbf{u}^{\bar{i}\bar{\kappa}}}{2} + \psi^{\bar{i}\bar{\kappa}} \right) \right] \tag{23} \\
& + \sum_{\kappa \in \mathcal{J}_{cs}} \sum_{i \in \mathcal{J}_s} M^{is \rightarrow i\kappa} \left[\frac{1}{\theta^{\bar{s}}} \left(\mu^{\bar{i}\bar{s}} + K_E^{\bar{i}\bar{s}} + \frac{\mathbf{u}^{\bar{i}\bar{s}} \cdot \mathbf{u}^{\bar{i}\bar{s}}}{2} + \psi^{\bar{i}\bar{s}} + \frac{\boldsymbol{\sigma}^{\bar{s}} : \mathbf{C}^s}{3\rho^s j^s} \right) \right. \tag{24}
\end{aligned}$$

$$- \frac{1}{\theta^{\bar{\kappa}}} \left(\mu^{\bar{i}\bar{\kappa}} + K_E^{\bar{i}\bar{\kappa}} + \frac{\mathbf{u}^{\bar{i}\bar{\kappa}} \cdot \mathbf{u}^{\bar{i}\bar{\kappa}}}{2} + \psi^{\bar{i}\bar{\kappa}} \right) \Big] \quad 25$$

$$+ \sum_{\kappa \in \mathcal{J}_{cs}} \frac{1}{\theta^{\bar{s}}} \left\langle \left(\frac{\boldsymbol{\sigma}_s \cdot \mathbf{C}_s}{\rho_s j_s} - \frac{\mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s}{\rho_s} - \frac{\boldsymbol{\sigma}^{\bar{s}} \cdot \mathbf{C}^s}{3\rho^s j^s} \right) \rho_s (\mathbf{v}_s - \mathbf{v}_\kappa) \cdot \mathbf{n}_s \right\rangle_{\Omega_\kappa, \Omega} \quad 26$$

$$+ \sum_{\alpha \in \mathcal{J}_I} \sum_{i \in \mathcal{J}_s} \frac{i\alpha \rightarrow iwns}{M} \left[\frac{1}{\theta^{\bar{\alpha}}} \left(\mu^{\bar{i}\bar{\alpha}} + K_E^{\bar{i}\bar{\alpha}} + \frac{\mathbf{u}^{\bar{i}\bar{\alpha}} \cdot \mathbf{u}^{\bar{i}\bar{\alpha}}}{2} + \psi^{\bar{i}\bar{\alpha}} \right) \right. \quad 27$$

$$\left. - \frac{1}{\theta^{\bar{wns}}} \left(\mu^{\bar{iwns}} + K_E^{\bar{iwns}} + \frac{\mathbf{u}^{\bar{iwns}} \cdot \mathbf{u}^{\bar{iwns}}}{2} + \psi^{\bar{iwns}} \right) \right] \quad 28$$

$$- \sum_{\alpha \in \mathcal{J}_f} \sum_{\kappa \in \mathcal{J}_{c\alpha}} \left\{ Q_1^{\alpha \rightarrow \kappa} + G_0^{\alpha \rightarrow \kappa} + \sum_{i \in \mathcal{J}_s} \left(\bar{E}_{i\alpha}^{\bar{\kappa}} + K_{Ei\alpha}^{\bar{\kappa}} + \frac{\mathbf{u}_{i\alpha}^{\bar{\kappa}} \cdot \mathbf{u}_{i\alpha}^{\bar{\kappa}}}{2} + \psi_{i\alpha}^{\bar{\kappa}} \right) M^{i\alpha \rightarrow i\kappa} \right. \quad 29$$

$$+ \left[\mathbf{T}_0^{\alpha \rightarrow \kappa} + \sum_{i \in \mathcal{J}_s} \left(\frac{\mathbf{v}_\alpha^{\bar{\kappa}} - \mathbf{v}^{\bar{s}}}{2} + \mathbf{u}_{i\alpha}^{\bar{\kappa}} \right) M^{i\alpha \rightarrow i\kappa} \right] \cdot (\mathbf{v}_\alpha^{\bar{\kappa}} - \mathbf{v}^{\bar{s}}) \quad 30$$

$$\left. - \langle \mathbf{n}_\alpha \cdot (\mathbf{v}_\kappa - \mathbf{v}^{\bar{s}}) p_\alpha \rangle_{\Omega_\kappa, \Omega} \right\} \left(\frac{1}{\theta^{\bar{\alpha}}} - \frac{1}{\theta^{\bar{\kappa}}} \right) \quad 31$$

$$- \sum_{\kappa \in \mathcal{J}_{cs}} \left\{ Q_1^{s \rightarrow \kappa} + G_0^{s \rightarrow \kappa} + \sum_{i \in \mathcal{J}_s} \left(\bar{E}_{is}^{\bar{\kappa}} + K_{Eis}^{\bar{\kappa}} + \frac{\mathbf{u}_{is}^{\bar{\kappa}} \cdot \mathbf{u}_{is}^{\bar{\kappa}}}{2} + \psi_{is}^{\bar{\kappa}} \right) M^{is \rightarrow i\kappa} \right. \quad 32$$

$$+ \left[\mathbf{T}_0^{s \rightarrow \kappa} + \sum_{i \in \mathcal{J}_s} \left(\frac{\mathbf{v}_s^{\bar{\kappa}} - \mathbf{v}^{\bar{s}}}{2} + \mathbf{u}_{is}^{\bar{\kappa}} \right) M^{is \rightarrow i\kappa} \right] \cdot (\mathbf{v}_s^{\bar{\kappa}} - \mathbf{v}^{\bar{s}}) \quad 33$$

$$\left. + \langle \mathbf{n}_s \cdot (\mathbf{v}_\kappa - \mathbf{v}^{\bar{s}}) \mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s \rangle_{\Omega_\kappa, \Omega} \right\} \left(\frac{1}{\theta^{\bar{s}}} - \frac{1}{\theta^{\bar{\kappa}}} \right) \quad 34$$

$$- \sum_{\alpha \in \mathcal{J}_I} \left\{ Q_1^{\alpha \rightarrow wns} + G_0^{\alpha \rightarrow wns} + \sum_{i \in \mathcal{J}_s} \left(\bar{E}_{i\alpha}^{\bar{wns}} + K_{Ei\alpha}^{\bar{wns}} + \frac{\mathbf{u}_{i\alpha}^{\bar{wns}} \cdot \mathbf{u}_{i\alpha}^{\bar{wns}}}{2} + \psi_{i\alpha}^{\bar{wns}} \right) M^{i\alpha \rightarrow iwns} \right. \quad 35$$

$$+ \left[\mathbf{T}_0^{\alpha \rightarrow wns} + \sum_{i \in \mathcal{J}_s} \left(\frac{\mathbf{v}_\alpha^{\bar{wns}} - \mathbf{v}^{\bar{s}}}{2} + \mathbf{u}_{i\alpha}^{\bar{wns}} \right) M^{i\alpha \rightarrow iwns} \right] \cdot (\mathbf{v}_\alpha^{\bar{wns}} - \mathbf{v}^{\bar{s}}) \quad 36$$

$$\left. + \langle \mathbf{n}_\alpha \cdot (\mathbf{v}_{wns} - \mathbf{v}^{\bar{s}}) \gamma_\alpha \rangle_{\Omega_{wns}, \Omega} \right\} \left(\frac{1}{\theta^{\bar{\alpha}}} - \frac{1}{\theta^{\bar{wns}}} \right) \quad 37$$

$$+ \left[Q_1^* + \langle \mathbf{n}_s \cdot \mathbf{t}_s^* \cdot (\mathbf{v}_s^{\overline{wns}} - \mathbf{v}_s) \rangle_{\Omega_{wns}, \Omega} \right. \quad 38$$

$$\left. + \langle \mathbf{n}_s \cdot \mathbf{t}_s^* \cdot (\mathbf{v}_s - \mathbf{v}_{wns}) \rangle_{\Omega_{wns}, \Omega} \right] \left(\frac{1}{\theta^{\overline{s}}} - \frac{1}{\theta^{\overline{wns}}} \right) \quad 39$$

$$- \sum_{\alpha \in \mathcal{J}_f} \frac{1}{\theta^{\overline{\alpha}}} \left\{ \eta^{\overline{\alpha}} \nabla \theta^{\overline{\alpha}} - \nabla \left(\epsilon^{\overline{\alpha}} p^\alpha \right) \right. \quad 40$$

$$\left. + \sum_{i \in \mathcal{J}_s} \epsilon^{\overline{\alpha}} \rho^\alpha \omega^{i\overline{\alpha}} \left[\nabla \left(\mu^{i\overline{\alpha}} + K_E^{\overline{i\overline{\alpha}}} + \frac{\mathbf{u}^{i\overline{\alpha}} \cdot \mathbf{u}^{i\overline{\alpha}}}{2} + \psi^{i\overline{\alpha}} \right) + \mathbf{g}^{i\overline{\alpha}} \right] \right. \quad 41$$

$$\left. - \sum_{\kappa \in \mathcal{J}_{c\alpha}} \left[\mathbf{T}_0^{\alpha \rightarrow \kappa} - \sum_{i \in \mathcal{J}_s} \frac{(\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}})^{i\alpha \rightarrow i\kappa}}{2} M \right. \right. \quad 42$$

$$\left. + \sum_{i \in \mathcal{J}_s} \left(\mathbf{v}_\alpha^{\overline{\kappa}} + \mathbf{u}_{i\alpha}^{\overline{\kappa}} - \mathbf{v}^{\overline{s}} \right)^{i\alpha \rightarrow i\kappa} M \right] \left. \right\} \cdot (\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}}) \quad 43$$

$$- \sum_{\alpha \in \mathcal{J}_1} \frac{1}{\theta^{\overline{\alpha}}} \left\{ \eta^{\overline{\alpha}} \nabla \theta^{\overline{\alpha}} + \nabla \cdot \langle \mathbf{l}'_\alpha \gamma_\alpha \rangle_{\Omega_\alpha, \Omega} \right. \quad 44$$

$$\left. + \sum_{i \in \mathcal{J}_s} \epsilon^{\overline{\alpha}} \rho^\alpha \omega^{i\overline{\alpha}} \left[\nabla \left(\mu^{i\overline{\alpha}} + K_E^{\overline{i\overline{\alpha}}} + \frac{\mathbf{u}^{i\overline{\alpha}} \cdot \mathbf{u}^{i\overline{\alpha}}}{2} + \psi^{i\overline{\alpha}} \right) + \mathbf{g}^{i\overline{\alpha}} \right] \right. \quad 45$$

$$\left. + \sum_{\kappa \in \mathcal{J}_{c\alpha}^+} \left[\mathbf{T}_0^{\kappa \rightarrow \alpha} - \sum_{i \in \mathcal{J}_s} \frac{(\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}})^{i\kappa \rightarrow i\alpha}}{2} M + \sum_{i \in \mathcal{J}_s} \left(\mathbf{v}_\kappa^{\overline{\alpha}} + \mathbf{u}_{i\kappa}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}} \right)^{i\kappa \rightarrow i\alpha} M \right] \right. \quad 46$$

$$\left. - \left[\mathbf{T}_0^{\alpha \rightarrow wns} - \sum_{i \in \mathcal{J}_s} \frac{(\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}})^{i\alpha \rightarrow iwns}}{2} M + \sum_{i \in \mathcal{J}_s} \left(\mathbf{v}_\alpha^{\overline{wns}} + \mathbf{u}_{i\alpha}^{\overline{wns}} - \mathbf{v}^{\overline{s}} \right)^{i\alpha \rightarrow iwns} M \right] \right. \quad 47$$

$$\left. - \langle \eta_\alpha (\mathbf{l} - \mathbf{l}'_\alpha) \rangle_{\Omega_\alpha, \Omega} \cdot \nabla \theta^{\overline{\alpha}} \right. \quad 48$$

$$\left. - \sum_{i \in \mathcal{J}_s} \langle \rho_\alpha \omega_{i\alpha} (\mathbf{l} - \mathbf{l}'_\alpha) \rangle_{\Omega_\alpha, \Omega} \cdot \nabla \left(\mu^{i\overline{\alpha}} + K_E^{\overline{i\overline{\alpha}}} + \frac{\mathbf{u}^{i\overline{\alpha}} \cdot \mathbf{u}^{i\overline{\alpha}}}{2} + \psi^{i\overline{\alpha}} \right) \right\} \cdot (\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}}) \quad 49$$

$$- \frac{1}{\theta^{\overline{wns}}} \left\{ \eta^{\overline{wns}} \nabla \theta^{\overline{wns}} - \nabla \cdot \langle \mathbf{l}''_{wns} \gamma_{wns} \rangle_{\Omega_{wns}, \Omega} \right. \quad 50$$

$$\left. + \sum_{i \in \mathcal{J}_s} \epsilon^{\overline{wns}} \rho^{wns} \omega^{i\overline{wns}} \left[\nabla \left(\mu^{i\overline{wns}} + K_E^{\overline{i\overline{wns}}} + \frac{\mathbf{u}^{i\overline{wns}} \cdot \mathbf{u}^{i\overline{wns}}}{2} + \psi^{i\overline{wns}} \right) + \mathbf{g}^{i\overline{wns}} \right] \right. \quad 51$$

$$+ \sum_{\kappa \in \mathcal{I}_{cwns}^+} \left[\mathbf{T}_0^{\kappa \rightarrow wns} - \sum_{i \in \mathcal{I}_s} \frac{(\mathbf{v}^{\overline{wns}} - \mathbf{v}^{\overline{s}})}{2} \frac{i\kappa \rightarrow iwns}{M} \right] \quad 52$$

$$+ \sum_{i \in \mathcal{I}_s} \left(\mathbf{v}_{\kappa}^{\overline{wns}} + \mathbf{u}_{i\kappa}^{\overline{wns}} - \mathbf{v}^{\overline{s}} \right) \frac{i\kappa \rightarrow iwns}{M} \quad 53$$

$$- \langle \eta_{wns} (\mathbf{l} - \mathbf{l}_{wns}'') \rangle_{\Omega_{wns}, \Omega} \cdot \nabla \theta^{\overline{wns}} \quad 54$$

$$- \sum_{i \in \mathcal{I}_s} \langle \rho_{wns} \omega_{iwns} (\mathbf{l} - \mathbf{l}_{wns}'') \rangle_{\Omega_{wns}, \Omega} \cdot \nabla \left(\mu^{\overline{iwns}} + K_E^{\overline{iwns}} + \frac{\mathbf{u}^{\overline{iwns}} \cdot \mathbf{u}^{\overline{iwns}}}{2} + \psi^{\overline{iwns}} \right) \quad 55$$

$$- \langle \mathbf{t}_s^* \cdot \mathbf{n}_s \rangle_{\Omega_{wns}, \Omega} \cdot (\mathbf{v}^{\overline{wns}} - \mathbf{v}^{\overline{s}}) \quad 56$$

$$+ \frac{1}{\theta^{\overline{wn}}} \left\langle \left[p_w \mathbf{n}_w + p_n \mathbf{n}_n + \gamma_{wn} (\nabla' \cdot \mathbf{l}_{wn}') \right. \right. \quad 57$$

$$\left. + \sum_{i \in \mathcal{I}_s} \rho_{wn} \omega_{iwn} \mathbf{g}_{iwn} \cdot (\mathbf{l} - \mathbf{l}_{wn}') \right] \cdot (\mathbf{v}_{wn} - \mathbf{v}^{\overline{s}}) \right\rangle_{\Omega_{wn}, \Omega} \quad 58$$

$$+ \frac{1}{\theta^{\overline{ws}}} \left\langle \left[p_w \mathbf{n}_w - \mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s \mathbf{n}_s + \gamma_{ws} (\nabla' \cdot \mathbf{l}_{ws}') \right. \right. \quad 59$$

$$\left. + \sum_{i \in \mathcal{I}_s} \rho_{ws} \omega_{iws} \mathbf{g}_{iws} \cdot (\mathbf{l} - \mathbf{l}_{ws}') \right] \cdot (\mathbf{v}_{ws} - \mathbf{v}^{\overline{s}}) \right\rangle_{\Omega_{ws}, \Omega} \quad 60$$

$$+ \frac{1}{\theta^{\overline{ns}}} \left\langle \left[p_n \mathbf{n}_n - \mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s \mathbf{n}_s + \gamma_{ns} (\nabla' \cdot \mathbf{l}_{ns}') \right. \right. \quad 61$$

$$\left. + \sum_{i \in \mathcal{I}_s} \rho_{ns} \omega_{ins} \mathbf{g}_{ins} \cdot (\mathbf{l} - \mathbf{l}_{ns}') \right] \cdot (\mathbf{v}_{ns} - \mathbf{v}^{\overline{s}}) \right\rangle_{\Omega_{ns}, \Omega} \quad 62$$

$$- \frac{1}{\theta^{\overline{wns}}} \left\langle \left[\gamma_{wn} \mathbf{n}_{wn} + \gamma_{ws} \mathbf{n}_{ws} + \gamma_{ns} \mathbf{n}_{ns} + \gamma_{wns} (\nabla'' \cdot \mathbf{l}_{wns}'') \right. \right. \quad 63$$

$$\left. - \sum_{i \in \mathcal{I}_s} \rho_{wns} \omega_{iwns} \mathbf{g}_{iwns} \cdot (\mathbf{l} - \mathbf{l}_{wns}'') + \mathbf{n}_s \cdot \mathbf{t}_s^* \right] \cdot (\mathbf{v}_{wns} - \mathbf{v}^{\overline{s}}) \right\rangle_{\Omega_{wns}, \Omega} \quad 64$$

$$+ \frac{1}{\theta^{\overline{s}}} \left\langle \mathbf{n}_s \cdot (\mathbf{v}_s - \mathbf{v}_{wns}) \frac{\boldsymbol{\sigma}_s^* : \mathbf{C}_s}{j_s} \right\rangle_{\Omega_{wns}, \Omega} - \frac{1}{\theta^{\overline{s}}} \langle \mathbf{n}_s \cdot \mathbf{t}_s^* \cdot (\mathbf{v}_s - \mathbf{v}_{wns}) \rangle_{\Omega_{wns}, \Omega} \quad 65$$

$$- \frac{1}{\theta^{\bar{s}}} \langle \mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{l}'_{ws} \cdot (\mathbf{v}_s - \mathbf{v}^{\bar{s}}) \rangle_{\Omega_{ws}, \Omega} - \frac{1}{\theta^{\bar{s}}} \langle \mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{l}'_{ns} \cdot (\mathbf{v}_s - \mathbf{v}^{\bar{s}}) \rangle_{\Omega_{ns}, \Omega} \quad 66$$

$$+ \frac{1}{\theta^{\bar{s}}} \left\langle \left(\nabla \cdot \mathbf{t}_s - \nabla \sigma_s : \frac{\mathbf{C}_s}{j_s} \right) \cdot (\mathbf{v}_s - \mathbf{v}^{\bar{s}}) \right\rangle_{\Omega_s, \Omega} \quad 67$$

$$+ \sum_{\alpha \in \mathcal{J}_I} \frac{1}{\theta^{\bar{\alpha}}} \langle \eta_\alpha (\mathbf{v}_\alpha - \mathbf{v}^{\bar{\alpha}}) \cdot (\mathbf{l} - \mathbf{l}'_\alpha) \rangle_{\Omega_\alpha, \Omega} \cdot \nabla \theta^{\bar{\alpha}} \quad 68$$

$$+ \sum_{\alpha \in \mathcal{J}_I} \frac{1}{\theta^{\bar{\alpha}}} \nabla \cdot \langle (\mathbf{l} - \mathbf{l}'_\alpha) \cdot (\mathbf{v}_\alpha - \mathbf{v}^{\bar{\alpha}}) \gamma_\alpha \rangle_{\Omega_\alpha, \Omega} \quad 69$$

$$+ \sum_{\alpha \in \mathcal{J}_I} \frac{1}{\theta^{\bar{\alpha}}} \sum_{i \in \mathcal{J}_s} \langle \rho_\alpha \omega_{i\alpha} (\mathbf{v}_\alpha - \mathbf{v}^{\bar{\alpha}}) \cdot (\mathbf{l} - \mathbf{l}'_\alpha) \rangle_{\Omega_\alpha, \Omega} \cdot \nabla \left(\mu^{\bar{i}\alpha} + K_E^{\bar{i}\alpha} \right. \quad 70$$

$$\left. + \frac{\mathbf{u}^{\bar{i}\alpha} \cdot \mathbf{u}^{\bar{i}\alpha}}{2} + \psi^{\bar{i}\alpha} \right) \quad 71$$

$$+ \frac{1}{\theta^{\overline{wns}}} \langle \eta_{wns} (\mathbf{v}_{wns} - \mathbf{v}^{\overline{wns}}) \cdot (\mathbf{l} - \mathbf{l}''_{wns}) \rangle_{\Omega_{wns}, \Omega} \cdot \nabla \theta^{\overline{wns}} \quad 72$$

$$- \frac{1}{\theta^{\overline{wns}}} \nabla \cdot \langle (\mathbf{l} - \mathbf{l}''_{wns}) \cdot (\mathbf{v}_{wns} - \mathbf{v}^{\overline{wns}}) \gamma_{wns} \rangle_{\Omega_{wns}, \Omega} \quad 73$$

$$+ \frac{1}{\theta^{\overline{wns}}} \sum_{i \in \mathcal{J}_s} \langle \rho_{wns} \omega_{iwns} (\mathbf{v}_{wns} - \mathbf{v}^{\overline{wns}}) \cdot (\mathbf{l} - \mathbf{l}''_{wns}) \rangle_{\Omega_{wns}, \Omega} \cdot \nabla \left(\mu^{\overline{iwns}} + K_E^{\overline{iwns}} \right. \quad 74$$

$$\left. + \frac{\mathbf{u}^{\overline{iwns}} \cdot \mathbf{u}^{\overline{iwns}}}{2} + \psi^{\overline{iwns}} \right) = \sum_{\alpha \in \mathcal{J}} \Lambda^{\bar{\alpha}} \geq 0, \quad (11)$$

527 where N is the reference chemical species. The manipulations needed to
 528 derive this equation are similar to those that have been documented and
 529 used to derive CEIs for other porous medium systems [18]. Equation (11) is
 530 the final form of the CEI for a compositional two-fluid-phase porous medium
 531 system at the macroscale. Because of the general and exact nature of the
 532 CEI, it is a useful archival result that can be used as a starting point to
 533 derive closed models for this broad class of problems.

534 Equation (11) can be reduced to the CEI for single-fluid-phase porous
 535 medium systems with species transport [18, Chap. 10] when the second fluid

536 phase is neglected, or to the CEI for two-fluid-phase systems [18, Chap. 11]
 537 when compositional effects are not modeled.

538 4.2. SEI Approximations

539 Many terms in Eq. (11) are already in macroscale force-flux form, but
 540 some of the terms are not in this form. To bring all terms to a force-flux
 541 form, some SEI approximations are needed. SEI approximations are non-
 542 unique and subject to reassessment if the TCAT model fails to describe the
 543 proper system behaviour. We formulate a set of SEI approximations that
 544 reduces the CEI to a strict force-flux form for problems of interest in this
 545 work.

546 SEI Approximation 1 (Macroscopically Simple System).

547 *The system of concern is thermodynamically simple at the macroscale, such*
 548 *that the entropy source is equivalent to the sum of the heat source and devi-*
 549 *ation terms such that*

$$\begin{aligned}
 & \epsilon^{\bar{\bar{\alpha}}} b^\alpha - \frac{1}{\theta^{\bar{\bar{\alpha}}}} \left[\epsilon^{\bar{\bar{\alpha}}} h^\alpha + \left\langle \eta_\alpha \frac{D^{\bar{s}} (\theta_\alpha - \theta^{\bar{\bar{\alpha}}})}{Dt} \right\rangle_{\Omega_\alpha, \Omega} \right. \\
 & \quad \left. + \sum_{i \in \mathcal{J}_s} \left\langle \rho_\alpha \omega_{i\alpha} \frac{D^{\bar{s}}}{Dt} \left(\mu_{i\alpha} + \psi_{i\alpha} - \mu^{i\bar{\alpha}} - K_E^{i\bar{\alpha}} - \frac{\mathbf{u}^{i\bar{\alpha}} \cdot \mathbf{u}^{i\bar{\alpha}}}{2} - \psi^{i\bar{\alpha}} \right) \right\rangle_{\Omega_\alpha, \Omega} \right] = 0 \\
 & \hspace{25em} \text{for } \alpha \in \mathcal{J}_P, \quad (12)
 \end{aligned}$$

$$\begin{aligned}
 & \epsilon^{\bar{\bar{\alpha}}} b^\alpha - \frac{1}{\theta^{\bar{\bar{\alpha}}}} \left[\epsilon^{\bar{\bar{\alpha}}} h^\alpha + \left\langle \eta_\alpha \frac{D^{\bar{s}} (\theta_\alpha - \theta^{\bar{\bar{\alpha}}})}{Dt} \right\rangle_{\Omega_\alpha, \Omega} \right. \\
 & \quad \left. + \sum_{i \in \mathcal{J}_s} \left\langle \rho_\alpha \omega_{i\alpha} \frac{D^{\bar{s}}}{Dt} \left(\mu_{i\alpha} + \psi_{i\alpha} - \mu^{i\bar{\alpha}} - K_E^{i\bar{\alpha}} - \frac{\mathbf{u}^{i\bar{\alpha}} \cdot \mathbf{u}^{i\bar{\alpha}}}{2} - \psi^{i\bar{\alpha}} \right) \right\rangle_{\Omega_\alpha, \Omega} \right] = 0
 \end{aligned}$$

$$\text{for } \alpha \in \mathcal{J}_I, \quad (13)$$

$$\begin{aligned} & \epsilon^{\overline{wns}} b^{wns} - \frac{1}{\theta^{\overline{wns}}} \left[\epsilon^{\overline{wns}} h^{wns} + \left\langle \eta_{wns} \frac{D'^{\overline{s}} (\theta_{wns} - \theta^{\overline{wns}})}{Dt} \right\rangle_{\Omega_{wns}, \Omega} \right. \\ & + \sum_{i \in \mathcal{J}_s} \left\langle \rho_{wns} \omega_{iwns} \frac{D'^{\overline{s}}}{Dt} \left(\mu_{iwns} + \psi_{iwns} - \mu^{\overline{iwns}} - K_E^{\overline{iwns}} - \frac{\mathbf{u}^{\overline{iwns}} \cdot \mathbf{u}^{\overline{iwns}}}{2} \right. \right. \\ & \left. \left. - \psi^{\overline{iwns}} \right) \right\rangle_{\Omega_{wns}, \Omega} \left. \right] = 0, \end{aligned} \quad (14)$$

550 and the entropy flux is equivalent to the non-advective energy flux for all
551 entities, consisting of heat and mechanical contributions such that

$$\epsilon^{\overline{\alpha}} \boldsymbol{\varphi}^{\overline{\alpha}} - \frac{1}{\theta^{\overline{\alpha}}} \left[\epsilon^{\overline{\alpha}} \mathbf{q}^{\overline{\alpha}} + \epsilon^{\overline{\alpha}} \mathbf{q}_{\mathbf{g}0}^{\overline{\alpha}} + \sum_{i \in \mathcal{J}_s} \epsilon^{\overline{\alpha}} \rho^\alpha \omega^{i\overline{\alpha}} \left(\mu^{i\overline{\alpha}} + K_E^{i\overline{\alpha}} + \frac{\mathbf{u}^{i\overline{\alpha}} \cdot \mathbf{u}^{i\overline{\alpha}}}{2} \right) \mathbf{u}^{i\overline{\alpha}} \right] = 0$$

for $\alpha \in \mathcal{J}_{\setminus S}$, (15)

552 and

$$\begin{aligned} & \epsilon^{\overline{s}} \boldsymbol{\varphi}^{\overline{s}} - \frac{1}{\theta^{\overline{s}}} \left[\epsilon^{\overline{s}} \mathbf{q}^{\overline{s}} + \epsilon^{\overline{s}} \mathbf{q}_{\mathbf{g}0}^{\overline{s}} + \sum_{i \in \mathcal{J}_s} \epsilon^{\overline{s}} \rho^s \omega^{i\overline{s}} \left(\mu^{i\overline{s}} + K_E^{i\overline{s}} + \frac{\mathbf{u}^{i\overline{s}} \cdot \mathbf{u}^{i\overline{s}}}{2} \right) \mathbf{u}^{i\overline{s}} \right. \\ & \left. - \left\langle \left(\mathbf{t}_s - \frac{\boldsymbol{\sigma}_s \cdot \mathbf{C}_s}{j_s} \mathbf{I} \right) \cdot (\mathbf{v}_s - \mathbf{v}^{\overline{s}}) \right\rangle_{\Omega_s, \Omega} \right] = 0. \end{aligned} \quad (16)$$

553

554 Based on this approximation, the first 11 lines in Eq. (11) may be dropped.

555 SEI Approximation 2 (Entity Velocity Deviations).

556 Expressions involving the average over Ω_α , the domain of entity α , of a prod-
557 uct of a microscale quantity with the deviation velocity $\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}}$ are assumed
558 to be negligible.

559 As a consequence of this approximation, we have

$$\left\langle \left(\mathbf{t}_s - \frac{\boldsymbol{\sigma}_s : \mathbf{C}_s}{j_s} \mathbf{l} \right) \cdot (\mathbf{v}_s - \mathbf{v}^{\bar{s}}) \right\rangle_{\Omega_s, \Omega} = 0, \quad (17)$$

$$\left\langle \left(\nabla \cdot \mathbf{t}_s - \nabla \boldsymbol{\sigma}_s : \frac{\mathbf{C}_s}{j_s} \right) \cdot (\mathbf{v}_s - \mathbf{v}^{\bar{s}}) \right\rangle_{\Omega_s, \Omega} = 0, \quad (18)$$

$$\langle \eta_\alpha (\mathbf{v}_\alpha - \mathbf{v}^{\bar{\alpha}}) \cdot (\mathbf{l} - \mathbf{l}'_\alpha) \rangle_{\Omega_\alpha, \Omega} = 0 \quad \text{for } \alpha \in \mathcal{J}_I, \quad (19)$$

$$\langle (\mathbf{l} - \mathbf{l}'_\alpha) \cdot (\mathbf{v}_\alpha - \mathbf{v}^{\bar{\alpha}}) \gamma_\alpha \rangle_{\Omega_\alpha, \Omega} = 0 \quad \text{for } \alpha \in \mathcal{J}_I, \quad (20)$$

$$\langle \rho_\alpha \omega_{i\alpha} (\mathbf{v}_\alpha - \mathbf{v}^{\bar{\alpha}}) \cdot (\mathbf{l} - \mathbf{l}'_\alpha) \rangle_{\Omega_\alpha, \Omega} = 0 \quad \text{for } \alpha \in \mathcal{J}_I, \ i \in \mathcal{J}_s, \quad (21)$$

$$\langle \eta_{wns} (\mathbf{v}_{wns} - \mathbf{v}^{\overline{wns}}) \cdot (\mathbf{l} - \mathbf{l}''_{wns}) \rangle_{\Omega_{wns}, \Omega} = 0, \quad (22)$$

$$\langle (\mathbf{l} - \mathbf{l}''_{wns}) \cdot (\mathbf{v}_{wns} - \mathbf{v}^{\overline{wns}}) \gamma_{wns} \rangle_{\Omega_{wns}, \Omega} = 0, \quad (23)$$

560 and

$$\langle \rho_{wns} \omega_{iwns} (\mathbf{v}_{wns} - \mathbf{v}^{\overline{wns}}) \cdot (\mathbf{l} - \mathbf{l}''_{wns}) \rangle_{\Omega_{wns}, \Omega} = 0 \quad \text{for } i \in \mathcal{J}_s. \quad (24)$$

561 SEI Approximation 2 allows the elimination of lines 17 and 67–75 from
562 Eq. (11).

563 A concentrated solid stress $\mathbf{t}_s^*$ acts at the common curve on a smooth solid
564 surface. We assume that the equilibrium condition $\mathbf{n}_s \cdot \mathbf{t}_s^* \cdot \mathbf{l}'_{ss} = 0$ for $\mathbf{x} \in \Omega_{wns}$
565 holds even when the system is away from equilibrium. Taking into account
566 $\mathbf{l}'_{ss} = \mathbf{l} - \mathbf{n}_s \mathbf{n}_s$, we formulate the following approximation [18, Chap. 11.4.2].

567

568 SEI Approximation 3 (Concentrated Stress Constraint).

569 *The concentrated stress expressing interaction between the solid phase and*
570 *the common curve is given by*

$$\mathbf{n}_s \cdot \mathbf{t}_s^* = \mathbf{n}_s \cdot \mathbf{t}_s^* \cdot \mathbf{n}_s \mathbf{n}_s \quad \text{for } \mathbf{x} \in \Omega_{wns}. \quad (25)$$

571

572 This approximation is applied to rewrite the corresponding terms in lines 56
 573 and 64 of the CEI in Eq. (11).

574 **SEI Approximation 4 (Solid-Common Curve Velocities).**

575 *No direct mass exchange between the solid phase and the common curve is*
 576 *modeled by the condition*

$$\mathbf{n}_s \cdot (\mathbf{v}_s - \mathbf{v}_{wns}) = 0 \quad \text{for } \mathbf{x} \in \Omega_{wns}, \quad (26)$$

577 *and the average over the common curve of the concentrated stress multiplied*
 578 *by the unit normal $\mathbf{n}_s$ dotted with the difference between the solid velocity*
 579 *averaged over the common curve and the microscale solid velocity is negligible*

$$\langle \mathbf{n}_s \cdot \mathbf{t}_s^* \cdot \mathbf{n}_s \mathbf{n}_s \cdot (\mathbf{v}_s^{\overline{wns}} - \mathbf{v}_s) \rangle_{\Omega_{wns}, \Omega} = 0. \quad (27)$$

580

581 As a consequence of SEI Approximations 3 and 4, the last term in line 38
 582 and terms in lines 39 and 65 of Eq. (11) are eliminated.

583 **SEI Approximation 5 (Solid-Phase Surface Stress).**

584 *The stress at the surface of the solid phase given by $\mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{l}'_{\alpha s}$ for $\mathbf{x} \in \Omega_{\alpha s}$,*
 585 *$\alpha \in \mathcal{I}_f$ is small, as is the difference between the solid-surface velocity and*
 586 *the average solid-phase velocity, such that the average of their product can be*
 587 *neglected*

$$\langle \mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{l}'_{\alpha s} \cdot (\mathbf{v}_s - \mathbf{v}^{\bar{s}}) \rangle_{\Omega_{\alpha s}, \Omega} = 0 \quad \text{for } \alpha \in \mathcal{I}_f. \quad (28)$$

588

589 As a consequence of this approximation, line 66 of Eq. (11) can be eliminated.

590 **SEI Approximation 6 (Solid Stress and Mass Exchange).**

591 *The average of the deviation of the solid surface stress from its average in*
 592 *the solid phase multiplied by the mass exchange rate is negligible*

$$\left\langle \left(\frac{\boldsymbol{\sigma}_s : \mathbf{C}_s}{\rho_s j_s} - \frac{\mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s}{\rho_s} - \frac{\boldsymbol{\sigma}^{\bar{s}} : \mathbf{C}^s}{3\rho^s j^s} \right) \rho_s (\mathbf{v}_s - \mathbf{v}_\kappa) \cdot \mathbf{n}_s \right\rangle_{\Omega_\kappa, \Omega} = 0 \quad \text{for } \kappa \in \mathcal{I}_{cs}. \quad (29)$$

593

594 This approximation is reasonable for the solid phase that is slightly compress-
 595 ible and systems that undergo minor changes in solid-phase composition and
 596 exact when there is no mass exchange occurring at the solid surface. SEI
 597 Approximation 6 allows for the elimination line 26 from Eq. (11).

598 The next three approximations deal with the balance of forces at the
 599 fluid-fluid interface, at the fluid-solid interface, and at the common curve.
 600 We state the final expressions here and refer the reader to [18, Chap. 11.4.3]
 601 for the details.

602 **SEI Approximation 7 (wn Interface Conditions).**

603 *The balance of forces at the fluid-fluid interface can be approximated as fol-*
 604 *lows*

$$\begin{aligned} & \left\langle \left[p_w \mathbf{n}_w + p_n \mathbf{n}_n + \gamma_{wn} (\nabla' \cdot \mathbf{l}'_{wn}) + \sum_{i \in \mathcal{I}_s} \rho_{wn} \omega_{iwn} \mathbf{g}_{iwn} \cdot (\mathbf{l} - \mathbf{l}'_{wn}) \right] \right. \\ & \quad \left. \cdot (\mathbf{v}_{wn} - \mathbf{v}^{\bar{s}}) \right\rangle_{\Omega_{wn}, \Omega} \\ & \approx \left[\frac{D^{\bar{s}} \epsilon^{\bar{w}}}{Dt} - \chi_s^{\bar{w}\bar{s}} \frac{D^{\bar{s}} \epsilon}{Dt} - \frac{\gamma^{wn} \hat{k}_1^{wn} (\epsilon^{\bar{w}\bar{n}} - \epsilon_{\text{eq}}^{\bar{w}\bar{n}})}{p_w^{wn} - p_n^{wn} + \sum_{i \in \mathcal{I}_s} \rho^{wn} \omega^{i\bar{w}\bar{n}} (\mathbf{g}_{iwn} \cdot \mathbf{n}_w)^{\bar{w}\bar{n}}} \right] \end{aligned}$$

$$\times \left(p_w^{wn} - p_n^{wn} + \sum_{i \in \mathcal{I}_s} \rho^{wn} \omega^{i\overline{wn}} (\mathbf{g}_{iwn} \cdot \mathbf{n}_w)^{\overline{wn}} - \gamma^{wn} J_w^{wn} \right), \quad (30)$$

605 where $\chi_s^{\overline{ws}} = \epsilon^{\overline{ws}} / (\epsilon^{\overline{ws}} + \epsilon^{\overline{ns}})$ is the fraction of the solid surface in contact
 606 with phase w , ϵ is the porosity, $\epsilon_{\text{eq}}^{\overline{wn}}$ is the wn interfacial area at equilibrium,
 607 J_w^{wn} is the surface curvature, $\nabla' \cdot \mathbf{n}_w$, averaged over interface wn , $\hat{k}_1^{wn}$ is a
 608 positive parameter denoting the rate of relaxation of interfacial area, and
 609 $(\mathbf{g}_{iwn} \cdot \mathbf{n}_w)^{\overline{wn}} = \langle \mathbf{g}_{iwn} \cdot \mathbf{n}_w \rangle_{\Omega_{wn}, \Omega_{wn}}$.

610 **SEI Approximation 8 (ws and ns Interface Conditions).**

611 The balance of forces at fluid-solid interfaces can be approximated as

$$\begin{aligned} \left\langle \left[p_\alpha \mathbf{n}_\alpha - \mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s \mathbf{n}_s + \gamma_{\alpha s} (\nabla' \cdot \mathbf{l}'_{\alpha s}) + \sum_{i \in \mathcal{I}_s} \rho_{\alpha s} \omega_{i\alpha s} \mathbf{g}_{i\alpha s} \cdot (\mathbf{l} - \mathbf{l}'_{\alpha s}) \right] \right. \\ \left. \cdot (\mathbf{v}_{\alpha s} - \mathbf{v}^{\overline{s}}) \right\rangle_{\Omega_{\alpha s}, \Omega} \approx \left[p_\alpha^{\alpha s} + (\mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s)_s^{\alpha s} - \sum_{i \in \mathcal{I}_s} \rho^{\alpha s} \omega^{i\overline{\alpha s}} (\mathbf{g}_{i\alpha s} \cdot \mathbf{n}_s)^{\overline{\alpha s}} \right. \\ \left. + \gamma^{\alpha s} J_s^{\alpha s} \right] \chi_s^{\overline{\alpha s}} \frac{D^{\overline{s}} \epsilon}{Dt} \quad \text{for } \alpha \in \mathcal{I}_f. \end{aligned} \quad (31)$$

612

613 **SEI Approximation 9 (wns Common Curve Conditions).**

614 The balance of forces at the common curve can be approximated as

$$\begin{aligned} \left\langle \left[\gamma_{wn} \mathbf{n}_{wn} + \gamma_{ws} \mathbf{n}_{ws} + \gamma_{ns} \mathbf{n}_{ns} + \gamma_{wns} (\nabla'' \cdot \mathbf{l}''_{wns}) \right. \right. \\ \left. \left. - \sum_{i \in \mathcal{I}_s} \rho_{wns} \omega_{iwns} \mathbf{g}_{iwns} \cdot (\mathbf{l} - \mathbf{l}''_{wns}) + \mathbf{n}_s \cdot \mathbf{t}_s^* \cdot \mathbf{n}_s \mathbf{n}_s \right] \cdot (\mathbf{v}_{wns} - \mathbf{v}^{\overline{s}}) \right\rangle_{\Omega_{wns}, \Omega} \\ \approx \left[\gamma_{wn}^{wns} \cos \varphi^{\overline{ws}, \overline{wn}} + \gamma_{ws}^{wns} - \gamma_{ns}^{wns} + \gamma_{wns}^{wns} \kappa_G^{\overline{wns}} \right] \end{aligned}$$

$$\begin{aligned}
& - \sum_{i \in \mathcal{I}_s} \rho^{wns} \omega^{i\overline{wns}} (\mathbf{g}_{iwns} \cdot \mathbf{n}_{ws})^{\overline{wns}} \left] \left(\epsilon^{\overline{ws}} + \epsilon^{\overline{ns}} \right) \frac{D^{\overline{s}} \chi_s}{Dt} \right. \\
& + \left[\gamma_{wn}^{wns} \sin \varphi^{\overline{ws}, \overline{wn}} - \gamma^{wns} \kappa_N^{\overline{wns}} - (\mathbf{n}_s \cdot \mathbf{t}_s^* \cdot \mathbf{n}_s)_s^{wns} \right. \\
& \left. + \sum_{i \in \mathcal{I}_s} \rho^{wns} \omega^{i\overline{wns}} (\mathbf{g}_{iwns} \cdot \mathbf{n}_s)^{\overline{wns}} \right] \left(\frac{\epsilon^{\overline{wns}}}{\epsilon^{\overline{ws}} + \epsilon^{\overline{ns}}} \right) \frac{D^{\overline{s}} \epsilon}{Dt}, \tag{32}
\end{aligned}$$

615 where $\kappa_G^{\overline{wns}} = \langle \mathbf{l}_{wns} \cdot \nabla'' \mathbf{l}_{wns} \cdot \mathbf{n}_{ws} \rangle_{\Omega_{wns}, \Omega}$ and $\kappa_N^{\overline{wns}} = \langle \mathbf{l}_{wgs} \cdot \nabla'' \mathbf{l}_{wgs} \cdot \mathbf{n}_s \rangle_{\Omega_{wns}, \Omega}$
 616 are the macroscale geodesic and normal curvatures, respectively, and $\varphi^{\overline{ws}, \overline{wn}}$
 617 is the macroscale measure of the contact angle between ws and wn interfaces.

618

619 SEI Approximations 7–9 can be applied to lines 57–64 of Eq. (11).

620 Additional simplifications of the CEI can be observed to be in the form of
 621 averages of microscale quantities that involve dyadic products of unit tensors.
 622 These dyadic products are called orientation tensors, because they relate
 623 to the orientation of the entity. These product terms are not accessible
 624 without detailed microscale knowledge of the system, but approximations
 625 are possible.

626 SEI Approximation 10 (Geometric Orientation Products).

627 *Averages of products involving the microscale geometric orientation tensors,*

$$\mathbf{G}_\alpha = \mathbf{I} - \mathbf{l}'_\alpha \quad \text{for } \alpha \in \mathcal{I}_I, \mathbf{x} \in \Omega_\alpha, \tag{33}$$

$$\mathbf{G}_{wns} = \mathbf{I} - \mathbf{l}''_{wns}, \mathbf{x} \in \Omega_{wns}, \tag{34}$$

628 and a microscale property f_α of entity α can be approximated as the product
 629 of the macroscale orientation tensor and averaged property f^α such that

$$\langle \mathbf{G}_\alpha f_\alpha \rangle_{\Omega_\alpha, \Omega} = \epsilon^{\overline{\alpha}} \mathbf{G}^\alpha f^\alpha \quad \text{for } \alpha \in \mathcal{I}_I, \tag{35}$$

$$\langle \mathbf{G}_{wns} f_{wns} \rangle_{\Omega_{wns}, \Omega} = \epsilon^{\overline{wns}} \mathbf{G}^{wns} f^{wns}. \quad (36)$$

630

631 This approximation can be applied to lines 13, 14, 44, 48–50, 54 and 55 in
 632 Eq. (11) for f corresponding to ρ , γ , and η .

633 **SEI Approximation 11 (Pressure/Tension Products).**

634 *The product of a microscale pressure or surface tension of entity α with*
 635 *$\mathbf{n}_\alpha \cdot (\mathbf{v}_\kappa - \mathbf{v}^{\bar{s}})$ where $\kappa \in \mathcal{I}_{\alpha}^-$ that is averaged over entity κ may be written as*
 636 *a product of the averages of these factors*

$$\langle \mathbf{n}_\alpha \cdot (\mathbf{v}_{wn} - \mathbf{v}^{\bar{s}}) p_\alpha \rangle_{\Omega_{wn}, \Omega} = \left(\frac{D^{\bar{s}} \epsilon^{\bar{\alpha}}}{Dt} - \chi_s^{\bar{\alpha}\bar{s}} \frac{D^{\bar{s}} \epsilon}{Dt} \right) p_\alpha^{wn} \quad \text{for } \alpha \in \mathcal{I}_f, \quad (37)$$

$$\langle \mathbf{n}_\alpha \cdot (\mathbf{v}_{\alpha s} - \mathbf{v}^{\bar{s}}) p_\alpha \rangle_{\Omega_{\alpha s}, \Omega} = \chi_s^{\bar{\alpha}\bar{s}} \frac{D^{\bar{s}} \epsilon}{Dt} p_\alpha^{\alpha s} \quad \text{for } \alpha \in \mathcal{I}_f, \quad (38)$$

$$\langle \mathbf{n}_s \cdot (\mathbf{v}_{\alpha s} - \mathbf{v}^{\bar{s}}) \mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s \rangle_{\Omega_{\alpha s}, \Omega} = -\chi_s^{\bar{\alpha}\bar{s}} \frac{D^{\bar{s}} \epsilon}{Dt} (\mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s)_s^{\alpha s} \quad \text{for } \alpha \in \mathcal{I}_f, \quad (39)$$

$$\begin{aligned} \langle \mathbf{n}_{wn} \cdot (\mathbf{v}_{wns} - \mathbf{v}^{\bar{s}}) \gamma_{wn} \rangle_{\Omega_{wns}, \Omega} = & \left[\left(\epsilon^{\bar{ws}} + \epsilon^{\bar{ns}} \right) \frac{D^{\bar{s}} \chi_s^{\bar{ws}}}{Dt} \cos \varphi^{\bar{ws}, \bar{wn}} \right. \\ & \left. + \frac{\epsilon^{\bar{wns}}}{\epsilon^{\bar{ws}} + \epsilon^{\bar{ns}}} \frac{D^{\bar{s}} \epsilon}{Dt} \sin \varphi^{\bar{ws}, \bar{wn}} \right] \gamma_{wn}^{wns}, \end{aligned} \quad (40)$$

$$\langle \mathbf{n}_{\alpha s} \cdot (\mathbf{v}_{wns} - \mathbf{v}^{\bar{s}}) \gamma_{\alpha s} \rangle_{\Omega_{wns}, \Omega} = \left(\epsilon^{\bar{ws}} + \epsilon^{\bar{ns}} \right) \frac{D^{\bar{s}} \chi_s^{\bar{\alpha}\bar{s}}}{Dt} \gamma_{\alpha s}^{wns} \quad \text{for } \alpha \in \mathcal{I}_f. \quad (41)$$

637

638 This approximation allows for evaluation of averages that appear in lines 31,
 639 34, and 37 of the CEI in Eq. (11).

640 SEI Approximations 1–11 are not unique. If better approximations, or
 641 exact expressions, are discovered in the future, then they need only be applied
 642 to the CEI as a starting point for developing an improved SEI formulation.

643 4.3. General SEI

644 The general SEI is an approximation to the CEI where all the terms
 645 are written as products of macroscale forces and fluxes. It is the starting
 646 point for formulation of closure relations and derivation of solvable closed
 647 macroscale models. The form of the general SEI depends on the set of SEI
 648 approximations employed. Application of SEI Approximations 1–11 to the
 649 CEI given in Eq. (11) yields the following SEI

$$\begin{aligned}
 & \sum_{\alpha \in \mathcal{J}_f} \frac{1}{\theta^{\bar{\alpha}}} \left(\epsilon^{\bar{\alpha}} \mathbf{t}^{\bar{\alpha}} + \epsilon^{\bar{\alpha}} p^{\alpha} \mathbf{I} \right) : \mathbf{d}^{\bar{\alpha}} + \frac{1}{\theta^{\bar{s}}} \left(\epsilon^{\bar{s}} \mathbf{t}^{\bar{s}} - \epsilon^{\bar{s}} \mathbf{t}^s \right) : \mathbf{d}^{\bar{s}} & 1 \\
 & + \sum_{\alpha \in \mathcal{J}_I} \frac{1}{\theta^{\bar{\alpha}}} \left[\epsilon^{\bar{\alpha}} \mathbf{t}^{\bar{\alpha}} - \epsilon^{\bar{\alpha}} \gamma^{\alpha} (\mathbf{I} - \mathbf{G}^{\alpha}) \right] : \mathbf{d}^{\bar{\alpha}} & 2 \\
 & + \frac{1}{\theta^{\bar{w}\bar{n}\bar{s}}} \left[\epsilon^{\bar{w}\bar{n}\bar{s}} \mathbf{t}^{\bar{w}\bar{n}\bar{s}} + \epsilon^{\bar{w}\bar{n}\bar{s}} \gamma^{wns} (\mathbf{I} - \mathbf{G}^{wns}) \right] : \mathbf{d}^{\bar{w}\bar{n}\bar{s}} & 3 \\
 & - \sum_{\alpha \in \mathcal{J}} \left[\epsilon^{\bar{\alpha}} \mathbf{q}^{\bar{\alpha}} + \epsilon^{\bar{\alpha}} \mathbf{q}^{\bar{\alpha}} \quad \bar{\alpha} \rho^{\alpha} \omega^{i\bar{\alpha}} \left(\mu^{i\bar{\alpha}} + K_E^{i\bar{\alpha}} + \frac{\mathbf{u}^{i\bar{\alpha}} \cdot \mathbf{u}^{i\bar{\alpha}}}{2} \right) \mathbf{u}^{i\bar{\alpha}} \right] \cdot \nabla \left(\frac{1}{\theta^{\bar{\alpha}}} \right) & 4 \\
 & - \sum_{\alpha \in \mathcal{J}} \sum_{i \in \mathcal{J}_s \setminus N} \frac{1}{\theta^{\bar{\alpha}}} \epsilon^{\bar{\alpha}} \rho^{\alpha} \omega^{i\bar{\alpha}} \mathbf{u}^{i\bar{\alpha}} \cdot \nabla \left[\mu^{i\bar{\alpha}} + K_E^{i\bar{\alpha}} + \frac{\mathbf{u}^{i\bar{\alpha}} \cdot \mathbf{u}^{i\bar{\alpha}}}{2} + \psi^{i\bar{\alpha}} \right. & 5 \\
 & \quad \left. - \left(\mu^{\bar{N}\alpha} + K_E^{\bar{N}\alpha} + \frac{\mathbf{u}^{\bar{N}\alpha} \cdot \mathbf{u}^{\bar{N}\alpha}}{2} + \psi^{\bar{N}\alpha} \right) \right] & 6 \\
 & - \sum_{\alpha \in \mathcal{J}} \sum_{i \in \mathcal{J}_s} \frac{1}{\theta^{\bar{\alpha}}} \left(\mu^{i\bar{\alpha}} + K_E^{i\bar{\alpha}} + \frac{\mathbf{u}^{i\bar{\alpha}} \cdot \mathbf{u}^{i\bar{\alpha}}}{2} + \psi^{i\bar{\alpha}} \right) \epsilon^{\bar{\alpha}} r^{i\alpha} & 7 \\
 & + \sum_{\alpha \in \mathcal{J}} \sum_{i \in \mathcal{J}_s} \frac{1}{\theta^{\bar{\alpha}}} \langle r_{i\alpha} \psi_{i\alpha} \rangle_{\Omega_{\alpha}, \Omega} & 8 \\
 & + \sum_{\alpha \in \mathcal{J}_f} \sum_{\kappa \in \mathcal{J}_{c\alpha}} \sum_{i \in \mathcal{J}_s} M^{i\alpha \rightarrow i\kappa} \left[\frac{1}{\theta^{\bar{\alpha}}} \left(\mu^{i\bar{\alpha}} + K_E^{i\bar{\alpha}} + \frac{\mathbf{u}^{i\bar{\alpha}} \cdot \mathbf{u}^{i\bar{\alpha}}}{2} + \psi^{i\bar{\alpha}} \right) \right. & 9 \\
 & \quad \left. - \frac{1}{\theta^{\bar{\kappa}}} \left(\mu^{i\bar{\kappa}} + K_E^{i\bar{\kappa}} + \frac{\mathbf{u}^{i\bar{\kappa}} \cdot \mathbf{u}^{i\bar{\kappa}}}{2} + \psi^{i\bar{\kappa}} \right) \right] & 10
 \end{aligned}$$

$$\begin{aligned}
& + \sum_{\kappa \in \mathcal{J}_{cs}} \sum_{i \in \mathcal{J}_s} M \left[\frac{1}{\theta^{\bar{s}}} \left(\mu^{\bar{i}s} + K_E^{\bar{i}s} + \frac{\mathbf{u}^{\bar{i}s} \cdot \mathbf{u}^{\bar{i}s}}{2} + \psi^{\bar{i}s} + \frac{\boldsymbol{\sigma}^{\bar{s}} \cdot \mathbf{C}^s}{3\rho^s j^s} \right) \right. \\
& \quad \left. - \frac{1}{\theta^{\bar{\kappa}}} \left(\mu^{\bar{i}\kappa} + K_E^{\bar{i}\kappa} + \frac{\mathbf{u}^{\bar{i}\kappa} \cdot \mathbf{u}^{\bar{i}\kappa}}{2} + \psi^{\bar{i}\kappa} \right) \right] \tag{11} \\
& + \sum_{\alpha \in \mathcal{J}_I} \sum_{i \in \mathcal{J}_s} M \left[\frac{1}{\theta^{\bar{\alpha}}} \left(\mu^{\bar{i}\alpha} + K_E^{\bar{i}\alpha} + \frac{\mathbf{u}^{\bar{i}\alpha} \cdot \mathbf{u}^{\bar{i}\alpha}}{2} + \psi^{\bar{i}\alpha} \right) \right. \\
& \quad \left. - \frac{1}{\theta^{\bar{wns}}} \left(\mu^{\bar{iwns}} + K_E^{\bar{iwns}} + \frac{\mathbf{u}^{\bar{iwns}} \cdot \mathbf{u}^{\bar{iwns}}}{2} + \psi^{\bar{iwns}} \right) \right] \tag{12} \\
& - \sum_{\alpha \in \mathcal{J}_f} \left\{ Q_1^{\alpha \rightarrow wn} + G_0^{\alpha \rightarrow wn} + \sum_{i \in \mathcal{J}_s} \left(\bar{E}_{i\alpha}^{\bar{wn}} + K_{Ei\alpha}^{\bar{wn}} + \frac{\mathbf{u}_{i\alpha}^{\bar{wn}} \cdot \mathbf{u}_{i\alpha}^{\bar{wn}}}{2} + \psi_{i\alpha}^{\bar{wn}} \right) M \right. \\
& \quad \left. + \left[\mathbf{T}_0^{\alpha \rightarrow wn} + \sum_{i \in \mathcal{J}_s} \left(\frac{\mathbf{v}_{\alpha}^{\bar{wn}} - \mathbf{v}^{\bar{s}}}{2} + \mathbf{u}^{\bar{wn}} \right) \right] \cdot \left(\frac{\mathbf{v}_{\alpha}^{\bar{wn}} - \mathbf{v}^{\bar{s}}}{2} + \mathbf{u}^{\bar{wn}} \right) \right. \\
& \quad \left. - \left(\frac{D^{\bar{s}} \epsilon^{\bar{\alpha}}}{Dt} - \chi_s^{\bar{\alpha s}} \frac{D^{\bar{s}} \epsilon}{Dt} \right) p_{\alpha}^{wn} \right\} \left(\frac{1}{\theta^{\bar{\alpha}}} - \frac{1}{\theta^{\bar{wn}}} \right) \tag{13} \\
& - \sum_{\alpha \in \mathcal{J}_f} \left\{ Q_1^{\alpha \rightarrow \alpha s} + G_0^{\alpha \rightarrow \alpha s} + \sum_{i \in \mathcal{J}_s} \left(\bar{E}_{i\alpha}^{\bar{\alpha s}} + K_{Ei\alpha}^{\bar{\alpha s}} + \frac{\mathbf{u}_{i\alpha}^{\bar{\alpha s}} \cdot \mathbf{u}_{i\alpha}^{\bar{\alpha s}}}{2} + \psi_{i\alpha}^{\bar{\alpha s}} \right) M \right. \\
& \quad \left. + \left[\mathbf{T}_0^{\alpha \rightarrow \alpha s} + \sum_{i \in \mathcal{J}_s} \left(\frac{\mathbf{v}_{\alpha}^{\bar{\alpha s}} - \mathbf{v}^{\bar{s}}}{2} + \mathbf{u}_{i\alpha}^{\bar{\alpha s}} \right) M \right] \cdot (\mathbf{v}_{\alpha}^{\bar{\alpha s}} - \mathbf{v}^{\bar{s}}) \right. \\
& \quad \left. - \chi_s^{\bar{\alpha s}} \frac{D^{\bar{s}} \epsilon}{Dt} p_{\alpha}^{\alpha s} \right\} \left(\frac{1}{\theta^{\bar{\alpha}}} - \frac{1}{\theta^{\bar{\alpha s}}} \right) \tag{14} \\
& - \sum_{\kappa \in \mathcal{J}_{cs}} \left\{ Q_1^{s \rightarrow \kappa} + G_0^{s \rightarrow \kappa} + \sum_{i \in \mathcal{J}_s} \left(\bar{E}_{is}^{\bar{\kappa}} + K_{Eis}^{\bar{\kappa}} + \frac{\mathbf{u}_{is}^{\bar{\kappa}} \cdot \mathbf{u}_{is}^{\bar{\kappa}}}{2} + \psi_{is}^{\bar{\kappa}} \right) M \right. \\
& \quad \left. + \left[\mathbf{T}_0^{s \rightarrow \kappa} + \sum_{i \in \mathcal{J}_s} \left(\frac{\mathbf{v}_s^{\bar{\kappa}} - \mathbf{v}^{\bar{s}}}{2} + \mathbf{u}_{is}^{\bar{\kappa}} \right) M \right] \cdot (\mathbf{v}_s^{\bar{\kappa}} - \mathbf{v}^{\bar{s}}) \right. \\
& \quad \left. - \chi_s^{\bar{\kappa}} \frac{D^{\bar{s}} \epsilon}{Dt} (\mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s)^{\kappa}_s \right\} \left(\frac{1}{\theta^{\bar{s}}} - \frac{1}{\theta^{\bar{\kappa}}} \right) \tag{15}
\end{aligned}$$

$$- \left\{ \overset{wn \rightarrow wns}{Q_1} + \overset{wn \rightarrow wns}{G_0} + \sum_{i \in \mathcal{I}_s} \left(\overline{E}_{iwn}^{\overline{wns}} + K_{Eiwn}^{\overline{wns}} + \frac{\mathbf{u}_{iwn}^{\overline{wns}} \cdot \mathbf{u}_{iwn}^{\overline{wns}}}{2} + \psi_{iwn}^{\overline{wns}} \right) \overset{iwn \rightarrow iwns}{M} \right. \quad 24$$

$$+ \left[\overset{wn \rightarrow wns}{\mathbf{T}_0} + \sum_{i \in \mathcal{I}_s} \left(\frac{\mathbf{v}_{wn}^{\overline{wns}} - \mathbf{v}^{\overline{s}}}{2} + \mathbf{u}_{iwn}^{\overline{wns}} \right) \overset{iwn \rightarrow iwns}{M} \right] \cdot (\mathbf{v}_{wn}^{\overline{wns}} - \mathbf{v}^{\overline{s}}) \quad 25$$

$$+ \left[\left(\epsilon^{\overline{ws}} + \epsilon^{\overline{ns}} \right) \frac{D^{\overline{s}} \chi_s^{\overline{ws}}}{Dt} \cos \varphi^{\overline{ws}, \overline{wn}} \right. \quad 26$$

$$\left. + \frac{\epsilon^{\overline{wns}}}{\epsilon^{\overline{ws}} + \epsilon^{\overline{ns}}} \frac{D^{\overline{s}} \epsilon}{Dt} \sin \varphi^{\overline{ws}, \overline{wn}} \right] \gamma_{wn}^{wns} \left\} \left(\frac{1}{\theta^{\overline{wn}}} - \frac{1}{\theta^{\overline{wns}}} \right) \quad 27$$

$$- \sum_{\alpha \in \mathcal{I}_f} \left\{ \overset{\alpha s \rightarrow wns}{Q_1} + \overset{\alpha s \rightarrow wns}{G_0} + \sum_{i \in \mathcal{I}_s} \left(\overline{E}_{i\alpha s}^{\overline{wns}} + K_{Ei\alpha s}^{\overline{wns}} + \frac{\mathbf{u}_{i\alpha s}^{\overline{wns}} \cdot \mathbf{u}_{i\alpha s}^{\overline{wns}}}{2} + \psi_{i\alpha s}^{\overline{wns}} \right) \overset{i\alpha s \rightarrow iwns}{M} \right. \quad 28$$

$$+ \left[\overset{\alpha s \rightarrow wns}{\mathbf{T}_0} + \sum_{i \in \mathcal{I}_s} \left(\frac{\mathbf{v}_{\alpha s}^{\overline{wns}} - \mathbf{v}^{\overline{s}}}{2} + \mathbf{u}_{i\alpha s}^{\overline{wns}} \right) \overset{i\alpha s \rightarrow iwns}{M} \right] \cdot (\mathbf{v}_{\alpha s}^{\overline{wns}} - \mathbf{v}^{\overline{s}}) \quad 29$$

$$+ \left(\epsilon^{\overline{ws}} + \epsilon^{\overline{ns}} \right) \frac{D^{\overline{s}} \chi_s^{\overline{\alpha s}}}{Dt} \gamma_{\alpha s}^{wns} \left\} \left(\frac{1}{\theta^{\overline{\alpha s}}} - \frac{1}{\theta^{\overline{wns}}} \right) \quad 30$$

$$- \overset{s \rightarrow wns}{Q_1^*} \left(\frac{1}{\theta^{\overline{s}}} - \frac{1}{\theta^{\overline{wns}}} \right) \quad 31$$

$$- \sum_{\alpha \in \mathcal{I}_f} \frac{1}{\theta^{\overline{\alpha}}} \left\{ \eta^{\overline{\alpha}} \nabla \theta^{\overline{\alpha}} - \nabla \left(\epsilon^{\overline{\alpha}} p^\alpha \right) \right. \quad 32$$

$$+ \sum_{i \in \mathcal{I}_s} \epsilon^{\overline{\alpha}} \rho^\alpha \omega^{i\overline{\alpha}} \left[\nabla \left(\mu^{i\overline{\alpha}} + K_E^{i\overline{\alpha}} + \frac{\mathbf{u}^{i\overline{\alpha}} \cdot \mathbf{u}^{i\overline{\alpha}}}{2} + \psi^{i\overline{\alpha}} \right) + \mathbf{g}^{i\overline{\alpha}} \right] \quad 33$$

$$- \sum_{\kappa \in \mathcal{I}_{c\alpha}} \left[\overset{\alpha \rightarrow \kappa}{\mathbf{T}_0} - \sum_{i \in \mathcal{I}_s} \frac{(\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}})^{i\alpha \rightarrow i\kappa}}{2} \overset{i\alpha \rightarrow i\kappa}{M} \right. \quad 34$$

$$+ \sum_{i \in \mathcal{I}_s} \left(\mathbf{v}_\alpha^{\overline{\kappa}} + \mathbf{u}_{i\alpha}^{\overline{\kappa}} - \mathbf{v}^{\overline{s}} \right) \overset{i\alpha \rightarrow i\kappa}{M} \left. \right\} \cdot (\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}}) \quad 35$$

$$- \sum_{\alpha \in \mathcal{I}_I} \frac{1}{\theta^{\overline{\alpha}}} \left\{ \eta^{\overline{\alpha}} (\mathbf{I} - \mathbf{G}^\alpha) \cdot \nabla \theta^{\overline{\alpha}} + \nabla \cdot [(\mathbf{I} - \mathbf{G}^\alpha) \epsilon^{\overline{\alpha}} \gamma^\alpha] \right. \quad 36$$

$$\begin{aligned}
& + \sum_{i \in \mathcal{I}_s} \epsilon^{\bar{\alpha}} \rho^{\alpha} \omega^{i\bar{\alpha}} (\mathbf{I} - \mathbf{G}^{\alpha}) \cdot \nabla \left(\mu^{i\bar{\alpha}} + K_E^{\bar{\alpha}} + \frac{\mathbf{u}^{i\bar{\alpha}} \cdot \mathbf{u}^{i\bar{\alpha}}}{2} + \psi^{i\bar{\alpha}} \right) + \sum_{i \in \mathcal{I}_s} \epsilon^{\bar{\alpha}} \rho^{\alpha} \omega^{i\bar{\alpha}} \mathbf{g}^{i\bar{\alpha}} \quad 37 \\
& + \sum_{\kappa \in \mathcal{I}_{c\alpha}^+} \left[\mathbf{T}_0^{\kappa \rightarrow \alpha} - \sum_{i \in \mathcal{I}_s} \frac{(\mathbf{v}^{\bar{\alpha}} - \mathbf{v}^{\bar{s}})}{2} \frac{i\kappa \rightarrow i\alpha}{M} + \sum_{i \in \mathcal{I}_s} \left(\mathbf{v}_{\kappa}^{\bar{\alpha}} + \mathbf{u}_{i\kappa}^{\bar{\alpha}} - \mathbf{v}^{\bar{s}} \right) \frac{i\kappa \rightarrow i\alpha}{M} \right] \quad 38 \\
& - \left[\mathbf{T}_0^{\alpha \rightarrow wns} - \sum_{i \in \mathcal{I}_s} \frac{(\mathbf{v}^{\bar{\alpha}} - \mathbf{v}^{\bar{s}})}{2} \frac{i\alpha \rightarrow iwns}{M} \right. \quad 39 \\
& \quad \left. + \sum_{i \in \mathcal{I}_s} \left(\mathbf{v}_{\alpha}^{\bar{wns}} + \mathbf{u}_{i\alpha}^{\bar{wns}} - \mathbf{v}^{\bar{s}} \right) \frac{i\alpha \rightarrow iwns}{M} \right] \cdot (\mathbf{v}^{\bar{\alpha}} - \mathbf{v}^{\bar{s}}) \quad 40 \\
& - \frac{1}{\theta^{\bar{wns}}} \left\{ \eta^{\bar{wns}} (\mathbf{I} - \mathbf{G}^{wns}) \cdot \nabla \theta^{\bar{wns}} - \nabla \cdot [(\mathbf{I} - \mathbf{G}^{wns}) \epsilon^{\bar{wns}} \gamma^{wns}] \right. \quad 41 \\
& \quad + \sum_{i \in \mathcal{I}_s} \epsilon^{\bar{wns}} \rho^{wns} \omega^{i\bar{wns}} (\mathbf{I} - \mathbf{G}^{wns}) \cdot \nabla \left(\mu^{i\bar{wns}} + K_E^{\bar{wns}} + \frac{\mathbf{u}^{i\bar{wns}} \cdot \mathbf{u}^{i\bar{wns}}}{2} + \psi^{i\bar{wns}} \right) \quad 42 \\
& \quad + \sum_{i \in \mathcal{I}_s} \epsilon^{\bar{wns}} \rho^{wns} \omega^{i\bar{wns}} \mathbf{g}^{i\bar{wns}} \quad 43 \\
& \quad + \sum_{\kappa \in \mathcal{I}_{cwns}^+} \left[\mathbf{T}_0^{\kappa \rightarrow wns} - \sum_{i \in \mathcal{I}_s} \frac{(\mathbf{v}^{\bar{wns}} - \mathbf{v}^{\bar{s}})}{2} \frac{i\kappa \rightarrow iwns}{M} \right. \quad 44 \\
& \quad \quad \left. + \sum_{i \in \mathcal{I}_s} \left(\mathbf{v}_{\kappa}^{\bar{wns}} + \mathbf{u}_{i\kappa}^{\bar{wns}} - \mathbf{v}^{\bar{s}} \right) \frac{i\kappa \rightarrow iwns}{M} \right] \quad 45 \\
& \quad \left. - \langle \mathbf{n}_s \cdot \mathbf{t}_s^* \cdot \mathbf{n}_s \mathbf{n}_s \rangle_{\Omega_{wns}, \Omega} \right\} \cdot (\mathbf{v}^{\bar{wns}} - \mathbf{v}^{\bar{s}}) \quad 46 \\
& + \frac{1}{\theta^{\bar{wn}}} \left[\frac{D^{\bar{s}} \epsilon^{\bar{w}}}{Dt} - \chi_s^{\bar{ws}} \frac{D^{\bar{s}} \epsilon}{Dt} - \frac{\gamma^{wn} \hat{k}_1^{wn} (\epsilon^{\bar{wn}} - \epsilon_{eq}^{\bar{wn}})}{p_w^{wn} - p_n^{wn} + \sum_{i \in \mathcal{I}_s} \rho^{wn} \omega^{i\bar{wn}} (\mathbf{g}_{iwn} \cdot \mathbf{n}_w)^{\bar{wn}}} \right] \quad 47 \\
& \quad \times \left(p_w^{wn} - p_n^{wn} + \sum_{i \in \mathcal{I}_s} \rho^{wn} \omega^{i\bar{wn}} (\mathbf{g}_{iwn} \cdot \mathbf{n}_w)^{\bar{wn}} - \gamma^{wn} J_w^{wn} \right) \quad 48 \\
& + \frac{1}{\theta^{\bar{ws}}} \chi_s^{\bar{ws}} \frac{D^{\bar{s}} \epsilon}{Dt} \left[p_w^{ws} + (\mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s)_s^{ws} - \sum_{i \in \mathcal{I}_s} \rho^{ws} \omega^{i\bar{ws}} (\mathbf{g}_{iws} \cdot \mathbf{n}_s)^{\bar{ws}} + \gamma^{ws} J_s^{ws} \right] \quad 49
\end{aligned}$$

$$+ \frac{1}{\theta^{\overline{\overline{ns}}}} \chi_s^{\overline{\overline{ns}}} \frac{D^{\overline{s}} \epsilon}{Dt} \left[p_n^{ns} + (\mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s)_s^{ns} - \sum_{i \in \mathcal{I}_s} \rho^{ns} \omega^{i\overline{\overline{ns}}} (\mathbf{g}_{ins} \cdot \mathbf{n}_s)^{\overline{\overline{ns}}} + \gamma^{ns} J_s^{ns} \right] \quad 50$$

$$- \frac{1}{\theta^{\overline{\overline{wns}}}} \left(\epsilon^{\overline{\overline{ws}}} + \epsilon^{\overline{\overline{ns}}} \right) \frac{D^{\overline{s}} \chi_s^{\overline{\overline{ws}}}}{Dt} \left[\gamma_{wn}^{wns} \cos \varphi^{\overline{\overline{ws,wn}}} + \gamma_{ws}^{wns} - \gamma_{ns}^{wns} \right] \quad 51$$

$$+ \gamma^{wns} \kappa_G^{\overline{\overline{wns}}} - \sum_{i \in \mathcal{I}_s} \rho^{wns} \omega^{i\overline{\overline{wns}}} (\mathbf{g}_{iwns} \cdot \mathbf{n}_{ws})^{\overline{\overline{wns}}} \right] \quad 52$$

$$- \frac{1}{\theta^{\overline{\overline{wns}}}} \left(\frac{\epsilon^{\overline{\overline{wns}}}}{\epsilon^{\overline{\overline{ws}}} + \epsilon^{\overline{\overline{ns}}}} \right) \frac{D^{\overline{s}} \epsilon}{Dt} \left[\gamma_{wn}^{wns} \sin \varphi^{\overline{\overline{ws,wn}}} - \gamma^{wns} \kappa_N^{\overline{\overline{wns}}} \right] \quad 53$$

$$- \langle \mathbf{n}_s \cdot \mathbf{t}_s^* \cdot \mathbf{n}_s \rangle_{\Omega_{wns}, \Omega_{wns}} + \sum_{i \in \mathcal{I}_s} \rho^{wns} \omega^{i\overline{\overline{wns}}} (\mathbf{g}_{iwns} \cdot \mathbf{n}_s)^{\overline{\overline{wns}}} \right] \quad 54$$

$$= \sum_{\alpha \in \mathcal{I}} \Lambda^{\overline{\overline{\alpha}}} \geq 0. \quad (42)$$

650 The SEI given in Eq. (42) is a general SEI that can be exploited to derive
 651 closure relationships for a wide range of models that are in agreement with
 652 the primary restrictions and SEI approximations imposed. In particular,
 653 this SEI allows the development of closed solvable models for two-fluid-phase
 654 flow and species transport in non-isothermal reactive porous medium systems
 655 when different entities may have different temperatures at the macroscale.
 656 For modeling more restrictive applications, the generality of the system can
 657 be reduced by introducing secondary restrictions. These restrictions further
 658 simplify the SEI, and lead to an easier formulation of closure relations.

659 The general SEI given by Eq. (42) is derived using an approach that is in
 660 principle similar to the approach developed and used for simpler systems such
 661 as a compositional single-fluid-phase porous medium system [18, Chap. 10]
 662 and a non-compositional two-fluid-phase system [18, Chap. 11]. While the
 663 simpler cases are limiting cases of the system in this work, the new results can
 664 be reduced to the simpler cases under appropriate simplifying conditions. We

note that some improvements on the previously derived forms have also been made, for example to the exchange terms and velocity fluctuation terms.

5. Restricted Applications

Secondary restrictions limit physical processes that will be modeled. They specify the number of species, chemical reactivity of the system, energy transfer, etc. Application of these restrictions reduces the SEI to a system of interest, eliminates certain terms in the conservation equations, and results in a simplified closed model formulation. The objective of this section is to provide two specific SEIs for compositional two-fluid-phase porous medium systems specified by the set of secondary restrictions under local thermal equilibrium at the macroscale and under isothermal conditions.

5.1. Secondary Restrictions

To illustrate how the general SEI given by Eq. (42) can be simplified, we present a set of secondary restrictions that follow.

Secondary Restriction 1 (Body Force Potential).

The macroscale body force vector for a species in an entity, $\mathbf{g}^{i\bar{\alpha}}$, and the average of the body force potential, $\psi^{i\bar{\alpha}}$, are considered to be independent of chemical species, $\mathbf{g}^{i\bar{\alpha}} = \mathbf{g}^{\bar{\alpha}}$, $\psi^{i\bar{\alpha}} = \psi^{\bar{\alpha}}$ for $i \in \mathcal{I}_s$, $\alpha \in \mathcal{I}$.

Secondary Restriction 2 (Deviation Velocities).

Deviation and dispersion velocities are restricted to be small enough so that their products and magnitude squared may be neglected.

686 As a consequence of this restriction, the kinetic energy due to velocity fluc-
 687 tuations, the inner product of the dispersion velocity with itself, and the
 688 products of mass exchange terms with the dispersion velocity may be elimi-
 689 nated. Secondary Restriction 2 is reasonable for slow flows.

690 **Secondary Restriction 3 (Massless Interfaces and Common Curve).**

691 *Interfaces and the common curve are restricted to be massless such that*
 692 *$\rho^\alpha = 0$ for $\alpha \in \mathcal{I}_I$, and $\rho^{wns} = 0$.*

693 According to this restriction, no mass exists or accumulates in the interfaces
 694 and common curve, and any mass transferred from one phase to an interface
 695 is directly transferred into the adjacent phase.

696 **Secondary Restriction 4 (Non-reactive System).**

697 *The system of concern is constrained such that no chemical reactions develop*
 698 *within entities.*

699 **Secondary Restriction 5 (Energy due to Mechanical Processes).**

700 *The non-advective energy flux associated with mechanical processes in the*
 701 *system is restricted to be negligibly small so that $\mathbf{q}_{\mathbf{g}_0}^{\bar{\alpha}} = 0$ for $\alpha \in \mathcal{I}$.*

702 **Secondary Restriction 6 (Binary System).**

703 *The system is restricted such that each fluid phase contains two chemical*
 704 *species denoted as A and B .*

705 **Secondary Restriction 7 (Solid Properties).**

706 *The deformation, movement, and composition changes of the solid are negli-*
 707 *gible.*

708 This restriction indicates that the deformation and movement of the solid
 709 phase can be neglected in the analysis, the solid is composed of single chem-
 710 ical species, and mass transfer does not occur between solid phase and other
 711 system entities. Such a case eliminates the need to model any of the solid
 712 properties.

713 **Secondary Restriction 8 (Homogeneous System).**

714 *The system is considered to be homogeneous at the macroscale so that the*
 715 *subscale deviation terms in the macroscale Gibbs–Duhem equation can be*
 716 *neglected resulting in*

$$\eta^{\bar{\alpha}} d\theta^{\bar{\alpha}} - \epsilon^{\bar{\alpha}} df^{\alpha} + \sum_{i \in \mathcal{I}_s} \epsilon^{\bar{\alpha}} \rho^{\alpha} \omega^{i\bar{\alpha}} d\mu^{i\bar{\alpha}} = 0, \quad (43)$$

717 *where $f^{\alpha} = p^{\alpha}$ when $\alpha \in \mathcal{I}_f$, $f^{\alpha} = -\gamma^{\alpha}$ when $\alpha \in \mathcal{I}_l$, and $f^{wns} = \gamma^{wns}$. For*
 718 *the solid phase the Gibbs–Duhem equation is*

$$\eta^{\bar{s}} d\theta^{\bar{s}} + \epsilon^{\bar{s}} \frac{\mathbf{C}^s}{j^s} : d\boldsymbol{\sigma}^{\bar{s}} + \sum_{i \in \mathcal{I}_s} \epsilon^{\bar{s}} \rho^s \omega^{i\bar{s}} d\mu^{i\bar{s}} = 0. \quad (44)$$

719

720 We will consider two cases: (i) a non-isothermal system under assumption
 721 of local thermal equilibrium when the temperatures for all entities are the
 722 same but change in space and time, and (ii) an isothermal system when the
 723 temperature is constant.

724 *5.2. SEI for Non-isothermal System*

725 **Secondary Restriction 9 (Local Thermal Equilibrium).**

726 *The system is restricted to the case where the temperature of each entity is*
 727 *the same at each point, $\theta^{\bar{\alpha}} = \theta$ for $\alpha \in \mathcal{I}$, but the gradient of the temperature*
 728 *may be non-zero.*

729 Application of Secondary Restrictions 1–9 to the general SEI given in
 730 Eq. (42), taking into account that

$$\nabla \mu^{\bar{i}\bar{\alpha}} = \nabla \mu^{\bar{i}\bar{\alpha}} \Big|_{\theta} + \theta \left(\bar{H}^{\bar{i}\bar{\alpha}} - \mu^{\bar{i}\bar{\alpha}} \right) \nabla \left(\frac{1}{\theta} \right) \quad \text{for } \alpha \in \mathcal{J}_f, \quad (45)$$

731 and neglecting higher order terms that are products of two or more forces,
 732 yields the following simplified SEI

$$\begin{aligned} & \sum_{\alpha \in \mathcal{J}_f} \frac{1}{\theta} \left(\epsilon^{\bar{\alpha}} \mathbf{t}^{\bar{\alpha}} + \epsilon^{\bar{\alpha}} p^{\alpha} \mathbf{l} \right) : \mathbf{d}^{\bar{\alpha}} + \frac{1}{\theta} \left(\epsilon^{\bar{s}} \mathbf{t}^{\bar{s}} - \epsilon^{\bar{s}} \mathbf{t}^s \right) : \mathbf{d}^{\bar{s}} & 1 \\ & + \sum_{\alpha \in \mathcal{J}_I} \frac{1}{\theta} \left[\epsilon^{\bar{\alpha}} \mathbf{t}^{\bar{\alpha}} - \epsilon^{\bar{\alpha}} \gamma^{\alpha} (\mathbf{l} - \mathbf{G}^{\alpha}) \right] : \mathbf{d}^{\bar{\alpha}} & 2 \\ & + \frac{1}{\theta} \left[\epsilon^{\bar{w}\bar{n}\bar{s}} \mathbf{t}^{\bar{w}\bar{n}\bar{s}} + \epsilon^{\bar{w}\bar{n}\bar{s}} \gamma^{wns} (\mathbf{l} - \mathbf{G}^{wns}) \right] : \mathbf{d}^{\bar{w}\bar{n}\bar{s}} & 3 \\ & - \left[\sum_{\alpha \in \mathcal{J}} \epsilon^{\bar{\alpha}} \mathbf{q}^{\bar{\alpha}} + \sum_{\alpha \in \mathcal{J}_f} \epsilon^{\bar{\alpha}} \rho^{\alpha} \omega^{A\bar{\alpha}} \left(\bar{H}^{\bar{A}\bar{\alpha}} - \bar{H}^{\bar{B}\bar{\alpha}} \right) \mathbf{u}^{\bar{A}\bar{\alpha}} \right] \cdot \nabla \left(\frac{1}{\theta} \right) & 4 \\ & - \sum_{\alpha \in \mathcal{J}_f} \frac{1}{\theta} \epsilon^{\bar{\alpha}} \rho^{\alpha} \omega^{A\bar{\alpha}} \mathbf{u}^{\bar{A}\bar{\alpha}} \cdot \nabla \left(\mu^{\bar{A}\bar{\alpha}} \Big|_{\theta} - \mu^{\bar{B}\bar{\alpha}} \Big|_{\theta} \right) & 5 \\ & + \sum_{i \in \{A, B\}} \frac{1}{\theta} \overset{iw \rightarrow iwn}{M} \left[\mu^{\bar{i}\bar{w}} + \psi^{\bar{w}} - \left(\mu^{\bar{i}\bar{n}} + \psi^{\bar{n}} \right) \right] & 6 \\ & - \sum_{\alpha \in \mathcal{J}_f} \frac{1}{\theta} \left\{ -p^{\alpha} \nabla \epsilon^{\bar{\alpha}} + \epsilon^{\bar{\alpha}} \rho^{\alpha} (\nabla \psi^{\bar{\alpha}} + \mathbf{g}^{\bar{\alpha}}) - \sum_{\kappa \in \mathcal{J}_{c\alpha}} \overset{\alpha \rightarrow \kappa}{\mathbf{T}}_0 \right\} \cdot (\mathbf{v}^{\bar{\alpha}} - \mathbf{v}^{\bar{s}}) & 7 \\ & - \sum_{\alpha \in \mathcal{J}_I} \frac{1}{\theta} \left\{ \gamma^{\alpha} \nabla \cdot \left[\epsilon^{\bar{\alpha}} (\mathbf{l} - \mathbf{G}^{\alpha}) \right] + \sum_{\kappa \in \mathcal{J}_{c\alpha}^+} \overset{\kappa \rightarrow \alpha}{\mathbf{T}}_0 - \overset{\alpha \rightarrow wns}{\mathbf{T}}_0 \right\} \cdot (\mathbf{v}^{\bar{\alpha}} - \mathbf{v}^{\bar{s}}) & 8 \\ & - \frac{1}{\theta} \left\{ -\gamma^{wns} \nabla \cdot \left[\epsilon^{\bar{w}\bar{n}\bar{s}} (\mathbf{l} - \mathbf{G}^{wns}) \right] + \sum_{\kappa \in \mathcal{J}_{cwns}^+} \overset{\kappa \rightarrow wns}{\mathbf{T}}_0 \right. & 9 \\ & \quad \left. - \langle \mathbf{n}_s \cdot \mathbf{t}_s^* \cdot \mathbf{n}_s \mathbf{n}_s \rangle_{\Omega_{wns}, \Omega} \right\} \cdot (\mathbf{v}^{\bar{w}\bar{n}\bar{s}} - \mathbf{v}^{\bar{s}}) & 10 \\ & + \frac{1}{\theta} \left[\frac{D^{\bar{s}} \epsilon^{\bar{w}}}{Dt} - \frac{\gamma^{wn} \hat{k}_1^{wn} \left(\epsilon^{\bar{w}\bar{n}} - \epsilon_{eq}^{\bar{w}\bar{n}} \right)}{p_w^{wn} - p_n^{wn}} \right] (p_w^{wn} - p_n^{wn} - \gamma^{wn} J_w^{wn}) & 11 \end{aligned}$$

$$\begin{aligned}
& -\frac{1}{\theta} \left(\epsilon^{\overline{ws}} + \epsilon^{\overline{ns}} \right) \frac{D^{\overline{s}} \chi_s^{\overline{ws}}}{Dt} \left[\gamma_{wn}^{ws} \cos \varphi^{\overline{ws}, \overline{wn}} + \gamma_{ws}^{ws} - \gamma_{ns}^{ws} + \gamma^{ws} \kappa_G^{\overline{wns}} \right] \\
& = \sum_{\alpha \in \mathcal{J}} \Lambda^{\overline{\alpha}} \geq 0,
\end{aligned} \tag{46}$$

733 where $\overline{H}^{i\overline{\alpha}}$ is the macroscale partial mass enthalpy of species i in entity α .

734 5.3. SEI for Isothermal System

735 A further restricted system applies for the case in which temperatures
736 are essentially constant. Under this condition, the system can be assumed
737 to be isothermal, which results in an even simpler SEI than that shown in
738 Eq. (46).

739 Secondary Restriction 10 (Isothermal System).

740 *Temperatures of all entities are equal and constant such that $\theta^{\overline{\alpha}} = \theta$ for $\alpha \in \mathcal{J}$,*
741 *and the derivatives of temperature are zero, $\nabla \theta = 0$ for $\alpha \in \mathcal{J}$.*

742 Secondary Restriction 10 reduces the SEI in Eq. (46) further as follows

$$\begin{aligned}
& \sum_{\alpha \in \mathcal{J}_f} \frac{1}{\theta} \left(\epsilon^{\overline{\alpha}} \mathbf{t}^{\overline{\alpha}} + \epsilon^{\overline{\alpha}} p^{\alpha} \mathbf{I} \right) : \mathbf{d}^{\overline{\alpha}} + \frac{1}{\theta} \left(\epsilon^{\overline{s}} \mathbf{t}^{\overline{s}} - \epsilon^{\overline{s}} \mathbf{t}^s \right) : \mathbf{d}^{\overline{s}} \\
& + \sum_{\alpha \in \mathcal{J}_I} \frac{1}{\theta} \left[\epsilon^{\overline{\alpha}} \mathbf{t}^{\overline{\alpha}} - \epsilon^{\overline{\alpha}} \gamma^{\alpha} (\mathbf{I} - \mathbf{G}^{\alpha}) \right] : \mathbf{d}^{\overline{\alpha}} \\
& + \frac{1}{\theta} \left[\epsilon^{\overline{wns}} \mathbf{t}^{\overline{wns}} + \epsilon^{\overline{wns}} \gamma^{wns} (\mathbf{I} - \mathbf{G}^{wns}) \right] : \mathbf{d}^{\overline{wns}} \\
& - \sum_{\alpha \in \mathcal{J}_f} \frac{1}{\theta} \epsilon^{\overline{\alpha}} \rho^{\alpha} \omega^{A\overline{\alpha}} \mathbf{u}^{A\overline{\alpha}} \cdot \nabla \left(\mu^{A\overline{\alpha}} \Big|_{\theta} - \mu^{B\overline{\alpha}} \Big|_{\theta} \right) \\
& + \sum_{i \in \{A, B\}} \frac{1}{\theta} M^{iw \rightarrow iwn} \left[\mu^{i\overline{w}} + \psi^{i\overline{w}} - \left(\mu^{i\overline{n}} + \psi^{i\overline{n}} \right) \right] \\
& - \sum_{\alpha \in \mathcal{J}_f} \frac{1}{\theta} \left\{ -p^{\alpha} \nabla \epsilon^{\overline{\alpha}} + \epsilon^{\overline{\alpha}} \rho^{\alpha} (\nabla \psi^{\overline{\alpha}} + \mathbf{g}^{\overline{\alpha}}) - \sum_{\kappa \in \mathcal{J}_{c\alpha}} \mathbf{T}_0^{\alpha \rightarrow \kappa} \right\} \cdot (\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}})
\end{aligned} \tag{1-6}$$

$$\begin{aligned}
& - \sum_{\alpha \in \mathcal{J}_I} \frac{1}{\theta} \left\{ \gamma^\alpha \nabla \cdot \left[\epsilon^{\bar{\alpha}} (\mathbf{I} - \mathbf{G}^\alpha) \right] + \sum_{\kappa \in \mathcal{J}_{c\alpha}^+} \mathbf{T}_0^{\kappa \rightarrow \alpha} - \mathbf{T}_0^{\alpha \rightarrow wns} \right\} \cdot (\mathbf{v}^{\bar{\alpha}} - \mathbf{v}^{\bar{s}}) \quad 7 \\
& - \frac{1}{\theta} \left\{ - \gamma^{wns} \nabla \cdot \left[\epsilon^{\overline{wns}} (\mathbf{I} - \mathbf{G}^{wns}) \right] + \sum_{\kappa \in \mathcal{J}_{cwns}^+} \mathbf{T}_0^{\kappa \rightarrow wns} \right. \quad 8 \\
& \quad \left. - \langle \mathbf{n}_s \cdot \mathbf{t}_s^* \cdot \mathbf{n}_s \mathbf{n}_s \rangle_{\Omega_{wns}, \Omega} \right\} \cdot (\mathbf{v}^{\overline{wns}} - \mathbf{v}^{\bar{s}}) \quad 9 \\
& + \frac{1}{\theta} \left[\frac{D^{\bar{s}} \epsilon^{\overline{w}}}{Dt} - \frac{\gamma^{wn} \hat{k}_1^{wn} (\epsilon^{\overline{wn}} - \epsilon_{eq}^{\overline{wn}})}{p_w^{wn} - p_n^{wn}} \right] (p_w^{wn} - p_n^{wn} - \gamma^{wn} J_w^{wn}) \quad 10 \\
& - \frac{1}{\theta} (\epsilon^{\overline{ws}} + \epsilon^{\overline{ns}}) \frac{D^{\bar{s}} \chi_s^{\overline{ws}}}{Dt} \left[\gamma_{wn}^{wns} \cos \varphi^{\overline{ws}, \overline{wn}} + \gamma_{ws}^{wns} - \gamma_{ns}^{wns} + \gamma^{wns} \kappa_G^{\overline{ws}} \right] \quad 11 \\
& = \sum_{\alpha \in \mathcal{J}} \Lambda^{\bar{\alpha}} \geq 0. \quad (47)
\end{aligned}$$

6. Model Closure

The SEI expressions given in Eqs. (46) and (47) are written in force-flux form and can be used to guide the formulation of closure relations. The selection of the closure relations is non-unique. As a first approximation to ensure that the entropy production rate is non-negative, we consider the fluxes to be either a constant or a linear function of the forces. If the resultant models are found to be inadequate for some case of concern, more general closure relations can be developed to produce alternative models.

6.1. Closure Relations

Closure approximations will be posited zero-order with respect to the macroscale rate of strain tensor and first-order with respect to all other forces being considered. Neglect of the rate of strain in constitutive relations for porous medium flow is appropriate if viscous forces at the boundary of the

756 solid phase are dominant, which implies that the system is macroscopically
 757 inviscid. This approximation is reasonable because the boundaries of the sys-
 758 tem are insignificant compared to the fluid-solid boundaries within the porous
 759 medium system. Put another way velocity variations that exist at the mic-
 760 roscales because of viscous effects that result in velocity variations between
 761 solid grains do not result in systematic macroscale trends in velocity—the
 762 fine scale detail vanishes in the averaging process. Because of this obser-
 763 vation, we will use a zero-order closure for the flux multiplying the rate of
 764 strain tensor. Similarly, the starting point for other closure relations will
 765 be a first-order approximation. We will include Onsager-like cross coupling
 766 where certain fluxes depend upon more than one force. Because of conditions
 767 on the system (e.g., massless interfaces and common curve, non-deforming
 768 solid phase) many cross-coupling terms can be neglected. Linear closure rela-
 769 tions are a reasonable starting point and have been found adequate for many
 770 systems investigated to date.

771 The zero-order closure approximations for the stress tensors can be writ-
 772 ten as

$$\mathbf{t}^{\bar{\alpha}} = -p^{\alpha} \mathbf{I} \quad \text{for } \alpha \in \mathcal{J}_f, \quad (48)$$

$$\mathbf{t}^{\bar{s}} = \mathbf{t}^s, \quad (49)$$

$$\mathbf{t}^{\bar{\alpha}} = \gamma^{\alpha} (\mathbf{I} - \mathbf{G}^{\alpha}) \quad \text{for } \alpha \in \mathcal{J}_I, \quad (50)$$

773 and

$$\mathbf{t}^{\overline{wgs}} = -\gamma^{wgs} (\mathbf{I} - \mathbf{G}^{wgs}), \quad (51)$$

774 where the macroscale geometric orientation tensors for the interfaces and
 775 common curve can be approximated as $\mathbf{G}^{\alpha} = \mathbf{I}/3$ for $\alpha \in \mathcal{J}_I$, and $\mathbf{G}^{wgs} = 2\mathbf{I}/3$

776 for the case in which the microscale interfaces and common curves have no
 777 preferred orientation.

778 A first-order closure approximation for the dispersion velocity is given by

$$\omega^{A\bar{\alpha}} \mathbf{u}^{\bar{A}\bar{\alpha}} = -\hat{\mathbf{D}}_{AB}^{\alpha} \cdot \nabla \left(\mu^{\bar{A}\bar{\alpha}} \Big|_{\theta} - \mu^{\bar{B}\bar{\alpha}} \Big|_{\theta} \right) \quad \text{for } \alpha \in \mathcal{J}_f, \quad (52)$$

779 where $\hat{\mathbf{D}}_{AB}^{\alpha}$ are second-rank symmetric positive semidefinite binary dispersion
 780 tensors which reduce to scalars if the diffusion process is isotropic.

781 For non-isothermal systems, a first-order closure for aggregate non-advective
 782 heat flux is

$$\sum_{\alpha \in \mathcal{J}} \epsilon^{\bar{\alpha}} \mathbf{q}^{\bar{\alpha}} + \sum_{\alpha \in \mathcal{J}_f} \epsilon^{\bar{\alpha}} \rho^{\alpha} \omega^{A\bar{\alpha}} \left(\overline{H^{A\bar{\alpha}}} - \overline{H} \right) \quad \overline{A\bar{\alpha}} = -\hat{\mathbf{K}}_{\theta} \cdot \nabla \left(\frac{1}{\theta} \right), \quad (53)$$

783 where $\hat{\mathbf{K}}_{\theta}$ is a second-rank symmetric positive semidefinite effective heat con-
 784 ductivity tensor. When the system of interest is isothermal, the closure re-
 785 lation given in Eq. (53) is not needed.

786 The transfer of mass of species i can be approximated as

$$\overset{iw \rightarrow iwn}{M} = \hat{K}_M^i \left[\mu^{\bar{i}w} + \psi^{\bar{w}} - \left(\mu^{\bar{i}n} + \psi^{\bar{n}} \right) \right] \quad \text{for } i \in \{A, B\}, \quad (54)$$

787 where $\hat{K}_M^i$ is a non-negative scalar mass transfer coefficient.

788 The fluxes in Eqs. (46) and (47), which contain transfer of momentum
 789 terms, depend on more than one force. The momentum transferred from
 790 the fluid phase to the interface is directly transferred to the adjacent phase.
 791 Therefore, the fluxes associated with the fluid phases are approximated as
 792 linear functions of both fluid-phase velocities relative to the macroscale solid
 793 phase velocity. According to Secondary Restriction 7, the solid is immobile
 794 and the solid-phase velocity is zero, such that

$$-p^{\alpha} \nabla \epsilon^{\bar{\alpha}} + \epsilon^{\bar{\alpha}} \rho^{\alpha} (\nabla \psi^{\bar{\alpha}} + \mathbf{g}^{\bar{\alpha}}) - \sum_{\kappa \in \mathcal{J}_{c\alpha}} \overset{\alpha \rightarrow \kappa}{\mathbf{T}}_0 = - \sum_{\kappa \in \mathcal{J}_f} \hat{\mathbf{R}}_{\kappa}^{\alpha} \cdot \mathbf{v}^{\bar{\kappa}} \quad \text{for } \alpha \in \mathcal{J}_f, \quad (55)$$

795 where $\hat{\mathbf{R}}_\kappa^\alpha$ are second-rank symmetric positive semidefinite resistance tensors.
 796 Resistance tensors depend on the morphology of the porous medium system.
 797 The fluxes associated with interfaces depend also on the adjacent phase
 798 velocities, since interfaces can move when adjacent phases move, which leads
 799 to

$$\gamma^\alpha \nabla \cdot \left[\epsilon^{\bar{\alpha}} (\mathbf{I} - \mathbf{G}^\alpha) \right] + \sum_{\kappa \in \mathcal{J}_{c\alpha}^+} \mathbf{T}_0^{\kappa \rightarrow \alpha} - \mathbf{T}_0^{\alpha \rightarrow wns} = -\hat{\mathbf{R}}_\alpha^\alpha \cdot \mathbf{v}^{\bar{\alpha}} - \sum_{\kappa \in \mathcal{J}_{c\alpha}^+} \hat{\mathbf{R}}_\kappa^\alpha \cdot \mathbf{v}^{\bar{\kappa}} \quad \text{for } \alpha \in \mathcal{J}_I. \quad (56)$$

800 Similar conclusions can be made for the common curve

$$\begin{aligned} & -\gamma^{wns} \nabla \cdot \left[\epsilon^{\overline{wns}} (\mathbf{I} - \mathbf{G}^{wns}) \right] + \sum_{\kappa \in \mathcal{J}_{cwns}^+} \mathbf{T}_0^{\kappa \rightarrow wns} + \mathbf{T}^{s \rightarrow wns} = -\hat{\mathbf{R}}_{wns}^{wns} \cdot \mathbf{v}^{\overline{wns}} \\ & - \sum_{\kappa \in \mathcal{J}_f} \hat{\mathbf{R}}_\kappa^{wns} \cdot \mathbf{v}^{\bar{\kappa}}, \end{aligned} \quad (57)$$

801 where $\mathbf{T}^{s \rightarrow wns} = -\langle \mathbf{n}_s \cdot \mathbf{t}_s^* \cdot \mathbf{n}_s \mathbf{n}_s \rangle_{\Omega_{wns}, \Omega}$.

802 Capillary effects at the fluid-fluid interface can be approximated without
 803 cross-coupling as

$$\frac{\partial \epsilon^{\bar{w}}}{\partial t} - \frac{\gamma^{wn} \hat{k}_1^{wn} \left(\epsilon^{\overline{wn}} - \epsilon_{\text{eq}}^{\overline{wn}} \right)}{p_w^{wn} - p_n^{wn}} = \hat{c}^{wn} (p_w^{wn} - p_n^{wn} - \gamma^{wn} J_w^{wn}), \quad (58)$$

804 where $\hat{c}^{wn}$ is a non-negative closure coefficient, and zero solid-phase velocity
 805 is taken into account.

806 The final grouping of terms accounts for an imbalance in the surface
 807 tension forces acting at the common curve in a direction tangent to the solid
 808 surface resulting in the approximation

$$\frac{\partial \chi_s^{\overline{ws}}}{\partial t} = -\hat{c}^{wns} \left(\gamma_{wn}^{wns} \cos \varphi^{\overline{ws}, \overline{wn}} + \gamma_{ws}^{wns} - \gamma_{ns}^{wns} + \gamma^{wns} \kappa_G^{\overline{wns}} \right), \quad (59)$$

809 where $\hat{c}^{wns}$ is a non-negative surface wetting parameter.

810 The SEI (46) used for specification of the closure relations contains group-
 811 ings of terms that appear in single-phase systems with chemical species and
 812 non-compositional two-phase systems. Therefore, certain closure relations
 813 presented in this section are similar to those developed for these more simple
 814 cases, and we refer the reader to [18, Chap. 10.10.1, 11.5.3] for comparison.

815 6.2. Closed Set of Conservation Equations

816 The macroscale conservation equations presented in section 3 can be writ-
 817 ten in a closed form taking into account the closure relations developed in
 818 section 6.1 and simplified according to the secondary restrictions specified in
 819 sections 5.1–5.3. In addition, several other terms can be neglected according
 820 to the expected system behaviour that will be detailed in turn.

821 Species Mass Conservation

822 Application of the closure relations given by Eqs. (52) and (54) together
 823 with Secondary Restrictions 1, 4, 6, and 7 allows the conservation of mass
 824 equation, Eq. (1), for species A and B in the fluid phase α to be written as

$$\begin{aligned} & \frac{D^{\bar{\alpha}} \left(\epsilon^{\bar{\alpha}} \rho^{\alpha} \omega^{A\bar{\alpha}} \right)}{Dt} + \epsilon^{\bar{\alpha}} \rho^{\alpha} \omega^{A\bar{\alpha}} \mathbf{l} : \mathbf{d}^{\bar{\alpha}} - \nabla \cdot \left[\epsilon^{\bar{\alpha}} \rho^{\alpha} \hat{\mathbf{D}}_{AB}^{\alpha} \cdot \nabla \left(\mu^{\overline{A\alpha}} \Big|_{\theta} - \mu^{\overline{B\alpha}} \Big|_{\theta} \right) \right] \\ & + \hat{K}_M^A \left[\mu^{\overline{A\alpha}} + \psi^{\bar{\alpha}} - \left(\mu^{\overline{A\beta}} + \psi^{\bar{\beta}} \right) \right] = 0 \quad \text{for } \alpha, \beta \in \mathcal{J}_f, \alpha \neq \beta, \end{aligned} \quad (60)$$

825 and

$$\begin{aligned} & \frac{D^{\bar{\alpha}} \left(\epsilon^{\bar{\alpha}} \rho^{\alpha} \omega^{B\bar{\alpha}} \right)}{Dt} + \epsilon^{\bar{\alpha}} \rho^{\alpha} \omega^{B\bar{\alpha}} \mathbf{l} : \mathbf{d}^{\bar{\alpha}} - \nabla \cdot \left[\epsilon^{\bar{\alpha}} \rho^{\alpha} \hat{\mathbf{D}}_{AB}^{\alpha} \cdot \nabla \left(\mu^{\overline{B\alpha}} \Big|_{\theta} - \mu^{\overline{A\alpha}} \Big|_{\theta} \right) \right] \\ & + \hat{K}_M^B \left[\mu^{\overline{B\alpha}} + \psi^{\bar{\alpha}} - \left(\mu^{\overline{B\beta}} + \psi^{\bar{\beta}} \right) \right] = 0 \quad \text{for } \alpha, \beta \in \mathcal{J}_f, \alpha \neq \beta. \end{aligned} \quad (61)$$

826 According to Secondary Restriction 7, we do not need to model any solid
 827 phase properties. Therefore, solid phase mass conservation equation does not
 828 enter the set of system equations.

829 Since the interfaces and common curve are considered to be massless,
 830 Secondary Restriction 3 reduces the conservation of mass equation for inter-
 831 faces to a jump condition between phases at the interface. For the fluid-fluid
 832 interface, we have $\overset{iw \rightarrow iwn}{M} = - \overset{in \rightarrow iwn}{M}$ for $i \in \{A, B\}$. Due to Secondary Re-
 833 striction 7, there is no mass exchange at the fluid-solid interfaces, and thus
 834 mass conservation equations for these entities will not be modeled. The com-
 835 mon curve conservation of mass equation can also be removed from the set
 836 of equations because it becomes trivially zero.

837 *Momentum Conservation*

838 Application of the closure relations given in Eq. (48), Eqs. (54) and (55),
 839 and the secondary restrictions listed in section 5.1 allows the momentum
 840 conservation equations, Eq. (2), to be written for fluid phases as

$$\begin{aligned} & \frac{D^{\bar{\alpha}} \left(\epsilon^{\bar{\alpha}} \rho^{\alpha} \mathbf{v}^{\bar{\alpha}} \right)}{Dt} + \epsilon^{\bar{\alpha}} \rho^{\alpha} \mathbf{v}^{\bar{\alpha}} \mathbf{l} : \mathbf{d}^{\bar{\alpha}} \\ & + \sum_{i \in \{A, B\}} \hat{K}_M^i \left[\mu^{\bar{i}\bar{\alpha}} + \psi^{\bar{\alpha}} - \left(\mu^{\bar{i}\bar{\beta}} + \psi^{\bar{\beta}} \right) \right] \left(\mathbf{v}_{\alpha}^{\bar{w}\bar{n}} + \mathbf{u}_{i\alpha}^{\bar{w}\bar{n}} \right) \\ & + \epsilon^{\bar{\alpha}} \nabla p^{\alpha} + \epsilon^{\bar{\alpha}} \rho^{\alpha} \nabla \psi^{\bar{\alpha}} + \hat{\mathbf{R}}_w^{\alpha} \cdot \mathbf{v}^{\bar{w}} + \hat{\mathbf{R}}_n^{\alpha} \cdot \mathbf{v}^{\bar{n}} = 0 \quad \text{for } \alpha, \beta \in \mathcal{J}_f, \alpha \neq \beta. \end{aligned} \quad (62)$$

841 Fluid flow through porous media is typically slow such that the inertial terms
 842 and the higher order term in the second line in Eq. (62) can be neglected,
 843 yielding the following simplified momentum conservation equations for the
 844 fluid phases

$$\epsilon^{\bar{\alpha}} \nabla p^{\alpha} + \epsilon^{\bar{\alpha}} \rho^{\alpha} \nabla \psi^{\bar{\alpha}} + \hat{\mathbf{R}}_w^{\alpha} \cdot \mathbf{v}^{\bar{w}} + \hat{\mathbf{R}}_n^{\alpha} \cdot \mathbf{v}^{\bar{n}} = 0 \quad \text{for } \alpha \in \mathcal{J}_f. \quad (63)$$

845 As stated in Secondary Restriction 7, the solid phase is considered to be
 846 non-deformable, rigid, and immobile. Therefore, the momentum conserva-
 847 tion equation for the solid phase is not modeled. According to Secondary
 848 Restriction 3, the interfaces and common curves are massless. Thus, they do
 849 not contribute any momentum, and the conservation of momentum equations
 850 for these entities are not explicitly included in the model formulation.

851 For isothermal systems of interest, the temperature is constant. For non-
 852 isothermal systems, we need to consider energy conservation equations.

853 As an alternative, instead of modeling the total energy conservation equa-
 854 tion, the equation of change of internal energy can be formulated as

$$\mathcal{U}_{**}^{\bar{\alpha}} := \mathcal{E}_{**}^{\bar{\alpha}} - \mathbf{v}^{\bar{\alpha}} \cdot \mathcal{P}_{**}^{\bar{\alpha}} + \sum_{i \in \mathcal{J}_s} \frac{\mathbf{v}^{\bar{\alpha}} \cdot \mathbf{v}^{\bar{\alpha}}}{2} \mathcal{M}_{**}^{\bar{i}\bar{\alpha}} = 0 \quad \text{for } \alpha \in \mathcal{J}, \quad (64)$$

855 where $\mathcal{M}_{**}^{\bar{i}\bar{\alpha}}$, $\mathcal{P}_{**}^{\bar{\alpha}}$, and $\mathcal{E}_{**}^{\bar{\alpha}}$ are defined in Eqs. (1)–(3), respectively. Substitut-
 856 ing these equations into Eq. (64), taking into account slow flows that allow
 857 one to neglect the terms containing velocity difference squared, considering
 858 $\mathbf{g}^{i\bar{\alpha}} = \mathbf{g}^{\bar{\alpha}}$ for $i \in \mathcal{J}_s$, $\alpha \in \mathcal{J}$ due to Secondary Restriction 1, and assuming no
 859 sources of energy $h^\alpha = h_0^{\bar{\alpha}} = 0$, we get

$$\begin{aligned} \mathcal{U}_{**}^{\bar{\alpha}} = & \frac{D^{\bar{\alpha}} E^{\bar{\alpha}}}{Dt} + E^{\bar{\alpha}} \mathbf{l} : \mathbf{d}^{\bar{\alpha}} - \sum_{\kappa \in \mathcal{J}_{c\alpha}} \sum_{i \in \mathcal{J}_s} M^{\kappa \rightarrow i\alpha} \overline{E_i^{\bar{\alpha}, \kappa}} - \sum_{\kappa \in \mathcal{J}_{c\alpha}} Q_1^{\kappa \rightarrow \alpha} \\ & - \frac{1}{2} \sum_{\beta \in \mathcal{J}_{c\alpha}^-} \sum_{\kappa \in \mathcal{J}_{c\beta}^-} Q_1^{* \kappa \rightarrow \alpha} - \frac{1}{2} \sum_{\beta \in \mathcal{J}_{c\alpha}^+} \sum_{\kappa \in \mathcal{J}_{c\beta}^+} Q_1^{* \kappa \rightarrow \alpha} \\ & - \epsilon^{\bar{\alpha}} \mathbf{t}^{\bar{\alpha}} : \mathbf{d}^{\bar{\alpha}} - \nabla \cdot (\epsilon^{\bar{\alpha}} \mathbf{q}^{\bar{\alpha}}) = 0 \quad \text{for } \alpha \in \mathcal{J}. \end{aligned} \quad (65)$$

860 According to Secondary Restriction 9, we have only one temperature.
 861 Therefore, we obtain an energy conservation equation for the system by
 862 summing up all the energy conservation equations for the entities so that

the exchange terms cancel yielding

$$\sum_{\alpha \in \mathcal{J}} \left[\frac{D^{\bar{\alpha}} E^{\bar{\alpha}}}{Dt} + E^{\bar{\alpha}} \mathbf{l} : \mathbf{d}^{\bar{\alpha}} - \epsilon^{\bar{\alpha}} \mathbf{t}^{\bar{\alpha}} : \mathbf{d}^{\bar{\alpha}} - \nabla \cdot (\epsilon^{\bar{\alpha}} \mathbf{q}^{\bar{\alpha}}) \right] = 0. \quad (66)$$

According to Secondary Restriction 7, the solid phase is immobile, thus $\mathbf{d}^{\bar{s}} = 0$. The constraint on massless interfaces and common curve stated in Secondary Restriction 3 means that there is no flow of an interface/common curve entity in the direction tangent to the interface/common curve. The fact that the solid is fixed means that there will be no flow of the interface in the direction normal to the solid surface either, and thus $\mathbf{d}^{\bar{\alpha s}} = 0$ for $\alpha \in \mathcal{J}_f$. The velocity of the massless wn interface is only in the direction normal to the interface, thus the rate of strain for this entity survives. A massless common curve has zero velocity tangent to the curve and normal to the solid, but can have a non-zero velocity tangent to the solid phase. Therefore, the rate of strain tensor for the common curve must be retained. Taking these facts into account and applying the closure relations given in Eq. (48) and Eqs. (50)–(53), the following results

$$\begin{aligned} & \sum_{\alpha \in \mathcal{J}} \left[\frac{D^{\bar{\alpha}} E^{\bar{\alpha}}}{Dt} + E^{\bar{\alpha}} \mathbf{l} : \mathbf{d}^{\bar{\alpha}} \right] + \sum_{\alpha \in \mathcal{J}_f} \epsilon^{\bar{\alpha}} p^{\alpha} \mathbf{l} : \mathbf{d}^{\bar{\alpha}} - \epsilon^{\bar{wn}} \gamma^{wn} (\mathbf{l} - \mathbf{G}^{wn}) : \mathbf{d}^{\bar{wn}} \\ & + \epsilon^{\bar{wns}} \gamma^{wns} (\mathbf{l} - \mathbf{G}^{wns}) : \mathbf{d}^{\bar{wns}} + \nabla \cdot \left[\hat{\mathbf{K}}_{\theta} \cdot \nabla \left(\frac{1}{\theta} \right) \right] \\ & - \sum_{\alpha \in \mathcal{J}_f} \nabla \cdot \left[\epsilon^{\bar{\alpha}} \rho^{\alpha} \left(\bar{H}^{\bar{A}\alpha} - \bar{H}^{\bar{B}\alpha} \right) \hat{\mathbf{D}}_{AB}^{\alpha} \cdot \nabla \left(\mu^{\bar{A}\alpha} \Big|_{\theta} - \mu^{\bar{B}\alpha} \Big|_{\theta} \right) \right] = 0. \quad (67) \end{aligned}$$

The conservation equations (60), (61), (63), and (67) that build the basis of the closed model contain more unknowns than equations. To reduce the number of unknowns, additional relationships will be applied. These are the identities between certain variables, the equations of state, and the evolution equations.

882 *Identities, Equations of State and Evolution Equations*

883 An identity between the volume fractions of the fluid phases is

$$\epsilon^{\bar{n}} = \epsilon - \epsilon^{\bar{w}}. \quad (68)$$

884 The mass fractions of a species in a phase are connected for a binary system
885 yielding

$$\omega^{B\bar{\alpha}} = 1 - \omega^{A\bar{\alpha}} \quad \text{for } \alpha \in \{w, n\}. \quad (69)$$

886 Usually, porous medium models are written in terms of fluid-phase satura-
887 tions, $s^{\bar{\alpha}}$, which are defined as

$$s^{\bar{\alpha}} = \frac{\epsilon^{\bar{\alpha}}}{\epsilon} \quad \text{for } \alpha \in \mathcal{I}_f. \quad (70)$$

888 Equations of state provide additional constitutive relationships necessary
889 to close the model. We will write these expressions in functional forms. Fluid
890 densities are functions of pressure and temperature

$$\rho^\alpha = \rho^\alpha(\theta, p^\alpha) \quad \text{for } \alpha \in \{w, n\}. \quad (71)$$

891 Internal energies are in addition functions of densities and interfacial/curvilinear
892 tensions

$$\begin{aligned} E^{\bar{\alpha}} &= E^{\bar{\alpha}}(\theta, p^\alpha, \rho^\alpha) \quad \text{for } \alpha \in \{w, n\}, & E^{\bar{s}} &= E^{\bar{s}}(\theta, \mathbf{t}^{\bar{s}}, \rho^s), \\ E^{\bar{\alpha}} &= E^{\bar{\alpha}}(\theta, \gamma^\alpha, \rho^\alpha) \quad \text{for } \alpha \in \{wn, ws, ns, wns\}, \end{aligned} \quad (72)$$

893 where the solid density ρ^s , solid phase stress tensor $\mathbf{t}^{\bar{s}}$, curvilinear and inter-
894 facial densities ρ^α and tensions γ^α are given constants.

895 Chemical potentials and enthalpies are in addition functions of mass frac-
896 tions

$$\mu^{i\bar{\alpha}} = \mu^{i\bar{\alpha}}(\theta, p^\alpha, \rho^\alpha \omega^{i\bar{\alpha}}) \quad \text{for } i \in \{A, B\}, \alpha \in \{w, n\}, \quad (73)$$

897 and

$$\overline{H}^{i\alpha} = \overline{H}^{i\alpha}(\theta, p^\alpha, \rho^\alpha \omega^{i\alpha}) \quad \text{for } i \in \{A, B\}, \alpha \in \{w, n\}. \quad (74)$$

898 A non-isothermal system described by the conservation equations (60),
 899 (61), (63), and (67), identities (68)–(70), and equations of state (71)–(74)
 900 contains the following unknowns

$$\mathcal{V}_\theta = \left\{ s^{\overline{w}}, \omega^{A\overline{w}}, \omega^{A\overline{n}}, \mathbf{v}^{\overline{w}}, \mathbf{v}^{\overline{n}}, p^w, p^n, \epsilon^{\overline{wn}}, \epsilon^{\overline{wns}}, \theta \right\}. \quad (75)$$

901 For an isothermal system, the temperature θ is a constant model parameter,
 902 and thus no energy conservation equation is needed. The model described
 903 by the conservation equations (60), (61), and (63), identities (68)–(70), and
 904 equations of state (71) and (73) contain the following vector of variables

$$\mathcal{V} = \left\{ s^{\overline{w}}, \omega^{A\overline{w}}, \omega^{A\overline{n}}, \mathbf{v}^{\overline{w}}, \mathbf{v}^{\overline{n}}, p^w, p^n \right\}. \quad (76)$$

905 For the non-isothermal case, three additional equations are needed to close
 906 the model, and one additional equation for the isothermal case.

907 This can be done by considering Eq. (58), which introduces the following
 908 unknowns $\epsilon^{\overline{wn}}$, $\epsilon_{\text{eq}}^{\overline{wn}}$, J_w^{wn} , p_w^{wn} , and p_n^{wn} to the above lists.

909 The surface averaged pressures can be approximated by the volume av-
 910 erages such that

$$p_w^{wn} \approx p^w, \quad \text{and} \quad p_n^{wn} \approx p^n. \quad (77)$$

911 Capillary pressure is a function of wetting-phase saturation and fluid-fluid
 912 interfacial area

$$p^c = -\gamma^{wn} J_w^{wn} = p^c(s^{\overline{w}}, \epsilon^{\overline{wn}}), \quad (78)$$

913 and an equilibrium interfacial area can be expressed in the following func-
 914 tional form

$$\epsilon_{\text{eq}}^{\overline{wn}} = \epsilon_{\text{eq}}^{\overline{wn}}(p^n - p^w, s^{\overline{w}}). \quad (79)$$

915 Inclusion of the fluid-fluid interfacial area $\epsilon^{\overline{\overline{wn}}}$ requires an additional equa-
 916 tion for the evolution of this variable that can be derived applying averaging
 917 theorems to the identity function [18, Chap. 8.6]. This equation for non-
 918 deformable immobile solids can be written as

$$\begin{aligned} \frac{\partial \epsilon^{\overline{\overline{wn}}}}{\partial t} + \nabla \cdot \left(\epsilon^{\overline{\overline{wn}}} \mathbf{w}^{\overline{\overline{wn}}} \right) - J_w^{wn} \epsilon \frac{\partial s^{\overline{\overline{w}}}}{\partial t} - \hat{k}^{wn} \left(\epsilon_{\text{eq}}^{\overline{\overline{wn}}} - \epsilon^{\overline{\overline{wn}}} \right) \\ - \cos \varphi^{\overline{\overline{ws,wn}}} \left(\epsilon^{\overline{\overline{ws}}} + \epsilon^{\overline{\overline{ns}}} \right) \frac{\partial \chi_s^{\overline{\overline{ws}}}}{\partial t} = 0, \end{aligned} \quad (80)$$

919 where the macroscale contact angle $\varphi^{\overline{\overline{ws,wn}}}$ and the total solid surface $\epsilon^{\overline{\overline{ws}}} +$
 920 $\epsilon^{\overline{\overline{ns}}}$ are specified constants, $\mathbf{w}^{\overline{\overline{wn}}}$ is the average macroscale interface velocity
 921 normal to the interface, and parameters $\hat{k}^{wn}$ and $\hat{k}_1^{wn}$ are related as

$$\hat{k}^{wn} = \left(\frac{J_w^{wn} \gamma^{wn}}{p_w^{wn} - p_n^{wn}} - 1 \right) \hat{k}_1^{wn}. \quad (81)$$

922 The average macroscale interface velocity normal to the interface can be
 923 approximated as

$$\mathbf{w}^{\overline{\overline{wn}}} \approx \mathbf{G}^{wn} \cdot \left(\hat{A}^w \mathbf{v}^{\overline{w}} + \hat{A}^n \mathbf{v}^{\overline{n}} \right), \quad (82)$$

924 where the interfacial velocity parameters $\hat{A}^w$ and $\hat{A}^n$ depend on the ratio of
 925 the wetting fluid to non-wetting viscosities and the saturations.

926 For massless interfaces, the velocity of the interface is primarily due to
 927 the movement of the interface rather than movement within the interface.
 928 Therefore, we can make the approximation

$$\mathbf{v}^{\overline{\overline{wn}}} \approx \mathbf{w}^{\overline{\overline{wn}}}. \quad (83)$$

929 To compute $\partial \chi_s^{\overline{\overline{ws}}} / \partial t$ needed in Eq. (80), closure relation given by Eq. (59)
 930 can be applied, where $\gamma_{wn}^{wns} \approx \gamma^{wn}$, $\gamma_{ws}^{wns} \approx \gamma^{ws}$, and $\gamma_{ns}^{wns} \approx \gamma^{ns}$ are given
 931 constants.

At this stage, the isothermal model is closed. However, the non-isothermal model needs one more additional equation that is the evolution equation for the common curve [18, Chap. 8.6.3], which can be written for non-deformable and immobile solid phase as

$$\frac{\partial \epsilon^{\overline{wns}}}{\partial t} + \nabla \cdot (\epsilon^{\overline{wns}} \mathbf{w}^{\overline{wns}}) + \kappa_G^{wns} (\epsilon^{\overline{ws}} + \epsilon^{\overline{ns}}) \frac{\partial \chi_s^{\overline{ws}}}{\partial t} - \hat{k}^{wns} (\epsilon_{\text{eq}}^{\overline{wns}} - \epsilon^{\overline{wn}}) = 0, \quad (84)$$

where κ_G^{wns} , $\hat{k}^{wns}$ and $\epsilon_{\text{eq}}^{\overline{wns}}$ are given.

The velocity $\mathbf{w}^{\overline{wns}}$ can be approximated as

$$\mathbf{w}^{\overline{wns}} \approx (\mathbf{G}^{wns} - \mathbf{G}^{ws}) \cdot (\hat{B}^w \mathbf{v}^{\overline{w}} + \hat{B}^n \mathbf{v}^{\overline{n}}), \quad (85)$$

where $\hat{B}^w$ and $\hat{B}^n$ are the common curve velocity coefficients related to the velocities of the fluid phases.

For a massless common curve, we can make the following approximation

$$\mathbf{v}^{\overline{wns}} \approx \mathbf{w}^{\overline{wns}}. \quad (86)$$

At this point, the non-isothermal model is closed as well.

The generality of the model developed in this section provides opportunities for an interested researcher to examine a variety of systems, e.g., a non-dilute species transport in single-phase porous medium systems [13]. Applications of this earlier work is a current area of research. The cases of surfactant-enhanced mobilization and dissolution could benefit from the improved modeling framework detailed in this work that includes interfaces. We note that formulating fluxes generally as a function of a set of forces in addition to just the conjugate forces – the approach for example in Fick’s law – provides opportunities for an expanded, higher fidelity, and more generally applicable analysis.

952 7. Discussion and Conclusions

953 Because of the increasing importance of the subsurface as a source of wa-
954 ter and energy, it is important to be able to formulate models that account
955 for the physical mechanisms that drive the flow of fluid phases and the trans-
956 port of chemical species and energy within those phases. Currently employed
957 models, for the most part, are based on understanding of different systems
958 at the scale of interest or on system behavior at a smaller scale. For exam-
959 ple, the equations of flow are direct extensions of the form of Darcy’s law
960 developed for single-phase fluid flow in porous media. The context in which
961 Darcy’s equation was developed did not have to account for interactions be-
962 tween fluids or any fluid-fluid interfaces. Transport of chemical species has
963 been modeled mostly based on assuming that Fick’s law, proposed at the
964 microscale, applies at the macroscale. Unfortunately, experiments and the
965 behavior of real systems have shown that this extension is inadequate in some
966 cases because of heterogeneities in porous media, the presence of non-dilute
967 solutes, and the topology and morphology of the fluid phases. A comprehen-
968 sive theoretical basis for modeling transport in two-fluid-phase porous media
969 system is needed.

970 In the present manuscript, we have provided a consistent and rigorous
971 theoretical basis for the description of two-fluid-phase systems where the
972 phases can exchange mass, momentum, and energy. The approach employed
973 is TCAT, which leads to equations that describe the evolution of chemical
974 species, phases, interfaces between phases, and common curves at the porous
975 medium scale. The TCAT equations are derived by averaging appropriate
976 microscale conservation equations and consistent thermodynamic microscale

977 relations. Thus the transition in scale of the equations is rigorous, but is
978 accompanied by the need to formulate macroscale closure relations and to
979 account for microscale processes as they evidence themselves at the larger
980 scale. Although the work required to obtain the closure relations is some-
981 what daunting, the fact that all assumptions that underlie an equation sys-
982 tem must be explicitly identified provides both a path to model improvement
983 and an opportunity to assess the validity of assumptions inherent in current
984 models. Indeed, the general equations obtained here can be reduced to com-
985 mon models, but this reduction can only be achieved by applying additional
986 assumptions that neglect aspects of the physics that are represented in the
987 general framework derived in this work.

988 Thus, the work in this manuscript has developed macroscale conservation
989 and balance equations as well as a general SEI that can be used to suggest
990 suitable forms of closure relations. Of course, one could posit closure relations
991 without recourse to the entropy constraint, but satisfaction of the SEI ensures
992 that the proposed forms are physically reasonable. As an example of the use
993 of the SEI, a particular set of conservation equations were developed subject
994 to some primary and secondary restrictions imposed on the system. Although
995 the list of simplifications is significant, the resultant formulation leaves a large
996 set of systems that can still be analyzed with more fidelity than would be
997 obtained using current models.

998 Of particular value here is the incorporation of interface and common
999 curve dynamics into the model. These are typically not accounted for in ex-
1000 isting models, and no other existing formulation results in precisely defined
1001 variables that are consistent between the microscale and the macroscale.

1002 However, the curvature of these interfaces impacts capillary pressure, an im-
1003 portant quantity for correct description of drainage and imbibition in porous
1004 media systems. The extent of these interfaces is also important in that these
1005 surfaces are the location of exchange of mass between the fluid phases. If one
1006 is seeking to stimulate interphase mass transfer, a useful approach involves
1007 increasing the area between the phases. Equations for evolution of interfacial
1008 areas are provided based on the TCAT approach.

1009 The equations derived provide a complete set of conservation, thermo-
1010 dynamic, and kinematic equations that can be exercised in computational
1011 models. Support for the parameterization of the equations can come through
1012 smaller scale simulation and experimentation as well as upscaling of those
1013 results. The task that remains to incorporate the results of this analysis into
1014 production models is significant, but the development of a sound theoretic-
1015 al framework provides an opportunity to discern the limitations of current
1016 models and to evaluate the most important processes to study if the models
1017 are to be improved.

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1023 References

- 1024 [1] M. Acosta, C. Merten, G. Eigenberger, H. Class, R. Helmig, B. Thoben,
1025 and H. Müller-Steinhagen. Modeling non-isothermal two-phase multi-
1026 component flow in the cathode of PEM fuel cells. *Journal of Power*
1027 *Sources*, 9:1123–1141, 2006.
- 1028 [2] K. Aziz and A. Settari. *Petroleum Reservoir Simulation*. Applied Science
1029 Publ., Ltd., London, 1979.
- 1030 [3] J. Bear. *Dynamics of Fluids in Porous Media*. Elsevier, New York, 1972.
- 1031 [4] P. Berg, A. Novruzi, and O. Volkov. Reaction kinetics at the triple-
1032 phase boundary in PEM fuel cells. *Journal of Fuel Cell Science and*
1033 *Technology*, 5:021007, 2008.
- 1034 [5] B. Berkowitz and H. Scher. On characterization of anomalous dispersion
1035 in porous and fractured media. *Water Resources Research*, 31(6):1461–
1036 1466, 1995.
- 1037 [6] R. B. Bird, W. E. Stewart, and E. N. Lightfoot. *Transport Phenomena*,
1038 *2nd Edition*. Wiley, New York, 2002.
- 1039 [7] J. Birkholzer, J. Houseworth, and C. Tsang. Geologic disposal of high-
1040 level radioactive waste: status, key issues, and trends. *The Annual*
1041 *Review of Environment and Resources*, 37:79–106, 2012.
- 1042 [8] N. Chapman and A. Hooper. The disposal of radioactive wastes under-
1043 ground. *Proceedings of the Geologists’ Association*, 123(1):46–63, 2012.

- 1044 [9] S. R. De Groot and P. Mazur. *Non-equilibrium Thermodynamics*. Dover,
1045 New York, 1984.
- 1046 [10] R. A. Freeze and J. A. Cherry. *Groundwater*. Prentice-Hall, Inc., En-
1047 glewood Cliffs, NJ, 1979.
- 1048 [11] W. G. Gray and C. T. Miller. Thermodynamically constrained aver-
1049 aging theory approach for modeling flow and transport phenomena in
1050 porous medium systems: 1. Motivation and overview. *Advances in Wa-*
1051 *ter Resources*, 28(2):161–180, 2005.
- 1052 [12] W. G. Gray and C. T. Miller. Thermodynamically constrained aver-
1053 aging theory approach for modeling flow and transport phenomena in
1054 porous medium systems: 3. Single-fluid-phase flow. *Advances in Water*
1055 *Resources*, 29(11):1745–1765, 2006.
- 1056 [13] W. G. Gray and C. T. Miller. Thermodynamically constrained averaging
1057 theory approach for modeling flow and transport phenomena in porous
1058 medium systems: 5. Single-fluid-phase transport. *Advances in Water*
1059 *Resources*, 32(5):681–711, 2009.
- 1060 [14] W. G. Gray and C. T. Miller. Thermodynamically constrained averaging
1061 theory approach for heat transport in single-fluid-phase porous media
1062 systems. *Journal of Heat Transfer*, 131(10):101002, 2009.
- 1063 [15] W. G. Gray and C. T. Miller. Thermodynamically constrained averaging
1064 theory approach for modeling flow and transport phenomena in porous
1065 medium systems: 7. Single-phase megascale flow models. *Advances in*
1066 *Water Resources*, 32(8):1121–1142, 2009.

- 1067 [16] W. G. Gray and C. T. Miller. Thermodynamically constrained averaging
1068 theory approach for modeling flow and transport phenomena in porous
1069 medium systems: 8. Interface and common curve dynamics. *Advances*
1070 *in Water Resources*, 33(12):1427–1443, 2010.
- 1071 [17] W. G. Gray and C. T. Miller. TCAT analysis of capillary pressure in
1072 non-equilibrium, two-fluid-phase, porous medium systems. *Advances in*
1073 *Water Research*, 34(6):770–778, 2011.
- 1074 [18] W. G. Gray and C. T. Miller. *Introduction to the Thermodynamically*
1075 *Constrained Averaging Theory for Porous Medium Systems*. Springer,
1076 2014.
- 1077 [19] W. G. Gray, C. T. Miller, and B. A. Schrefler. Averaging theory for de-
1078 scription of environmental problems: What have we learned? *Advances*
1079 *in Water Resources*, 51:123–138, 2013.
- 1080 [20] W. G. Gray, C. T. Miller, and B. A. Schrefler. Response to comment
1081 on "Averaging theory for description of environmental problems: What
1082 have we learned?". *Advances in Water Resources*, 52:331–333, 2013.
- 1083 [21] S. M. Hassanizadeh. On the transient non-Fickian dispersion theory.
1084 *Transport in Porous Media*, 23(1):107–124, 1996.
- 1085 [22] S. M. Hassanizadeh and W. G. Gray. Mechanics and thermodynamics
1086 of multiphase flow in porous media including interphase boundaries.
1087 *Advances in Water Resources*, 13(4):169–186, 1990.
- 1088 [23] S. M. Hassanizadeh and W. G. Gray. Toward an improved description

- 1089 of the physics of two-phase flow. *Advances in Water Resources*, 16(1):
1090 53–67, 1993.
- 1091 [24] S. M. Hassanizadeh and A. Leijnse. A non-linear theory of high-
1092 concentration-gradient dispersion in porous media. *Advances in Water*
1093 *Resources*, 18(4):203–215, 1995.
- 1094 [25] S. M. Hassanizadeh and T. Leijnse. On the modeling of brine transport
1095 in porous media. *Water Resources Research*, 24(3):321–330, 1988.
- 1096 [26] S. M. Hassanizadeh, M. A. Celia, and H. K. Dahle. Dynamic effect in the
1097 capillary pressure-saturation relationship and its impact on unsaturated
1098 flow. *Vadose Zone Journal*, 1:38–57, 2002.
- 1099 [27] R. Helmig. *Multiphase Flow and Transport Processes in the Subsur-*
1100 *face: A Contribution to the Modeling of Hydrosystems*. Springer-Verlag,
1101 Berlin, 1997.
- 1102 [28] A. B. S. Jackson, C. T. Miller, and W. G. Gray. Thermodynamically
1103 constrained averaging theory approach for modeling flow and transport
1104 phenomena in porous medium systems: 6. Two-fluid-phase flow. *Ad-*
1105 *vances in Water Resources*, 32(6):779–795, 2009.
- 1106 [29] A. S. Jackson, I. Rybak, R. Helmig, W. G. Gray, and C. T. Miller. Ther-
1107 modynamically constrained averaging theory approach for modeling flow
1108 and transport phenomena in porous medium systems: 9. Transition re-
1109 gion models. *Advances Water Resources*, 42:71–90, 2012.
- 1110 [30] L. W. Lake. *Enhanced Oil Recovery*. Prentice Hall, Englewood Cliffs,
1111 NJ, 1989.

- 1112 [31] C. T. Miller and W. G. Gray. Thermodynamically constrained averaging
1113 theory approach for modeling flow and transport phenomena in porous
1114 medium systems: 2. Foundation. *Advances in Water Resources*, 28(2):
1115 181–202, 2005.
- 1116 [32] C. T. Miller and W. G. Gray. Thermodynamically constrained averaging
1117 theory approach for modeling flow and transport phenomena in porous
1118 medium systems: 4. Species transport fundamentals. *Advances in Water*
1119 *Resources*, 31(3):577–597, 2008.
- 1120 [33] J. M. Nordbotten and M. A. Celia. *Geological Storage of CO₂: Modeling*
1121 *Approaches for Large-Scale Simulation*. John Wiley & Sons, 2012.
- 1122 [34] K. Vafai. *Porous Media: Applications in Biological Systems and Biotech-*
1123 *nology*. CRC Press, 2011.
- 1124 [35] C. J. van Duijn, L. A. Peletier, and R. J. Schotting. Brine transport
1125 in porous media:self-similar solutions. *Advances in Water Resources*, 22
1126 (3):285–297, 1998.
- 1127 [36] R. J. Wakeman and S. Tarleton. *Solid/Liquid Separation: Principles of*
1128 *Industrial Filtration*. Elsevier Science & Technology, 2005.
- 1129 [37] V. P. Zhdanov. Electrochemical reactions on catalyst particles with
1130 three-phase boundaries. *Physical Review E*, 67:042601, 2003.