Abstract

AN INTEGRAL CONTINUUM APPROACH TO THE FORMULATION OF FLOW AND TRANSPORT EQUATIONS IN POROUS MEDIA SYSTEMS

by

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Standard approaches exist in many fields of science and engineering for the description of multiphase flow and transport phenomena in porous media; we focus on multiphase subsurface systems in this work. The common approach to the formulation of balance equations for such systems is limited by several inconsistencies and approximations that affect the accuracy of these formulations in a manner and to an extent that is not well understood. The constitutive relations traditionally applied have evolved under restrictive assumptions and conditions yet are routinely applied to systems that are much different. Additionally, paradoxes exist in the commonly applied constitutive relations.

The integral continuum approach yields a complete formal averaging formulation of mass, momentum, and energy balance laws for volumes, interfaces, and contact lines. This formulation can be constrained by entropy balance relations to yield a more complete and thermodynamically consistent description of multiphase flow and transport phenomena than is available through standard approaches.

In this work, we: (1) review the standard approach for modeling multiphase flow and transport, noting inconsistencies and limitations; (2) outline the integral continuum approach at the microscale and macroscale; (4) compare and contrast the balance equations resulting from the approaches; (5) derive integral continuum balance equations, formally averaged from the microscale to the macroscale, for volumes,

interfaces, and contact lines; (6) apply the integral continuum balance equations to a two fluid-phase subsurface system; (7) constrain the application thermodynamically utilizing the methodology of *Coleman and Noll* [1963]; and (8) comment on the unresolved issues facing the application of integral continuum approaches, noting promising approaches for the resolution of these issues.

An Ode to Coffee

Coffee is the beverage of the people of God, and the cordial of his servants who thirst for wisdom. When coffee is infused into the bowl, it exhales the odor of musk, and is of the color of ink. The truth is not known except to the wise, who drink it from the foaming coffee cup. God has deprived fools of coffee, who with invincible obstinacy condemn it as injurious. In it will we drown our adversities, and in its fire our sorrows.

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Notation

Roman Letters

$a^{\alpha\beta}$	specific surface area, amount of $\alpha\beta$-interface per unit volume $[L^{-1}]$
A	physical surface of the interface $[L^2]$
A^α	Helmholtz free energy of the α-phase, $A^\alpha = E^\alpha_\psi - T^\alpha\eta^\alpha$ $[L^2T^{-2}]$
$A^{\alpha\beta}$	Helmholtz free energy of the $\alpha\beta$-interface, $A^{\alpha\beta} = E^{\alpha\beta}_\psi - T^{\alpha\beta}\eta^{\alpha\beta}$ $[L^2T^{-2}]$
$\mathcal{A}$	closed surface of integration $[L^2]$
$\mathcal{A}_{\alpha\alpha}$	surface at the external boundary of $\mathcal{V}_\alpha$ that coincides with the α-phase $[L^2]$
$\mathcal{A}_{\alpha\beta}$	surface at the interface between the α- and β-phases $[L^2]$
b^α	external entropy source term for the α-phase $[L^2T^{-3}K^{-1}]$
$b^{\alpha\beta}$	external entropy source term for the $\alpha\beta$-interface $[L^2T^{-3}K^{-1}]$
$b^{\alpha\beta\gamma}$	external entropy source term for the $\alpha\beta\gamma$ contact line $[L^2T^{-3}K^{-1}]$
C	indicating length of curve formed at the intersection of three phases $[L]$
$\mathcal{C}_{\alpha\beta}$	curve formed between the $\alpha\beta$-interface and the boundary of $\mathcal{V}$ $[L]$
$\mathcal{C}_{\alpha\beta\gamma}$	curve formed at the intersection of three phases $[L]$
d	indicating the microscale, on the order of 10^{-4} to 10^{-8} meters $[L]$
$\mathbf{D}^\alpha$	deformation rate tensor for the α-phase $[T^{-1}]$
$\mathbf{D}^{\alpha\beta}$	deformation rate tensor for the $\alpha\beta$-interface $[T^{-1}]$
$\mathbf{D}^{\alpha\beta\gamma}$	deformation rate tensor for the $\alpha\beta\gamma$ contact line $[T^{-1}]$

$\hat{e}^{\alpha}_{\alpha\beta}$	transfer of mass from the α-phase to the $\alpha\beta$-interface $[ML^{-3}T^{-1}]$
$\hat{e}^{\alpha\beta}_{\alpha\beta\gamma}$	transfer of mass from the $\alpha\beta$-interface to the $\alpha\beta\gamma$ contact line $[ML^{-3}T^{-1}]$
$\hat{e}^{\alpha\beta\gamma}_{\alpha\beta\gamma\lambda}$	transfer of mass from the $\alpha\beta\gamma$ contact line to the internal end-point $[ML^{-3}T^{-1}]$
E_{ψ}	total potential and kinetic energy in $\mathcal{V}$ $[L^2T^{-2}]$
$E^{\alpha\beta}_{\psi}$	total potential and kinetic energy in $\mathcal{A}$ $[L^2T^{-2}]$
$E^{\alpha\beta\gamma}_{\psi}$	total potential and kinetic energy in $\mathcal{C}$ $[L^2T^{-2}]$
$\mathbf{E}^s$	Lagrangian strain tensor of the solid phase $[-]$
$\mathbf{f}$	vector function of interest used for examples $[-]$
$\mathbf{f}^{\alpha\beta}$	vector function on a surface $[-]$
$\mathbf{f}^{\alpha\beta\gamma}$	vector function of a curve $[-]$
g	scalar function of interest used for examples $[-]$
$\mathbf{g}$	gravitational acceleration $[LT^{-2}]$
$\overline{g}^{\alpha}$	mass weighted average of the α-phase for the function g $[-]$
$\tilde{g}^{\alpha}$	fluctuation of the α-phase for the function g about some mean value $[-]$
$\langle g\rangle^{\alpha}$	volume average of the α-phase for the function g $[-]$
h	scalar function of interest used for examples $[-]$
$h_{\mathcal{V}1}$	represent an extensive fluid property such as mass, momentum, energy, or entropy within the volumes $\mathcal{V}1$
h^{α}	external supply of energy for the α-phase $[L^2T^{-3}]$
$h^{\alpha\beta}$	external supply of energy for the $\alpha\beta$-interface $[L^2T^{-3}]$
$h^{\alpha\beta\gamma}$	external supply of energy for the $\alpha\beta\gamma$ contact line $[L^2T^{-3}]$
$\hat{i}^{\alpha}_{\alpha\beta}$	non-advective flux of mass from the α-phase to the $\alpha\beta$-interface $[ML^{-3}T^{-1}]$
$\hat{i}^{\alpha\beta}_{\alpha\beta\gamma}$	non-advective flux of mass from the $\alpha\beta$-interface to the $\alpha\beta\gamma$ contact line $[ML^{-3}T^{-1}]$
$\hat{e}^{\alpha\beta\gamma}_{\alpha\beta\gamma\lambda}$	non-advective flux from the $\alpha\beta\gamma$ contact line to the internal end-point $[ML^{-3}T^{-1}]$

$\mathbf{I}$	unit isotropic tensor [−]
$\mathcal{I}_\alpha^\iota$	interphase mass transfer rate of species ι to the α-phase $[ML^{-3}T^{-1}]$
$\mathcal{I}_m^\alpha$	interphase exchange of momentum $[ML^{-2}T^{-2}]$
$\hat{I}_{\alpha\beta}^{\alpha}$	non-convective interaction between the α-phase and the $\alpha\beta$-interface [−]
$\hat{I}_{\alpha\beta\gamma}^{\alpha\beta}$	non-convective interaction between the $\alpha\beta$-interface and the $\alpha\beta\gamma$ contact line [−]
$\mathbf{j}$	non-advective flux $[ML^{-2}\mathrm{T}^{-1}]$
$\mathbf{j}_\alpha^\iota$	non-advective flux vector for species ι in the α-phase $[ML^{-2}T^{-1}]$
$\mathbf{j}_\psi$	non-advective flux of ψ across volume boundary $[\mathrm{T}^{-1}\mathrm{L}^{-}2]$
$\mathbf{j}_\psi^{\alpha\beta}$	non-advective flux of ψ across $\alpha\beta$-interface boundary $[\mathrm{T}^{-1}\mathrm{L}^{-}2]$
$\mathbf{j}_\psi^{\alpha\beta\gamma}$	non-advective flux of ψ across $\alpha\beta\gamma$ contact line boundary $[\mathrm{T}^{-1}\mathrm{L}^{-}2]$
k	intrinsic permeability of porous media $[L^2]$
k^*	scaled intrinsic permeability of porous media $[L^2]$
k^α	effective permeability of porous media to α phase $[L^2]$
$k^{r\alpha}$	relative permeability of porous media to α phase [−]
K^e	effective hydraulic conductivity $[LT^{-1}]$
K^g	geometric mean hydraulic conductivity $[LT^{-1}]$
$\mathbf{k}$	permeability tensor $[LT^{-1}]$
$\mathbf{K}$	multiphase relative permeability tensor $[LT^{-1}]$
l	indicating the macroscale, on the order of 10^{-1} to 10^{-4} meters $[L]$
$\mathbf{l}^{\alpha\beta}$	unit vector tangent to the surface and tangent to a curve, therefore being orthogonal to $\mathbf{n}^{\alpha\beta}$ $[L]$
$\mathbf{l}^*$	unit vector tangent to the curve $C_{\alpha\beta\gamma}$ at its endpoints within $\mathcal{V}$, positive in the direction out from the curve such that $\mathbf{l} \cdot \mathbf{l}^* = \pm 1$ $[L]$
$l^{\alpha\beta\gamma}$	specific length of the $\alpha\beta\gamma$-contact line, $C_{\alpha\beta\gamma}$, per unit volume $[L]$

L	indicating the megascale, on the order of tens of meters $[L]$
m	empirical parameter in van Genuchten p-S model $[-]$
M^{α}	mass of the α-phase $[M]$
$M^{\alpha\beta}$	mass of the $\alpha\beta$-interface $[M]$
n	empirical parameter in van Genuchten p-S model $[-]$
n_d	number of spatial dimensions $[-]$
n_p	number of phases $[-]$
n_s	number of species $[-]$
$\mathbf{n}^{\alpha}$	unit vector normal to the surface pointing outward $[L]$
$\mathbf{n}_b^{\alpha}$	unit vector normal to the α-phase volume, occurring at the REV boundary $(\mathcal{A}_{\alpha\alpha})$ pointing outward from the α-phase $[L]$
$\mathbf{n}^{\alpha\beta}$	unit vector tangent to the surface and normal to the $\alpha\beta\gamma$-contact line $[L]$
$\mathbf{n}_b^{\alpha\beta}$	unit vector tangent to the surface and normal to the surface boundary line $(C_{\alpha\beta})$ pointing outward $[L]$
$\mathbf{n}^{\alpha\beta\gamma}$	unit vector tangent to the curve $C_{\alpha\beta\gamma}$ at its endpoints within the REV
$\mathbf{n}_b^{\alpha\beta\gamma}$	unit vector tangent to the curve $C_{\alpha\beta\gamma}$ at its endpoints at the boundary of the REV
$\hat{\mathbf{n}}_{\alpha\beta}^{\alpha}$	entropy transfer from the α-phase to the $\alpha\beta$-interface $[ML^{-1}T^{-3}]$
$\hat{\mathbf{n}}_{\alpha\beta\gamma}^{\alpha\beta}$	entropy transfer from the $\alpha\beta$-interface to the $\alpha\beta\gamma$ contact line $[ML^{-1}T^{-3}]$
$\hat{\mathbf{n}}_{\alpha\beta\gamma\lambda}^{\alpha\beta\gamma}$	entropy transfer from the $\alpha\beta\gamma$ contact line to the internal end-point $[ML^{-1}T^{-3}]$
N	newton, measure of force $[MLT^{-2}]$
N	particle number $[-]$
$\mathbf{m}$	unit vector tangent to the surface and directed outward normal to a curve of interest $[L]$
p	pressure $[ML^{-1}\mathrm{T}^{-2}]$

p^{na}	capillary pressure, pressure of the non-wetting fluid minus the pressure of the wetting fluid $[ML^{-1}\mathrm{T}^{-2}]$
p^c	capillary pressure as defined in Eq. (5.108) $[ML^{-1}\mathrm{T}^{-2}]$
p^α	α-phase pressure $[ML^{-1}T^{-2}]$
$p^{\alpha\beta}$	pressure of the $\alpha\beta$-interface $[MT^{-2}]$
$p^{\alpha\beta\gamma}$	pressure of the $\alpha\beta\gamma$ contact line $[ML^{1}T^{-2}]$
$\mathcal{P}_{\alpha\beta\gamma}$	endpoints of $\mathcal{C}_{\alpha\beta\gamma}$ that are caused by the edge of $\mathcal{V}$ $[-]$
$\mathcal{P}_{\alpha\beta\gamma\lambda}$	internal endpoints of $\mathcal{C}_{\alpha\beta\gamma}$ $[-]$
$\mathcal{P}$	production of ψ within control volume $[M^{-1}]$
Pa	Pascal, measure of force per area $[ML^{-1}\mathrm{T}^{-2}]$
q	heat transferred to the system, $\delta q = T\eta$ $[L^2T^{-2}]$
$\hat{q}^{\alpha}_{\alpha\beta}$	heat transfer from the α-phase to the $\alpha\beta$-interface $[ML^{-1}T^{-3}]$
$\hat{q}^{*\alpha}_{\alpha\beta}$	heat and momentum transfer from the α-phase to the $\alpha\beta$-interface $[ML^{-1}T^{-3}]$
$\hat{q}^{\alpha\beta}_{\alpha\beta\gamma}$	heat transfer from the $\alpha\beta$-interface to the $\alpha\beta\gamma$ contact line $[ML^{-1}T^{-3}]$
$\hat{q}^{*\alpha\beta}_{\alpha\beta\gamma}$	heat and momentum transfer from the $\alpha\beta$-interface to the $\alpha\beta\gamma$ contact line $[ML^{-1}T^{-3}]$
$\hat{q}^{\alpha\beta\gamma}_{\alpha\beta\gamma\lambda}$	heat transfer from the $\alpha\beta\gamma$ contact line to the internal end-point $[ML^{-1}T^{-3}]$
$\hat{q}^{*\alpha\beta\gamma}_{\alpha\beta\gamma\lambda}$	heat and momentum transfer from the $\alpha\beta\gamma$ contact line to the internal end-point $[ML^{-1}T^{-3}]$
$\breve{q}$	electrical charge $[M^{-1}]$
$\mathbf{q}^\alpha_d$	darcy velocity of the α-phase, $\mathbf{q}^\alpha_d = \varepsilon\, s^\alpha\, \mathbf{v}^\alpha$ $[LT^{-1}]$
$\mathbf{q}^\alpha$	heat flux vector for the α-phase $[MT^{-3}]$
$\mathbf{q}^{\alpha\beta}$	heat flux vector for the $\alpha\beta$-interface $[MT^{-3}]$
$\mathbf{q}^{\alpha\beta\gamma}$	heat flux vector for the $\alpha\beta\gamma$ contact line $[MT^{-3}]$
$\mathbf{r}$	spatial position vector $\mathbf{r} = \mathbf{i}x + \mathbf{j}y + \mathbf{k}z$ $[L]$

$\mathbf{R}$	material position vector $\mathbf{R} = \mathbf{i}X + \mathbf{j}Y + \mathbf{k}Z$ $[L]$
$\mathbf{R}$	tensor of viscous drag forces $[MT^{-2}]$
$\mathbf{R}_{\mathbf{a}}^{\alpha}$	drag forces between the α-phase and the aqueous phase $[MT^{-2}]$
$\mathbf{R}^{\alpha\alpha}$	drag forces between the α-phase and the fixed solid phase $[MT^{-2}]$
$\mathbf{R}^{\alpha\beta}$	drag forces between the α-phase and the β-phase $[MT^{-2}]$
$\mathbf{R}_{\gamma\epsilon}^{\alpha\beta}$	drag forces between the $\alpha\beta$-interface and the $\gamma\epsilon$-interface $[MT^{-2}]$
$\mathcal{R}_{\alpha}^{\iota}$	reactions that produce species ι of the α-phase $[ML^{-3}T^{-1}]$
$\mathcal{R}_{e}^{\alpha}$	denotes energy produced in the α-phase from reactions $[ML^{-3}T^{-1}]$
R_s	mass transfer between NAPL and gas $[M]$
s^{α}	saturation of the α-phase $[-]$
S_s	specific storage $[L^{-1}]$
$\mathcal{S}_{\alpha}^{\iota}$	external source of species ι of the α phase $[M^{-1}]$
$\mathcal{S}_{m}^{\alpha}$	momentum transferred to the α-phase by a source (e.g., body forces) $[ML^{-2}T^{-2}]$
t	time $[T]$
$\hat{\mathbf{t}}_{\alpha\beta}^{\alpha}$	momentum transferred from the α-phase to the $\alpha\beta$-interface $[ML^{-1}T^{-2}]$
$\hat{\mathbf{t}}_{\alpha\beta\gamma}^{\alpha\beta}$	momentum transferred from the $\alpha\beta$-interface to the $\alpha\beta\gamma$ contact line $[ML^{-1}T^{-2}]$
$\hat{\mathbf{t}}_{\alpha\beta\gamma\lambda}^{\alpha\beta\gamma}$	momentum transferred from the $\alpha\beta\gamma$ contact line to the internal end point $[ML^{-1}T^{-2}]$
$\mathbf{t}^{\alpha}$	stress vector of the α-phase $[MT^{-2}]$
$\mathbf{t}^{\alpha\beta}$	stress vector of the $\alpha\beta$-interface $[MLT^{-2}]$
$\mathbf{t}^{\alpha\beta\gamma}$	stress vector of the $\alpha\beta\gamma$ contact line $[ML^{2}T^{-2}]$
T^{α}	temperature of the α-phase $[K]$
$T^{\alpha\beta}$	temperature of the $\alpha\beta$-interface $[K]$
$T^{\alpha\beta\gamma}$	temperature of the $\alpha\beta\gamma$ contact line $[K]$

$\mathbf{T}^{\alpha}$	stress tensor of the α-phase $[MT^{-2}]$
$\mathbf{T}^{\alpha\beta}$	stress tensor of the $\alpha\beta$-interface $[MLT^{-2}]$
$\mathbf{T}^{\alpha\beta\gamma}$	stress tensor of the $\alpha\beta\gamma$ contact line $[MLT^{-2}]$
$\mathbf{T}^{s}_{e}$	effective stress tensor for the solid phase $[MLT^{-2}]$
$\mathbf{v}$	velocity of the α-phase $[LT^{-1}]$
v^{α}	magnitude of the α-phase velocity vector $[L]$
$v^{\alpha\beta}$	magnitude of the $\alpha\beta$-interface velocity vector $[L]$
$v^{\alpha\beta\gamma}$	magnitude of the $\alpha\beta\gamma$ contact line velocity vector $[L]$
$\mathbf{v}^{\alpha\beta}$	velocity of the $\alpha\beta$-interface $[LT^{-1}]$
$\mathbf{v}^{\alpha\beta}_{\mathbf{b}}$	velocity of the boundary of the $\alpha\beta$-interface which is caused at the intersection of the interface and the edge of $\mathcal{V}$ $[LT^{-1}]$
$\mathbf{v}^{\alpha\beta\gamma}$	velocity of the $\alpha\beta\gamma$-contact line $[LT^{-1}]$
$\mathbf{v}^{\alpha\beta\gamma}_{b}$	velocity of $\mathcal{P}_{\alpha\beta\gamma}$ at the REV boundary of the $\alpha\beta$-interface $[LT^{-1}]$
$\mathbf{v}^{\alpha\beta\gamma\lambda}$	velocity of the point $\mathcal{P}_{\alpha\beta\gamma\lambda}$ $[LT^{-1}]$
V	volume $[L^3]$
$\mathcal{V}$	domains for integration about volumes $[L^3]$
w	work done by the system $[ML^2T^{-2}]$
$\mathbf{x}$	position vector $[L]$
x, y, z	spatial coordinates $[L]$
X, Y, Z	material position coordinates $[L]$
$\mathbf{z}$	unit vector in the upward direction $[L]$

Greek Letters

β	compressibility $[M^{-1}LT^2]$
ε	porosity $[-]$

ε^α	volume fraction of the α-phase $[-]$
η^α	entropy of the α-phase $[L^2T^{-2}K-1]$
$\eta^{\alpha\beta}$	entropy of the $\alpha\beta$-interface $[L^2T^{-2}K-1]$
$\eta^{\alpha\beta\gamma}$	entropy of the $\alpha\beta\gamma$ contact line $[L^2T^{-2}K-1]$
Λ	total entropy of the system $[L^2T^{-2}K-1]$
Λ^α	entropy production for the α-phase $[L^2T^{-2}K-1]$
$\Lambda^{\alpha\beta}$	entropy production for the $\alpha\beta$-interface $[L^2T^{-2}K-1]$
$\Lambda^{\alpha\beta\gamma}$	entropy production for the $\alpha\beta\gamma$ contact line $[L^2T^{-2}K-1]$
μ	chemical potential $[ML^2T^{-2}]$
μ^α	dynamic viscosity of the α-phase $[ML^{-1}T^{-1}]$
ν^α	kinematic viscosity of the α-phase $[L^2T^{-1}]$
ω_α^ι	mass fraction of species ι in the α-phase $[-]$
ϕ	electric potential $[ML^2T^{-2}]$
$\boldsymbol{\phi}^\alpha$	entropy flux vector for the α-phase $[MT^{-3}K]$
$\boldsymbol{\phi}^{\alpha\beta}$	entropy flux vector for the $\alpha\beta$-interface $[MT^{-3}K]$
$\boldsymbol{\phi}^{\alpha\beta}$	entropy flux vector for the $\alpha\beta\gamma$ contact line $[MT^{-3}K]$
Φ	pressure head which includes both pressure and gravity potentials $[L]$
ρ^α	mass density of the α-phase $[ML^{-3}]$
$\rho^{\alpha\beta}$	mass density of the $\alpha\beta$-interface $[ML^{-2}]$
$\rho^{\alpha\beta\gamma}$	mass density of the $\alpha\beta\gamma$ contact line $[ML^{-1}]$
ψ	scalar single fluid phase property $[M^{-1}]$
$\boldsymbol{\psi}$	vector single fluid phase property $[M^{-1}]$
Ω	wettability potential $[-]$
ω	mass fraction $[-]$
$\boldsymbol{\tau}^\alpha$	non-equilibrium portion of the momentum equation for the α-phase $[ML^{-1}T^{-2}]$

$\tau^{\alpha\beta}$	non-equilibrium portion of the momentum equation for the $\alpha\beta$-interface $[ML^{-1}T^{-2}]$

Roman Subscripts/Superscripts

a	aqueous-phase quantity
an	the aqueous-NAPL interface
as	the aqueous-solid interface
b	indicating a quantity on the boundary
e	energy qualifier
eq	equilibrium conditions
g	gas-phase quantity
le	linear-equilibrium conditions
m	microemulsion-phase quantity
m	momentum qualifier
n	nonaqueous-phase quantity
ne	non-equilibrium conditions
ns	the NAPL-solid interface
nw	nonwetting-phase quantity
s	solid-phase quantity
t	total liquid-phase quantity
T	transpose of a tensoral quantity
T	indicating a quantity at a constant temperature
w	wetting-phase quantity
wr	residual wetting-phase quantity

Greek Subscripts/Superscripts

α	phase qualifier
$\alpha\beta$	interface qualifier between the α and β phases
$\alpha\beta\gamma$	contact line qualifier between the α, β, and γ phases
$\alpha\beta\gamma\lambda$	endpoint of the $\alpha\beta\gamma$ contact line
$\alpha, \alpha\beta$	indicates variable at the interface subtracted for variable at the volume
ι	species qualifier

Abbreviations

BC	Brooks-Corey [*Brooks and Corey*, 1966] pressure-saturation relation
BD	Burdine's [*Burdine*, 1953] relative permeability model
C	Corey's [*Corey*, 1954] p−S−k relationship
Co	Coats' [*Coats*, 1980] p−S−k relationship
Comp	compressibility
Dim	dimensions
DCA	differential continuum approach
DNAPL	dense nonaqueous-phase liquid (denser than water)
E	Eckberg's [*Brooks and Corey*, 1966] *S-k* relationship
EOS	equation of state
FO	first-order interphase mass transfer relation
h-VG	hysteretic van Genuchten pressure-saturation relation
ICA	integral continuum approach
IMT	interphase mass transfer
Immob	immobile
KP	Kool and Parker's [*Kool and Parker*, 1987] p−S−k relationship

LE	local equilibrium
LHS	left hand side of an equation
LNAPL	light nonaqueous phase liquid (less dense than water)
LP	Lenhard and Parker's [*Lenhard and Parker*, 1987a, 1987b] p−S−k relationship
LV	Luckner, van Genuchten, and Nielsen p−S−k relationship
M	Mualem's [*Mualem*, 1976] relative permeability model
Mob	mobile
MPFT	multiphase flow and transport
NAPL	nonaqueous phase liquid
NWP	nonwetting phase
na	not applicable
ns	not specified
ODE	ordinary differential equation
P	Parker's [*Parker*, 1989] p−S−k relationship
PDE	partial differential equation
PLH	Pope, Lake, and Hirasaki p−S−k models
p−S	pressure-saturation relation
p−S−k	pressure-saturation-permeability relation
REV	representative elementary volume
RHS	right hand side of an equation
SFM	sharp-front model
S	Stone's p−S relation
S−k	saturation-permeability relation
t S−k	tabulated saturation-permeability relation

t p−S	tabulated pressure-saturation relation
VG	van Genuchten's [*van Genuchten et al.*, 1991] p−S relation

Mathematical Notation

f	a scalar
$\mathbf{f}$	a vector, boldface lower case
$\mathbf{F}$	a tensor, boldface upper case
$\hat{e}$	hat indicating a mass exchange term
$\overline{h}$	mean value of h
$\tilde{h}$	fluctuation of h about some mean value
$\langle\psi\rangle^{\alpha}$	volume average of ψ
$\overline{\psi}^{\alpha}$	mass average of ψ
$\langle\psi\rangle^{\alpha\beta}$	surface average of ψ
$\overline{\psi}^{\alpha\beta}$	mass average over surface of ψ
$\langle\psi\rangle^{\alpha\beta\gamma}$	contact line average of ψ
$\overline{\psi}^{\alpha\beta\gamma}$	mass average over contact line of ψ
$\cdot$	scalar dot product
$:$	tensor dot product
$\nabla\cdot$	divergence operator
∇	gradient operator
∇^{*}	indicates that differentiation takes place with respect to the material reference coordinates
$\dot{(\ )}$	simplified form of the material derivative with respect to the motion of the solid phase
$[\ ]_{ne}$	quantities which will be zero under non-equilibrium conditions

$[\ ]_{eq}$	quantities which will be zero under equilibrium conditions
$[\ ]_{lt}$	quantities which will be zero assuming linear theory at near equilibrium conditions
$\frac{D^{\alpha}\psi}{Dt}$	material derivative relative to the motion of the α-phase
$\frac{D^{\alpha\beta}\psi}{Dt}$	material derivative relative to the motion of the $\alpha\beta$-interface
$\frac{D^{\alpha\beta\gamma}\psi}{Dt}$	material derivative relative to the motion of the $\alpha\beta\gamma$-contact line
Δ	change in

Chapter 1

Introduction

"Very great rivers flow underground." Leonardo DaVinci

Groundwater is a valuable source of fresh water. As with any resource, groundwater is studied in an effort to optimize its benefits. The benefits of groundwater include a drinking water source, an irrigation source, and an industrial water source. Contaminants compromise these benefits to varying degrees depending upon the type of contaminant and the final use of the groundwater. To continue to utilize groundwater as a resource, engineers have studied the mechanics of groundwater flow and the movement of contaminants (transport). We first overview the standard approach for describing groundwater flow and transport and then investigate alternative approaches.

Groundwater has been used as a source of potable water since early biblical times. Despite the long history of water use, many misconceptions, from scientists as brilliant as Leonardo DaVinci, have prevailed in the imprecise physical description of fluids that flow through the pore spaces of granular material. The flow of a single fluid through porous media is the simplest to consider, yet is a very complex physical process. Moreover, the flow of multiple fluids coupled with the movement of dissolved chemical components (multiphase flow and transport) through porous media are problems of even greater complexity and importance [*Abriola and Pinder*, 1985a;

Parker and Lenhard, 1989; *Falta et al.*, 1992a]. However difficult the description of these systems may be, solutions will benefit society in many ways.

The flow of both single and multiple fluids through porous media is an issue in many fields of science. Hydrologists seek to quantify groundwater resources and potential water production. Petroleum engineers attempt to define the flow of multiple fluids and the movement of multiple components in order to maximize oil recovery. Environmental engineers are faced with the task of predicting the flow of multiple fluids and the movement of multiple components in order to design effective contaminant remediation schemes. An improved understanding of multiphase flow and transport will benefit all of these fields.

In order to understand the flow of fluids through porous media, physical equations have been constructed to describe the system. Common approaches exist for this description of fluid flow. Simplified analytical expressions for the flow of a single fluid date back to the early to mid 1900's [*Green and Ampt*, 1911; *Muskat et al.*, 1937; *Welge*, 1952]. These initial mathematical descriptions originated as researchers were motivated to describe roughly homogeneous aquifers that would produce the greatest yields of either petroleum or water. Solutions to the above equations predict bulk, or average, flows with deviations from the bulk flow generally ignored. These formulations take advantage of the fact that many assumptions are permissible when only the bulk flow in uniform aquifers is of concern. However, contaminant remediation problems involving multiphase flow and transport motivate the development of more rigorous descriptions that include deviations from the average flow.

Common approaches also exist for the mathematical description of multiphase flow and transport. Mass and momentum balance equations are written at a prescribed scale for the groundwater system. These equations are then combined with simplifying assumptions and constitutive relationships in order to approximate the movement of water and contaminants in the groundwater system. Multiphase flow and transport models require multiple constitutive relations to close the system of equations. Constitutive relations are approximate and often empirical. These relations increase both the number of equations and the total number of unknowns in the system; however, they supply sufficient information to close the system of equations by describing unknown quantities in terms of measurable parameters. Biological, chemical, and surface effects are also of concern but rigorous descriptions of these processes in groundwater systems do not yet exist for many systems of interest. Energy balances and thermodynamic relations in the groundwater system also lack a complete and rigorous development.

Theories based on conservation equations have been developed that predict the flow of two immiscible fluids [*Bear*, 1972; *Peaceman*, 1977; *Aziz and Settari*, 1979]. Theories that consider not only the flow of multiple fluids but also the movement of dissolved components have been formulated [*Streile and Simmons*, 1986; *Abriola*, 1989]. These common approach use a representative volume, often not specified but assumed to be related to the scale of measurement and a discretization of the system, about which balance equations are written. In order to solve the balance equations, constitutive relations are used to close the system of equations. The differential continuum approach, which will be overviewed in Chapter 3, is the common method for development of field-scale balance equations to predict fluid flow and species transport.

These common approaches used to describe multiphase flow and transport are based upon assumptions that are empirical and not valid for many systems of interest [*Arnold et al.*, 1990; *Gray and Hassanizadeh*, 1991a]. Little attention has been paid to the length-scale of the empirical formulations compared to the length-scale of the solution. A more rigorous and complete approach can be formulated which integrates over a representative elementary volume to produce mass, momentum, and energy balance equations that are formulated about volumes, interfacial areas, and contact lines [*Hassanizadeh and Gray*, 1979a, 1979b, 1980a; *Gray*, 1983; *Gray and Hassanizadeh*, 1991a, 1991b; *Hassanizadeh and Gray*, 1993b]. These balance equations are then supplemented with constitutive relations. The associated constitutive relations are thermodynamically constrained using an entropy inequality, the second law of thermodynamics, and other equilibrium thermodynamic relations [*Coleman and Noll*, 1963; *Hassanizadeh and Gray*, 1980a; *Gray and Hassanizadeh*, 1991b].

The objectives of this work are: (1) to summarize the standard formulations used in the description of fluid flow and species transport in multiphase porous media systems; (2) to outline methods to formulate complete statements of mass, momentum, energy, and entropy transport in single and multiple phase porous media systems; (3) to investigate formulations for a typical two fluid phase system; (4) to compare the proposed formulation with typical formulations; and (5) to suggest approaches for closing the resultant system of equations.

Chapter 2

Background

"My goal is simple. It is complete understanding of the universe, why it is as it is and why it exists at all." Stephen Hawking

2.1 Multiphase Flow and Species Transport

A typical spill scenario of interest to an environmental engineer is depicted in Figure 2.1 (similar depictions can be found in *Abriola and Pinder* [1985a]; *Corapcioglu and Baehr* [1987]; and *Celia et al.* [1993]). A spill event introduces multiple contaminants into the subsurface allowing the contaminants to be transported vertically toward the saturated zone, leading to multiphase flow and transport (MPFT). These contaminants may be soluble in water and become a component of the aqueous phase or may be highly insoluble in water and form a non-aqueous phase liquid (NAPL). Many released contaminants are toxic and pose a long-term health risk to drinking water supplies if left untreated. In light of the harmful consequences, the engineer is motivated to understand these complex system.

Spilled contaminants of large enough volume will flow downward by gravity. Some lateral movement will accompany the vertical flow. Residual contaminants may be trapped in void spaces by capillary forces as the bulk flow migrates down. Air, the

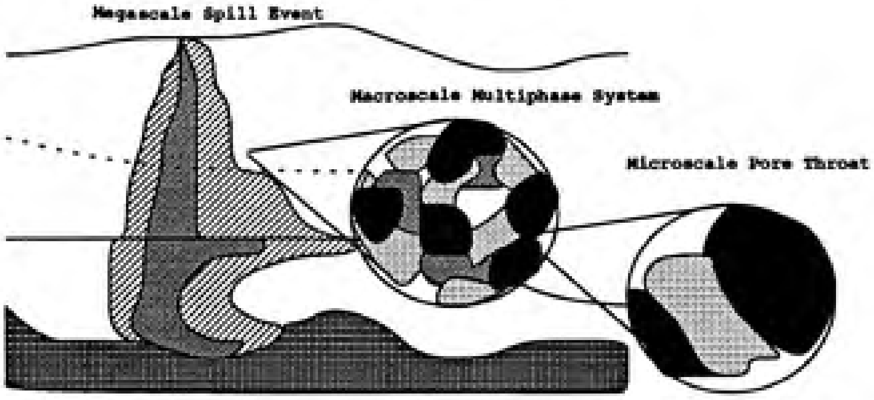


Figure 2.1: Depiction of Spill of a Typical Non-Aqueous Phase Liquid at Several Scales

contaminant, and recharge water may all be present in the pore spaces leading to a multiphase system. Volatilization and biodegradation of certain species may also occur over time.

Upon reaching the capillary fringe, an area in which water is held above the groundwater table by capillary forces, horizontal migration may begin depending on the density of the contaminant. NAPL that is less dense than water (LNAPL) will pool at the top of the groundwater table [*Schwille*, 1967; *van Dam*, 1967]. Contaminants may flow as a separate phase or may persist as trapped residual. The NAPL will slowly partition into the aqueous, gas, and solid phases. NAPL that is more dense than water (DNAPL) may flow downward through the saturated zone to the bottom confining layer of the aquifer [*Schwille*, 1988]. The contaminants may flow as a separate phase, persist as trapped residual, or partition into the aqueous phases. DNAPL may flow by gravity in a different direction than the direction of groundwater flow. Also, pools of DNAPL may be found in depressions in the underlying confining layer.

2.2 Modeling Multiphase Systems

The inherent complexity of multiphase systems and the marked heterogeneity that is characteristic of most natural environments [*Dagan*, 1989; *Christakos*, 1992; *Gelhar*, 1993], often over multiple scales [*Cushman*, 1990a], leads to a large and difficult set of problems that must be resolved before accurate simulation of multiphase subsurface transport phenomena can be expected. We know of no work that structures these crucial issues and offers potential approaches for advancement.

The accurate description of fluid flow and contaminant transport in many subsurface multiphase systems requires that consideration be given not only to mass and momentum balances but to energy and entropy constraints [*Hassanizadeh and Gray*, 1979b; *Bear and Bachmat*, 1986]. Furthermore, accurate descriptions require incorporation of physical phenomena that occur over several different length scales [*Plumb and Whitaker*, 1988; *Mayer and Miller*, 1992a; *Gray et al.*, 1993; *Lowry and Miller*, 1995]. Continuum assumptions provide a means of representing microscale phenomena at the macroscale and are necessary to resolve the infinite number of microscale events which affect MPFT [*Bear*, 1972; *Hassanizadeh and Gray*, 1979a; *Baveye and Sposito*, 1984]. Closure of the system of formulated balance equations, which is accomplished by providing equations of state (EOS) and constitutive relations, requires a sufficient number of equations such that all unknowns can be determined.

The accurate solution of field-scale multiphase flow and transport problems, with inherent heterogeneities in the system, is beyond current capabilities due to the overall number of equations which require solution and the number of parameters which need to be measured. Simplifying assumptions are therefore essential. Constitutive relations, used for closure, must be judiciously chosen to allow solution while retaining accuracy.

Typical constitutive relations for multiphase systems include pressure-saturation-permeability (p-S-k), interphase mass transfer, and solute reaction relations. EOS and constitutive relations, in net, supply sufficient information to close the system of equations by expressing unknown quantities in the balance equations in terms of accessible parameters. However, constitutive relationships are approximations of the system and are often tested for only subsets of the domain [*Miller et al.*, 1990; *Powers et al.*, 1992, 1994; *Imhoff et al.*, 1994b]. The use of EOS and constitutive relations is necessary but must be done judiciously.

Taking into consideration the above issues, the differential continuum formulation of MPFT models has become common in both the oil industry [*Peaceman*, 1977; *Aziz and Settari*, 1979; *Trangenstein and Bell*, 1989; *Brown et al.*, 1994; *Khan et al.*, 1994] and the groundwater literature [*Abriola and Pinder*, 1985a, 1985b; *Baehr and Corapcioglu*, 1987; *Corapcioglu and Baehr*, 1987; *Faust et al.*, 1988; *Sleep and Sykes*, 1989; *Celia and Binning*, 1992a, 1992b; *Mayer and Miller*, 1992b; *Sleep and Sykes*, 1993a, 1993b; *Huyakorn et al.*, 1994b]. Despite the difficulties and inaccuracies of averaging small scale phenomena at a larger representative scale [*Cushman*, 1986; *Gray and Hassanizadeh*, 1989; *Cushman*, 1990b; *Gray and Hassanizadeh*, 1991a, 1991b], most of the above formulations utilize a differential continuum description of MPFT.

Differential multiphase continuum approaches that are commonly used in the petroleum and groundwater fields can be grouped into three categories [*Abriola*, 1988]: (1) sharp-front models, (2) models that include capillarity but do not allow for varying composition, and (3) compositional models. The following is a review of the state of the art theoretical approaches used in these three approaches from the groundwater literature with additional references from the petroleum literature. This report will focus on the theory and assumptions that are necessary for a complete formulation of the governing MPFT equations, leaving the large body of literature that focuses on the optimal solution of flow and transport equations for later investigation. Each category of MPFT models is reviewed below with its premises, advantages, and shortcomings.

2.2.1 Sharp-Front Models

The sharp-front model (SFM) is an idealization of the physical system that assumes that fluids are immiscible [*El-Kadi*, 1992, 1994]. Models in the petroleum literature also commonly use the methodology of *Buckley and Leverett* [1941] and assume that the total flow of a system can be treated as a constant. The primary benefit of SFM is the relative ease with which an approximate infiltration solution can be obtained and the few parameters required. However, the SFM is inadequate for heterogeneous systems or for systems undergoing wetting and drainage [*Abriola*, 1988]. SFM prove suitable for preliminary assessment of chemical or NAPL spills [*Huyakorn et al.*, 1994a] but cannot be used to describe species transport or to design remediation schemes [*Pinder and Stothoff*, 1988].

The SFM approach has been applied to water infiltration [*Green and Ampt*, 1911], to salt water intrusion [*Pinder and Stothoff*, 1988], and to estimate the leading and trailing edges of an infiltrating NAPL [*Reible et al.*, 1990; *El-Kadi*, 1992, 1994]. An analytical approach introduced by *Buckley and Leverett* [1941] is widely used in the petroleum field. Other uses and advancements in SFM are noted in Table 2.1.

2.2.2 Multiphase Flow with Capillarity Models

Multiphase flow models which include the effects of capillarity and its affects on bulk fluid motion describe bulk fluid motion with more physically-realistic terms than the SFM. In the environmental field, two-phase flow was first described including capillarity in two dimensions in an effort to model the movement of immiscible contaminants [*Faust*, 1985; *Osborne and Sykes*, 1986]. A static air phase was included to investigate NAPL flow in the unsaturated zone [*Kuppusamy et al.*, 1987; *Celia and Binning*, 1992a]. Hysteretic constitutive relations for p-S-k relationships in two-phase flow were also investigated [*Parker and Lenhard*, 1989]. In the petroleum field, black-oil models consider three flowing phases (aqueous, NAPL, and air) with two components (water and oil) of interest [*Trangenstein and Bell*, 1989]. Table 2.2 references the major contributors to multiphase flow models that include capillarity.

All of the models described above and in Table 2.2 follow a similar methodology [*Abriola*, 1988]. First, differential equations conserving mass are written about a representative volume at the continuum scale. The existing multiphase flow with capillarity models include a balance equation for mass and an approximate momentum balance. Energy and entropy balance are ignored as well as interfaces between phases.

A more theoretically satisfying approach would contain balance equations for

Table 2.1: Sharp-front models

Work	Model Highlights
Green and Ampt [1911]	Sharp-front approximation of water infiltrating air filled pore spaces.
Buckley and Leverett [1941]	Two-phase flow equation that neglects diffusion caused by gravity and capillary forces and assumes that fluids are incompressible.
Welge [1952]	Analytical method for computing average saturation in two-phase flow systems in order to predict oil displacement.
Mull [1971]	Analytical work to access the behavior of fuel oil spills into the subsurface.
Corapcioglu and Hossain [1986]	The analytical work of Buckley and Leverett is extended to a two-dimensional simulation of DNAPL displacing groundwater.
Pinder and Stothoff [1988]	Show that the SFM does not adequately account for regimes of transient behavior.
Odeh [1989]	Incorporates relative permeability as part of a Buckley and Leverett analysis and looks at viscous fingering in one-dimension.
El-Kadi [1992]	SFM for NAPL flow through the unsaturated zone is developed and compared to models that include capillarity.
El-Kadi [1994]	Extends SFM for of initial accumulation and spreading of LNAPL.
Huyakorn et al. [1994a]	Applies vertical equilibrium to examine three dimensional SFM infiltration.
Sarma et al. [1994]	Examines Buckley and Leverett displacement in regards to unstable displacements.

Table 2.2: Multiphase flow with capillarity models

	Flowing		Constitutive Relations	
Work	Phases [a]	Dimensions	Compressibility	p-S-k[b]
[*Faust*, 1985]	a, n	2	a, n, s	BC
[*Faust et al.*, 1989]	a, n	3	a, n, s	BC
[*Kueper and Frind*, 1991]	a, n	2	none	BC
[*Huyakorn et al.*, 1994b]	a, g, n	3	a, g, n, s	VG/S, t S−k

[a] phases: a=aqueous, n=NAPL/oelic, g=gaseous, s=solid

[b] when present, a slash indicates p-S/S-k

BC=Brooks and Corey-type p-S-k relations; VG=van Genuchten p-S relation; S=Stone's three-phase extensions for p-S-k relations; and t S-k = tabulated S-k.

mass, momentum, energy, and entropy about representative elementary volumes, areas, and contact lines; making typical formulations incomplete [*Gray and Hassanizadeh*, 1991a; *Gray et al.*, 1993]. Second, the momentum balance applied in the multiphase flow with capillarity models is the extended form of Darcy's law that relates pressures and velocity. The application of Darcy's law limits the formulations as (1) Darcy's law cannot account for the dissipation of momentum [*Hassanizadeh and Gray*, 1993b], (2) Darcy's law was developed at scales and under conditions that are much different than those which are commonly encountered in multiphase flow [*Scheidegger*, 1974], and (3) Darcy's experiments were conducted with a single fluid while multiphase flow models use an *ad hoc* extension of Darcy's law using a single scaling term to describe the complicated physics of fluid-fluid interfaces [*Kalaydjian*, 1987]. Third, multiphase flow with capillarity models couple fluid saturations and relative permeability through capillary pressures, thereby allowing for a more detailed model than SFM [*Forsyth*, 1991], yet still yielding a variety of inconsistencies [*Gray and Hassanizadeh*, 1991a; *Illangasekara et al.*, 1992]. Additionally, most data from which the constitutive relations are constructed only covers a portion of the domain of interest [*Bear et al.*, 1987; *Parker and Lenhard*, 1990].

Multiphase flow models that include capillarity have proven useful for predicting secondary oil recovery and NAPL movement [*Kuppusamy et al.*, 1987]. These models will not be able to model chemical partitioning and transport, however, as the models are based on the assumption that phase composition is invariant [*Abriola*, 1988]. Furthermore, the equations are summed over all species, therefore the non-advective fluxes of individual species are not quantified. In order to model contaminant transport, balance equations for each chemical component of interest must be written. Such equations form the basis for compositional models, developed specifically to model interphase mass transport, surfactant enhanced fluid recovery, NAPL dissolution, and other chemically complex scenarios present in tertiary oil recovery and contaminant transport.

2.2.3 Compositional Methodology

Compositional models apply mass balance equations for individual components in the subsurface environment. Compositional models vary between the petroleum and environmental fields as the motivation for tracking individual constituents differs. In the petroleum field, the mobilization of oil that remains in the reservoir is profitable. A partial list of applications of compositional models in petroleum engineering are listed in Table 2.3. In the environmental field, the spreading of harmful contaminants is of primary interest. The spill of these contaminants is usually of a small enough nature that the flow of the immiscible fluid is short-lived. Therefore, compositional models are used to describe the spreading of dissolved contaminants often assuming that the NAPL phase is immobile. Applications of compositional models in environmental engineering are listed in Table 2.4.

Interphase mass transfer (IMT), considered in all of the cited compositional models, is a process of central importance for multiphase environmental systems; yet a fundamental understanding of IMT is not well developed. Limited experimental data exists for NAPL-aqueous phase mass transfer, while this process is of major importance. Mass transfer between a single-species residual NAPL and groundwater is commonly described with either local equilibrium (LE) or first-order (FO) rate models.

Table 2.3: Multiphase flow and transport models from the petroleum literature

	Mob./Immob.		Species		Constitutive Relations	
Work	Phases [a]	n_s	Into	Dim.	Comp.	p-S-k [b]
Pope and Nelson, 1978	$a, m, n/s$	6	a, m, n, s	1	*ns*	other / t S-k
Young and Stephenson, 1983	a, g, n	17	a, g, n	1	a, g, n	other
Camilleri *et al.*, 1987	$a, m, n/s$	19	a, m, n, s	3	a, m, n, s	PLH
Bhuyan *et al.*, 1990	$a, m, n/s$	32	a, m, n, s	3	a, g, n, s	BC
Brown *et al.*, 1994	$a, m, n/s$	4	a, m, n, s	3	none	BC
Khan *et al.*, 1994	$a, m, g/n$	7	a, m, g, n	3	a, g, n, s	BC

[a] phases: a=aqueous, n=NAPL/oleic, g=gaseous, m=(micro-)emulsion and s=solid; [b] when present, a slash indicates p-S/S-k; t p-S (or S-k) = tabulated p-S or S-k; *ns* = Not Specified; BC and Co refer to specific p-S-k relations defined in the Notation.

In Tables 2.3 and 2.4, LE models are used with the exceptions of *Sleep and Sykes* [1989]; *Guarnaccia and Pinder* [1992]; and *Mayer and Miller* [1992b]. Compositional descriptions generally utilize LE models that are scalar and independent of flow direction. The assumption of local chemical equilibrium relies on the reasoning that the time required to approach local chemical equilibrium is short in comparison to the rate at which transport occurs. The assumption of local equilibrium presupposes that the solute mass fraction, or concentration, in one phase implies the mass fraction in all other phases. When local equilibrium among phases is assumed, species transport equations may be summed over all phases and solved in terms of a single mass fraction.

However, LE models are empirical in nature, and based upon data that only cover a portion of the domain of interest. As a result, the appropriateness of the common assumption of linear and instantaneous solute component equilibrium among phases is questionable [*Miller and Weber*, 1986; *Sleep and Sykes*, 1989; *Powers et al.*, 1991]. The incorporation of FO rate models provides a more descriptive equilibrium representation.

More attention has been given to aqueous-solid interphase mass transfer (i.e. sorption) with recent reviews by *Brusseau and Rao* [1989] and *Weber et al.* [1991]. However, many complex systems are of interest for which experimental IMT data does not yet exist and therefore the associated constitutive relations may not accurately describe such systems.

In summary, even with the complexity of compositional modeling; many important, yet unresolved, questions in subsurface multiphase flow and transport systems exist. The additional mass and momentum equations written about each phase do not resolve the short-comings noted regarding multiphase flow models that included capillarity. All of the differential continuum approaches are limited by representing microscale processes with empirical macroscale relations. The actual physics cannot be completely described by the empirical relations and the thermodynamic consistency of these approaches cannot be assured.

2.2.4 Summary of Models

The state-of-the-art differential continuum MPFT models published to date are summarized in Tables 2.2, 2.3 and 2.4. These tables are intended to be illustrative of recent approaches taken in the environmental field, as well as a sampling from the petroleum literature. From these tables we can note several common trends in multiphase flow and transport modeling of environmental systems:

1. several two- and three-fluid-phase flow models have been published for both two and three spatial dimension systems;
2. all of the cited multiphase flow models simulate nonhysteretic p-S-k relations;
3. most multiphase flow and transport models in the environmental field use nonhysteretic forms of the p-S-k relations;
4. most models assume local equilibrium, but some first-order mass transfer formulations have been presented; and
5. typical reported simulation sizes are on the order of 10^2 to 10^4 nodes (data not shown in table).

Further examination of the differential continuum approach, which is utilized almost exclusively in the literature, will bring to light some theoretical difficulties which must be understood before more rigorous models can be developed and applied with reliability. The following chapter examines the underpinnings of the differential continuum approaches for modeling multiphase systems.

Table 2.4: Multiphase flow and transport models from the environmental literature

	Mob./Immob.		Species		Constitutive Relations	
Work	Phases [a]	n_s	Into	Dim.	Comp.	p-S-k [b]
Abriola and Pinder, 1985a,b	$a, n_1, n_2/g, s$	1	a, g, n_1	1	a, n_1, n_2	Co
Corapcioglu and Baehr, 1987;	$a/g, n, s$	8	a, g, n, s	1	none	other
Forsyth, 1988	$a, n/g$	1	a, g, n	2	s	other / t S-k
Sleep and Sykes, 1989	$a, g/n$	1	a, g	2	g	VG / BC
Kaluarachchi and Parker, 1990	$a, n/g, s$	2	a, g, n, s	2	a, g, n	P
Falta *et al.*, 1992	$a, g, n/s$	3	a, g, n, s	1	a, g, n	VG / S,C
Guarnaccia and Pinder, 1992	a, n	2	a, n	2	none	h-VG / KP,LV
Mayer and Miller, 1992	a, n	1	a, n	2	a, n	VG / P
Adenekan *et al.*, 1993	$a, g, n/s$	*ns*	a, g, n, s	3	a, g, n, s	C / P
Sleep and Sykes, 1993a,b	a, g, n	3	a, g, n	3	a, g, n	BC,VG / BC,P
Reeves and Abriola, 1994	any 2	3	a, g, n	2	a, g, n	VG / P
van Geel and Sykes, 1994	a, g, n	1	a, g, n	2	a, g, n	h-VG / LP
Sleep, 1995	a, n_1, n_2	3	a, n_1, n_2	1	none	t p-S / E
White *et al.*, 1995; Lenhard *et al.*, 1995	$a, n/g, s$	1	a, g, n, s	3	*ns*	h-VG , LP

[a] phases: a=aqueous, n=NAPL/oleic, g=gaseous, m=(micro-)emulsion and s=solid; [b] when present, a slash indicates p-S/S-k; t p-S (or S-k) = tabulated p-S or S-k; *ns* = Not Specified; BC, C, Co, E, KP, LP, LV, P, PLH, S, and VG refer to specific p-S-k data or relations and are defined in the Notation.

Chapter 3

The Differential Continuum Approach

"Since the measuring device has been constructed by the observer...we have to remember that what we observe is not nature in itself, but nature exposed to our method of questioning." Werner Karl Heisenberg

3.1 Approaches to Modeling Multiphase Systems

It will be useful to establish some terminology and mathematical notation before presenting approaches to modeling multiphase systems.

3.1.1 Length Scales

Three length-scales are of importance in the derivation of governing balance equations for flow and transport through porous media: (1) the microscale, d, (2) the macroscale, l, and (3) the megascale, L. Precise identification of these length scales is very difficult [*Gray et al.*, 1993] however the relations among them are defined as follows:

$$L \gg l \geq d \tag{3.1}$$

The microscale, d, is defined to be above a scale where molecular motion is important and standard fluid mechanics is applicable [*Bear*, 1972]. This is a valid continuum level for a single fluid about which balance equations can be applied. However, in order to write the balance equations, boundary conditions and the exchange of material across those boundaries must be defined and constitutive relations must be formulated at this scale. This is exactly the approach taken by pore-scale models [*Reeves and Celia*, 1996]. The level of information necessary to mathematically describe the complex geometry of each fluid and its respective boundaries severely limits the size of the domain that can be computationally described [*Lowry and Miller*, 1995]. Consequently, a microscale description of multiphase flow and transport in a contaminated aquifer system is precluded.

At the other end of the length spectrum, the megascale, L, provides for no spatial variations within the system [*Gray et al.*, 1993] and would be used to represent geologic layers or other areas that are assumed homogeneous. Thus, in describing geologic layers, the megascale may have varied magnitudes in the horizontal and vertical directions. The megascale describes the average changes that occur within the system as a result of boundary conditions. Megascopic solutions lack detail due to the inherent and complex heterogeneities within porous media systems.

Alternatively, the macroscale, a coarser level of averaging than the microscale and a much finer system than the megascale, is defined as a multiple phase continuum scale in an attempt to circumvent the difficulties associated with the other two scales. A volume at the macroscale must be larger than the microscale so that a sufficient number of pores are included to allow for a meaningful, statistical average of the multiple phases. The volume must also be much smaller than the size of flow domain that is being considered [*Bear*, 1972]. The macroscale is a valid continuum level for multiple fluids about which balance equations can be applied. However, to write balance equations, boundary conditions and the exchange of material across those boundaries must be defined and constitutive relations must be formulated at this scale. The description of boundary conditions and the development of constitutive relations has been completed with varied levels of rigor and accuracy.

The conventional approach for the macroscale derivation of MPFT equations use empirical constitutive theories to close the system of equations. These constitutive theories may violate the laws of thermodynamics and include inconsistencies [*Gray and Hassanizadeh*, 1991a, 1991b; *Hassanizadeh and Gray*, 1993a, 1993b; *Quintard and Whitaker*, 1994; *Miller et al.*, 1996].

As an alternative to the conventional macroscale approach, the integral continuum approach begins at the microscale to utilize the physics of the microscale that are important to the overall macroscale results [*Hassanizadeh and Gray*, 1979a, 1979b; *Cushman*, 1983]. Macroscale equations are derived by integrating microscale quantities over a macroscopic volume [*Slattery*, 1967]. Information at the microscale is averaged and carried forward to the macroscale as opposed to beginning at the macroscale and attempting to back calculate important features from the microscale. Sometimes, there is a tendency to think of the large-scale process as being dominated by the structure of the heterogeneities and that the small-scale phenomena are lost in the averaging procedure. In reality, the mathematics of the method of volume averaging clearly indicates that physical information at one scale is utilized at the next scale but filtered in the process [*Quintard and Whitaker*, 1990].

3.1.2 The Continuum Approach

The continuum approach seeks to define discrete microscale events at the macroscopic scale [*Bear*, 1972; *Bedford and Drumheller*, 1983; *Sahimi*, 1993]. The macroscopic description of flow and transport in porous media rests upon the assumptions that at the macroscale (1) physical properties of the porous media (such as density, porosity, permeability, pressure, etc.) can be associated with mathematical field variables and that (2) the time and space dependence of these field variables can be represented in the form of continuous, differential balance equations for mass, momentum, and energy [*Baveye and Sposito*, 1984]. By assuming the existence of a representative elementary volume (REV), as described by *Bear* [1972], the physical properties of the porous media at the macroscale are postulated to be invariant with small changes in the averaging volume. Alternatively, the mathematical field variables can be described by spatial random fields [*Dagan*, 1989; *Christakos*, 1992;

Christakos et al., 1993b; *Gelhar*, 1993; *Russo*, 1993; *Christakos et al.*, 1995], but the REV assumption provides the simplest means for equation development and will be used in this report.

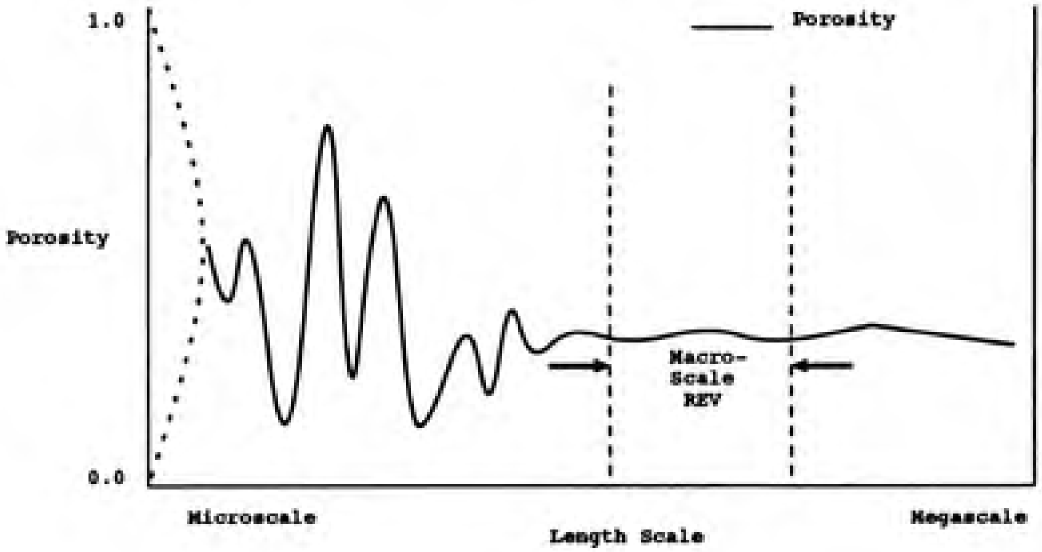


Figure 3.1: Hypothetical Porosities with Increasing Length Scale

The REV assumption generally combines two independent assumptions. The first assumption states that at a prescribed length scale each mathematical field variable describing the physical properties of the porous media system will reach a mean global value and this value will not be significantly changed by small changes in the length of the averaging volume [*Bear*, 1972; *Marle*, 1982]. The second assumption presumes that all mathematical field variables will attain this mean global value within the same range or window of macroscopic length scales. Figure 3.1 depicts hypothetical porosities (ratio of volume of voids to total volume) for a sampled porous media (similar depictions can be found in *Bear* [1972] and *de Marsily* [1986]). At the microscale, depending if the sample contains a solid piece or a void space, the porosity erratically jumps between one and zero. At the macroscale, the first assumption of a REV predicts that the porosity will approach a constant value and not be significantly changed by small changes in length. At lengths greater than the macroscale, megascale heterogeneities may influence the value of porosity. Figure 3.2

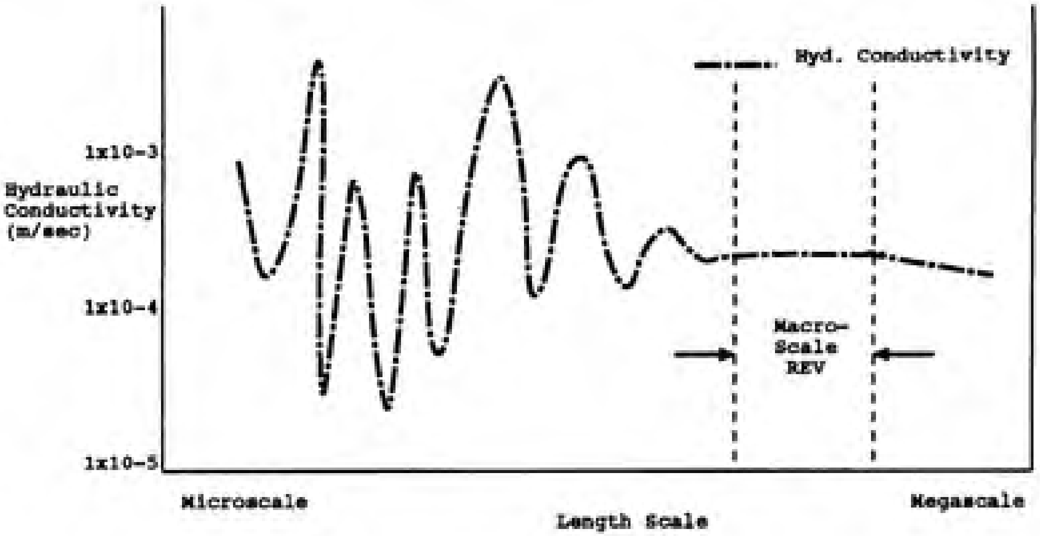


Figure 3.2: Hypothetical Hydraulic Conductivities with Increasing Length Scale

depicts hypothetical hydraulic conductivities for the same sampled porous media. At the microscale, hydraulic conductivity lacks meaning. At the macroscale, the first assumption of a REV predicts that the hydraulic conductivity will approach a constant value and not be significantly changed by small changes in length. The second REV assumption predicts that there exists a scale or window over which the REV assumptions apply for all properties of interest.

The REV assumption is commonly strengthened with several auxiliary hypotheses. First, it is assumed that the mean value of each property of interest is a constant value throughout the domain and its covariance depends only on the vector distance between two points in space (statistical homogeneity in the weak sense) [*Christakos*, 1992, p. 55]. A second hypothesis is the ergodic assumption, which further simplifies modeling. Ergodicity implies that the limit, as the number of physical measurements approaches infinity, of the calculated mean and covariance for the single available realization will approach the true mean and covariance of the system [*Christakos*, 1992]. Ergodicity requires statistical homogeneity but the reverse is not true. By assuming ergodicity we can replace the realization averages with the spatial average. To summarize, (1) we only have one realization for a given natural system, (2) we assume that average values exist at a length scale which can be determined, and (3) when we measure or calculate these field variables at this length scale, these values will be representative of the entire domain of interest.

The benefit of the REV assumption is the practical description of averaged microscale events at the macroscale [*Baveye and Sposito*, 1984; *Bachmat and Bear*, 1986]. Specifically, incorporation of the REV into multiphase flow and transport equation development through the continuum model (1) avoids specification of complex interphase boundaries, (2) describes physical processes in terms of differential equations allowing potential solution, and (3) defines macroscopic quantities that can be physically measured [*Bear and Bachmat*, 1991]. These three properties make continuum approaches used almost universally in the solution of multiphase flow and transport problems.

Several important limitations, many of which are inherent to various levels in all types of continuum models, arise from continuum approaches:

1. The REV assumption is likely not valid for many systems of concern because of expected trends in environmental systems [*Mayer and Miller*, 1992a; *Cushman and Ginn*, 1993; *Miller et al.*, 1996; *Yang et al.*, 1996].
2. Existing continuum models do not typically include complete problem statements, which would include balance equations for mass, momentum, and energy about a representative elementary volume, area, and contact lines [*Gray and Hassanizadeh*, 1991a; *Gray et al.*, 1993].
3. Existing continuum models assume that an REV exists without ensuring a range satisfying the REV assumptions can be found [*Baveye and Sposito*, 1984; *Bachmat and Bear*, 1986; *Bear and Bachmat*, 1991].
4. Most of the existing constitutive relationships in use are empirical in nature and often are based upon data that cover only a portion of the domain of interest [*Bell et al.*, 1986; *Miller et al.*, 1990, 1996].
5. Constitutive relationships are often developed at scales and under conditions

that are much different than those of prime concern [*Powers et al.*, 1992, 1994; *Imhoff et al.*, 1994b].

6. Many complex subsurface systems are of concern, such as the flow of surfactants or multiphase flow through fractured media, which are not accounted for in existing continuum models [*Mayer and Miller*, 1993, 1994; *Brown et al.*, 1994; *Farrell and Reinhard*, 1994a, 1994b; *Imhoff et al.*, 1994a; *Okuda et al.*, 1994; *Miller et al.*, 1996].

Trends are expected in environmental systems both over time (as shown in Figures 3.3 and 3.4 [*Baveye and Sposito*, 1984]) and as the length scale increases. Figure 3.3 shows the average saturation in an unsaturated porous media with the proposed macroscale boundaries. After infiltration, Figure 3.4 shows the same porous media which is now expected to have a decrease in the length scale of the macroscale [*Baveye and Sposito*, 1984]. Therefore, the existence of a REV is a topic of debate [*Baveye and Sposito*, 1984; *Sudicky*, 1986; *Mayer and Miller*, 1991; *Cushman and Ginn*, 1993; *Miller et al.*, 1996; *Yang et al.*, 1996]. Much attention has been given to the validity of the REV assumption for equations describing contaminant transport through heterogeneous, porous media systems [*Graham and McLaughlin*, 1989a, 1989b; *Ababou and Gelhar*, 1990; *Tompson and Gelhar*, 1990; *Deng et al.*, 1993]. Additionally, the implementation of REV based balance theories may not be practical due to an insufficient number of measurements of necessary quantities. Irregular variations, measuring difficulties, and economic limitations all but insure that the prediction of any quantity in a multiphase system is subject to uncertainty [*Dagan*, 1990].

The uncertainty and error associated with the REV assumption may be addressed in several different ways. One method for addressing the trends in environmental systems is to bound the relative error associated with the REV assumption [*Bear*, 1972; *Bachmat and Bear*, 1986; *Bear and Bachmat*, 1991]. The relative error is constrained by defining a lower and upper length-scale bound on the size of the REV for the system. The size of the REV is a function of the acceptable relative error levels, the size of the domain, and the spatial variability of the variable. Each additional mathematical field variables of the porous media will require bounds. If an overlapping REV

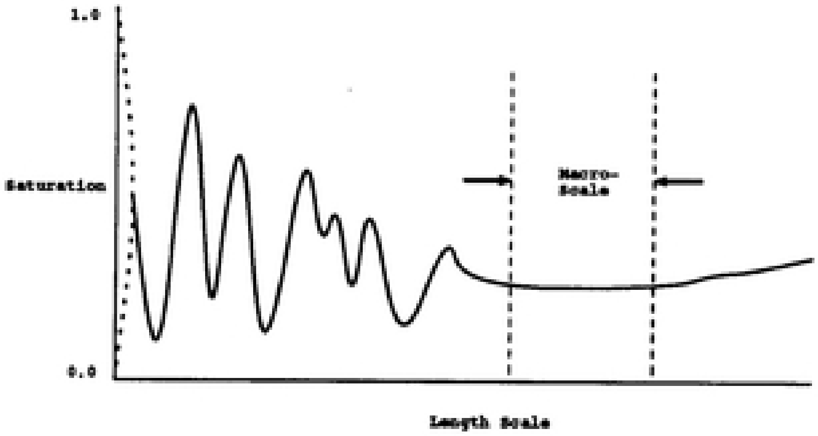


Figure 3.3: Average Saturation in Unsaturated Soil

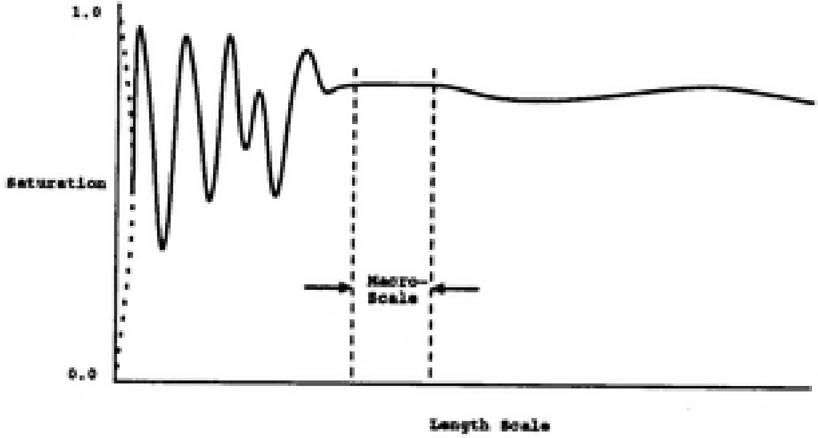


Figure 3.4: Average Saturation after Infiltration in Same Porous Media

can be found, the continuum assumption can be applied. However, bounds such as this have not been placed on the REV in current state-of-the-art continuum models due to the difficulty associated with defining the spatial variability of each variable.

Alternatively, instead of manipulating the size of the REV in an attempt to eliminate trends and fluctuations, we can choose to approximate the trends and fluctuations that are known to occur. This can be done in one of two ways. First, we may define fluctuations and trends through the constitutive relations [*Cushman and Ginn*, 1993; *Neuman and Orr*, 1993]. In this case, we will still operate under the premise that the continuum balance laws describing mass, momentum, energy, and entropy are correct. The revised form of the constitutive relations will then need to incorporate parameters that may fluctuate in space and time. Trends in space and time can be described with non-local laws [*Cushman and Ginn*, 1993]. For example, the traditional expression of Darcy's law is stated as [*Bear*, 1972, p. 123]:

$$\mathbf{q}_d = \varepsilon\,\mathbf{v} = -\left(\frac{\rho\, g\,\mathbf{k}}{\mu}\cdot\nabla\Phi\right) \tag{3.2}$$

where $\mathbf{q}_d$ is the Darcy velocity vector, $\mathbf{v}$ is the pore velocity vector, $\mathbf{k}$ is the permeability tensor, ρ is the fluid density, μ is the dynamic viscosity of the fluid, and Φ is the hydraulic head which includes both pressure and gravity potentials.

A non-local Darcy law may be substituted, which is expressed as [*Neuman and Orr*, 1993, p. 342]:

$$\mathbf{q}_d(\mathbf{x}) = \varepsilon\,\mathbf{v}(\mathbf{x}) = -\left(\frac{\rho\, g\,\mathbf{k}(\mathbf{x}-\mathbf{x}_0)}{\mu}\cdot\nabla\Phi(\mathbf{x}-\mathbf{x}_0)\right) \tag{3.3}$$

where $\mathbf{x}$ is a position vector and $\mathbf{x}-\mathbf{x}_0$ represents movement relative to a reference position. The non-local form of this constitutive relation allows the incorporation of trends in the porous media. Much work is still needed in the development of other constitutive relations incorporating the statistical moments of the porous media system to further quantify the fluctuation of variables.

A second approach acknowledges that the deterministic laws of continuum mechanics do not always provide an accurate description of multiphase flow and transport in porous media. To this end, some researchers are focusing on the case in which the REV does not exist but rather the porous media is described stochastically [*Dagan*, 1990; *Christakos et al.*, 1993a; *Indelman and Abramovich*, 1994]. For a stochastic description, the representation of variables will utilize random functions and the form of the governing will accordingly change [*de Marsily*, 1986; *Christakos*, 1992]. The use of random functions is a powerful method which studies the porous media system as one realization of a random process. Again using porosity as an example, porosity can be defined at a given point in space as the average over all possible realizations of its point value. The point value of porosity is either 0 in a pore space or 1 in a solid grain. An ensemble average or expected value of all realization will be the porosity for the system. Likewise, an ensemble average can be defined for other variables of interest. The mathematical field variables which govern the system no longer have to be statistically homogeneous as assumed in the REV approach, but may have trends in space and time. While this methodology has been derived for single phase flow in porous media systems [*Christakos et al.*, 1994a, 1994b], non-local equations and relations will be needed to define the stochastic representation of multiphase flow and transport equations as well as the stochastic representation of constitutive theory [*Hu and Cushman*, 1994]. Much important work remains to be done in this area.

The debate on the applicability of the REV assumption aside, this assumption is appealing in the pursuit of straightforward governing equations and easily attained numerical solutions. While the REV assumption is debated, it will be used in this report to avoid specification of interphase boundaries, to allow description of physical processes in terms of differential equations, and to define macroscopic quantities that can be experimentally measured.

3.1.3 Mathematical Notation

As equations are developed, the following notation will be followed unless in specific circumstances the standard convention dictates a deviation. Scalar variables will be represented with lower-case Roman and Greek letters (e.g., t, μ). Vector variables will be represented with bold-face lower-case Roman and Greek letters (e.g., $\mathbf{v}, \boldsymbol{\psi}$). Tensor quantities will be represented with bold-face upper-case Roman letters (e.g., T). Script capital Roman letters represent source, reaction, and production terms (e.g., $\mathcal{R}$). $\hat{\tau}$ is used as an exception to this rule as an interphase momentum exchange term. Phase qualifiers are denoted as a superscripted α, β, or γ unless the species are of interest, in which case the species will be superscripted and the phase qualifier will be the subscript.

The following mathematical identities will also lend clarity to equation manipulations [*Greenberg*, 1988]:

$$\frac{\partial (gh)}{\partial t} = g\,\frac{\partial h}{\partial t} + h\,\frac{\partial g}{\partial t} \tag{3.4}$$

$$\nabla \cdot (\mathbf{f}g) = \mathbf{f} \cdot \nabla g + g\,\nabla \cdot \mathbf{f} \tag{3.5}$$

where g and h are general scalar functions of interest and $\mathbf{f}$ represents a general vector function of interest.

3.2 Discrete Multiphase Continuum Approach for Multiphase Flow and Species Transport

The standard approach for the mathematical description of multiphase flow and transport is with a macroscale, differential continuum approach utilizing differential equations that are written about REV's [*Baehr and Corapcioglu*, 1987; *Sleep and Sykes*, 1989; *Domenico and Schwartz*, 1990]. Conservation equations can be written for mass, momentum, and energy. Constitutive relations are then used to close the system of equations and allow for solution.

3.2.1 Mass Balance

Following the methodology given by *Baehr and Corapcioglu* [1987] and *Sleep and Sykes* [1989, 1993a], the DCA can be applied to Figure 3.5 to derive the mass balance equation for a given species ι in the α-phase. Figure 3.5 depicts a differential volume with a volume of $(dx \times dy \times dz)$. We consider a general compositional formulation of multiphase flow and transport for systems comprised of n_p phases and n_s species

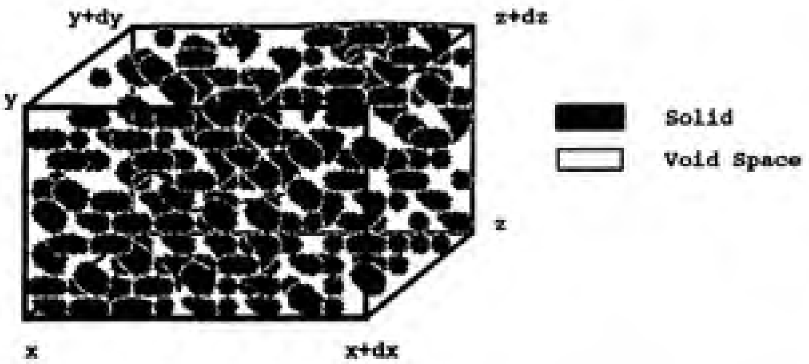


Figure 3.5: Macroscale Representative Elementary Volume

in which capillarity, interphase mass transfer, and complex phase behavior may be important. We will use $\alpha = a, n, g, s$ to denote an aqueous phase, a non-aqueous phase liquid (NAPL), a gas phase, and a solid phase; other phases are possible as well (e.g., colloidal, micro-emulsion).

Making use of the continuous, differentiable variables, a general species mass balance equation for a multiphase, multi-species system is written as [*Baehr and Corapcioglu*, 1987; *Sleep and Sykes*, 1989, 1993a]:

$$\frac{\partial}{\partial t}\left(\varepsilon^{\alpha}\rho^{\alpha}\omega_{\alpha}^{\iota}\right) = -\nabla\cdot\left(\varepsilon^{\alpha}\rho^{\alpha}\omega_{\alpha}^{\iota}\mathbf{v}^{\alpha}\right) - \nabla\cdot\mathbf{j}_{\alpha}^{\iota} + \mathcal{I}_{\alpha}^{\iota} + \mathcal{R}_{\alpha}^{\iota} + \mathcal{S}_{\alpha}^{\iota} \tag{3.6}$$

where ε^{α} represents the volume fraction of the α-phase, ε represent the porosity such that $\varepsilon = 1 - \varepsilon^{s}$ where the superscript s indicates the solid phase, ρ is the density, ω is the mass fraction, $\mathbf{v}$ is the velocity, $\mathbf{j}$ represents non-advective fluxes, $\mathcal{I}$ represents interphase mass transfer to the α-phase from another phase, $\mathcal{S}$ is a source term, $\mathcal{R}$ is the reaction term which represents mass produced. The superscript α indicates a phase unless a species is specified in which case the superscript ι indicates the species of interest and the subscript α indicates the phase. Eq. (3.6) states that the accumulation of mass over time in the α-phase in the REV is equal to the mass entering the system minus the mass leaving the system. Mass may leave the α-phase of the system through advective and non-advective means as well as through reactions, interphase mass transfer, and sink terms.

By definition of quantities, Equation (3.6) is subject to the following constraints

[*Abriola and Pinder*, 1985a]:

$$\begin{aligned} \sum_{\alpha} \varepsilon^{\alpha} &= 1 \\ \sum_{\alpha} \mathcal{I}_{\alpha}^{\iota} &= 0 \\ \sum_{\iota} \omega_{\alpha}^{\iota} &= 1 \\ \sum_{\iota} \mathbf{j}_{\alpha}^{\iota} &= 0 \\ \sum_{\iota} \mathcal{R}_{\alpha}^{\iota} &= 0 \end{aligned} \tag{3.7}$$

The constraints state that the sum of all mass fractions over all species of a given phase will equal one, the sum of all volume fractions over all phases will equal one, the net interphase mass transfer for a species ι over all phases will be zero, and net non-advective flux over all species will be zero.

Saturations are defined for a phase as the ratio of the volume fraction to the total void space. Therefore, the following identity will hold:

$$\sum_{\alpha,\alpha\neq s} s^{\alpha} = \sum_{\alpha,\alpha\neq s} \frac{\varepsilon^{\alpha}}{\varepsilon} = 1 \tag{3.8}$$

Consider a homogeneous porous media system that is fully saturated with an aqueous phase and NAPL, both of which are slightly compressible fluids in which density and void spaces are only functions of pressure.

First, beginning with Eq. (3.6) and summing over all species within a phase, the constraints in Eq. (3.7) state that the mass fraction, ω_{α}, will equal unity and the net non-advective flux will be zero yielding:

$$\frac{\partial}{\partial t}(\varepsilon^{\alpha}\rho^{\alpha}) = -\nabla\cdot(\varepsilon^{\alpha}\rho^{\alpha}\mathbf{v}^{\alpha}) + \sum_{\iota}(\mathcal{I}_{\alpha}^{\iota} + \mathcal{S}_{\alpha}^{\iota}) \tag{3.9}$$

Second, if interphase mass transfer is negligible:

$$\frac{\partial}{\partial t}(\varepsilon^{\alpha}\rho^{\alpha}) = -\nabla\cdot(\varepsilon^{\alpha}\rho^{\alpha}\mathbf{v}^{\alpha}) + \sum_{\iota}\mathcal{S}_{\alpha}^{\iota} \tag{3.10}$$

Next, expanding the accumulation and advection terms as:

$$\varepsilon^{\alpha}\frac{\partial\rho^{\alpha}}{\partial t} + \rho^{\alpha}\frac{\partial\varepsilon^{\alpha}}{\partial t} = -\rho^{\alpha}\nabla\cdot(\varepsilon^{\alpha}\mathbf{v}^{\alpha}) + \varepsilon^{\alpha}\mathbf{v}^{\alpha}\cdot\nabla(\rho^{\alpha}) + \sum_{\iota}\mathcal{S}_{\alpha}^{\iota} \tag{3.11}$$

Assuming that the fluids of interest are slightly compressible such that changes in density in space are negligible then Eq. (3.11) can be written as [*Abriola and Pinder*, 1985a]:

$$\varepsilon^{\alpha}\frac{\partial\rho^{\alpha}}{\partial t}+\rho^{\alpha}\frac{\partial\varepsilon^{\alpha}}{\partial t}=-\rho^{\alpha}\nabla\cdot(\varepsilon^{\alpha}\mathbf{v}^{\alpha})+\sum_{\iota}S_{\alpha}^{\iota} \tag{3.12}$$

Dividing by density and relating the density to pressure, under isothermal conditions, through a compressibility term yields [*de Marsily*, 1986]:

$$\varepsilon^{\alpha}\beta^{\alpha}\frac{\partial p^{\alpha}}{\partial t}+\frac{\partial\varepsilon^{\alpha}}{\partial t}=-\nabla\cdot(\varepsilon^{\alpha}\mathbf{v}^{\alpha})+\frac{\sum_{\iota}S_{\alpha}^{\iota}}{\rho^{\alpha}} \tag{3.13}$$

where β^{α} is the compressibility of the α-phase defined as $\beta^{\alpha}=(1/\rho^{\alpha})(\partial\rho^{\alpha}/\partial p^{\alpha})$, and p^{α} is the pressure of the α-phase.

The time derivative of the volume fraction can be related empirically at the macroscale through capillary pressures, which exist across interfaces between the multiple fluids [*Kool et al.*, 1987]. The differential continuum approach uses capillarity to account for interfacial effects that are not captured in the governing equations. Capillary pressure is defined as the pressure of the non-wetting fluid (NAPL) minus the pressure of the wetting fluid (aqueous) as:

$$p^{na}=p^{n}-p^{a} \tag{3.14}$$

Therefore, the volume fraction of the aqueous phase can be written in terms of capillary pressure as:

$$\frac{\partial\varepsilon^{a}}{\partial t}=\frac{\partial\varepsilon^{a}}{\partial p^{na}}\frac{\partial p^{na}}{\partial t}=\frac{\partial\varepsilon^{a}}{\partial p^{na}}\left(\frac{\partial p^{n}}{\partial t}-\frac{\partial p^{a}}{\partial t}\right) \tag{3.15}$$

Eq. (3.15) would have additional terms if additional interfaces existed. The use of capillary pressures reduces the two fluid flow equations to a single equation in which p-S-k relations are subsequently used to close the system of equations. To date, p-S-k relations are often based on data that only cover a portion of the domain in interest and are developed at scales and under conditions much different than those of primary concern in the groundwater environment [*Lenhard and Parker*, 1987a, 1988; *Lenhard et al.*, 1989; *Dane et al.*, 1992].

Eq. (3.15) is incorporated into Eq. (3.13) for the aqueous phase yielding:

$$\varepsilon^{a}\beta^{a}\frac{\partial p^{a}}{\partial t}+\frac{\partial\varepsilon^{a}}{\partial p^{na}}\left(\frac{\partial p^{n}}{\partial t}-\frac{\partial p^{a}}{\partial t}\right)=-\nabla\cdot(\varepsilon^{a}\mathbf{v}^{a})+\frac{\sum_{\iota}S_{a}^{\iota}}{\rho^{a}} \tag{3.16}$$

3.2.2 Momentum Balance

Momentum and energy balance equations about a volume may also be written for multiphase systems. Most environmental applications do not explicitly consider either of these balance equations. Rather the momentum equation enters into (3.16) by specification of an extended form of Darcy's law as a constitutive relation describing the velocity in terms of pressures [*Bear*, 1972]. Momentum flux and momentum dissipation are neglected through this approach. The standard application of Darcy's law also neglects anisotropy. To facilitate future comparison with the integral continuum approach, a complete momentum balance equation will be presented and reduced by means of several broad assumptions [*Hassanizadeh and Gray*, 1993b] down to Darcy's law.

The complete macroscopic momentum balance for a fluid phase is written in a similar fashion to the mass balance equation such that accumulation of momentum is equal to the net flux of momentum into the phase plus the net dispersion of momentum into the phase plus the net transfer of momentum into the phase via sources or reactions. Neglecting macroscopic inertial and viscous effects, the momentum balance is given as [*Bear*, 1972; *Allen*, 1985]:

$$\frac{\partial}{\partial t}(\varepsilon^\alpha \rho^\alpha \mathbf{v}^\alpha) = -\nabla \cdot (\varepsilon^\alpha \rho^\alpha \mathbf{v}^\alpha \mathbf{v}^\alpha) - \nabla \cdot \mathbf{T}^\alpha + \mathcal{I}_m^\alpha + \mathcal{S}_m^\alpha \qquad (3.17)$$

where the term on the left hand side (LHS) accounts for accumulation of momentum, the first term on the right hand side (RHS) accounts for the loss of momentum due to shear forces, $\mathbf{T}^\alpha$ is the stress tensor, $\mathcal{I}_m^\alpha$ represents an interphase exchange of momentum, and $\mathcal{S}_m^\alpha$ is momentum transferred to the α-phase by a source (e.g., body forces).

To reduce Eq. (3.17) to Darcy's law, we assume that there is no accumulation of momentum and that the momentum transfer within each fluid from shear stresses is negligible compared to the momentum exchange with respect to the solid matrix. Rearrangement yields:

$$\mathcal{I}_m^\alpha = \nabla \cdot \mathbf{T}^\alpha - \mathcal{S}_m^\alpha \qquad (3.18)$$

Assuming $\mathbf{T}^\alpha = p^\alpha \mathbf{I}$ [*Allen*, 1985] where p^α is pressure and $\mathbf{I}$ is the unit isotropic tensor. Next, if the only body force considered is gravity then $\mathcal{S}_m^\alpha = \rho^\alpha g \nabla \mathbf{z}$ where g is gravity positive downward and $\mathbf{z}$ is the unit vector in the upward direction [*Allen*, 1985]. These assumptions reduce the complete momentum balance equation to a form which is equivalent to averaging the microscopic Navier-Stokes equations [*Hassanizadeh and Gray*, 1993b] yielding:

$$\mathcal{I}_m^\alpha = \varepsilon^\alpha \left(\nabla p^\alpha + \rho^\alpha g \nabla \mathbf{z} \right) \tag{3.19}$$

In order to simplify Eq. (3.19) further to Darcy's law, a constitutive relation must be specified for $\mathcal{I}_m^\alpha$ to account for the drag exerted by adjacent phases on the α-phase [*Hassanizadeh and Gray*, 1993b]. This relation, relative to the fixed solid matrix, takes the form [*Hassanizadeh and Gray*, 1993b]:

$$\begin{gathered} \mathcal{I}_m^\alpha = -\mathbf{R}^{\alpha\alpha} \cdot \mathbf{v}^{\alpha,s} - \mathbf{R}^{\alpha\beta} \cdot \mathbf{v}^{\beta,s} \\ \alpha = a, n;\ \beta = a, n;\ \alpha \neq \beta \end{gathered} \tag{3.20}$$

where $\mathbf{R}$ is a tensor of viscous drag forces with $\mathbf{R}^{\alpha\alpha}$ representing the forces between the α-phase and the fixed solid phase and $\mathbf{R}^{\alpha\beta}$ representing the forces between the α-phase and the β-phase. Consistent with the above assumptions, $\mathbf{R}^{\alpha\beta} = 0$. Substitution of Eq. (3.20) into Eq. (3.19) then yields:

$$-\mathbf{R}^{\alpha\alpha} \cdot \mathbf{v}^{\alpha,s} = \varepsilon^\alpha \left(\nabla p^\alpha + \rho^\alpha g \nabla z \right) \tag{3.21}$$

Defining $\mathbf{R}^{\alpha\alpha} = (\varepsilon^\alpha)^2 \mu^\alpha / (\mathbf{k} k_{r\alpha})$ [*Hassanizadeh and Gray*, 1993b], yields the common form of Darcy's law as [*Abriola and Pinder*, 1985a; *Allen*, 1985; *Mayer and Miller*, 1990; *Hassanizadeh and Gray*, 1993b]:

$$\mathbf{q}_d^{\alpha,s} = \varepsilon^\alpha \mathbf{v}^{\alpha,s} = -\frac{\mathbf{k} k_{r\alpha}}{\mu^\alpha} \cdot \left(\nabla p^\alpha + \rho^\alpha g \nabla z \right) \tag{3.22}$$

where $\mathbf{q}_d^{\alpha,s}$ is the specific discharge relative to the solid phase, μ^α is the viscosity of the α-phase, $\mathbf{k}$ is the intrinsic permeability tensor of the α-phase, and $k_{r\alpha}$ is the relative permeability of the α-phase assuming an isotropic media, which is predicted by constitutive theory and an issue of much debate [*Bear et al.*, 1987; *Delshad and Pope*, 1989; *Demond and Roberts*, 1993; *Sarma et al.*, 1994]. For an isotropic media, the relative permeability can be well-defined as a scalar quantity [*Bear and Bachmat*, 1991]. However, for an anisotropic media, the relative permeability must be defined as a tensor quantity [*Miller et al.*, 1996]. This is yet to be done and will prove difficult experimentally.

Using the extended form of Darcy's law expressed in Eq. (3.22), assuming an isotropic media, and substituting into Eq. (3.16) for the aqueous phase gives:

$$\varepsilon^a\beta^a\frac{\partial p^a}{\partial t}+\frac{\partial\varepsilon^a}{\partial p^{na}}\left(\frac{\partial p^n}{\partial t}-\frac{\partial p^a}{\partial t}\right)=\nabla\cdot\left[\frac{\mathbf{k}k_{ra}}{\mu^a}\cdot(\nabla p^a+\rho^a g\nabla z)\right]+\frac{\sum_\iota S_a^\iota}{\rho^a} \tag{3.23}$$

Defining the specific storage of a control volume as $S_s = (\varepsilon^a\beta^a\rho^a g)$ allows the single phase fluid flow equation to be stated as [*Abriola and Pinder*, 1985a; *Domenico and Schwartz*, 1990]:

$$S_s\frac{\partial\Phi^a}{\partial t}=\nabla\cdot\left(\frac{\mathbf{k}\rho^a g}{\mu^a}\cdot\nabla\Phi^a\right)+\frac{\sum_\iota S_a^\iota}{\rho^a} \tag{3.24}$$

It can be easily seen that for a single fluid with no source terms, the above reduces to saturated, horizontal groundwater flow equation [*Freeze and Cherry*, 1979; *Corey*, 1994]:

$$S_s\frac{\partial\Phi^a}{\partial t}=\nabla\cdot\left(\frac{\mathbf{k}\rho^a g}{\mu^a}\cdot\nabla\Phi^a\right) \tag{3.25}$$

All of the cited immiscible flow models in Table 2.2 follow the above methodology to predict multiphase fluid flow in porous media. Emphasis has been placed on further refining constitutive relations to more accurately predict systems of concern.

3.2.3 Energy Balance

The differential continuum approach can be applied to Figure 3.5 to also derive an energy balance equation for a given species ι in the α-phase. Most multiphase environmental model formulations published to date do not consider an energy balance, but there are some notable exceptions [*Milly*, 1984a, 1984b; *Falta et al.*, 1992b, 1992a; *Panday and Corapcioglu*, 1994]. Making use of continuous, differentiable variables, the energy balance is written as [*Domenico and Schwartz*, 1990]:

$$\begin{aligned}\frac{\partial}{\partial t}\left[\varepsilon^\alpha\rho^\alpha\left(E_u^\alpha+\frac{(v^\alpha)^2}{2}\right)\right] = {} & - \nabla\cdot\left[\varepsilon^\alpha\rho^\alpha\mathbf{v}^\alpha\left(E_u^\alpha+\frac{(v^\alpha)^2}{2}\right)\right]+\nabla\cdot(\varepsilon^\alpha\mathbf{T}^\alpha\cdot\mathbf{v}^\alpha)\\ & - \nabla\cdot\mathbf{j}_\epsilon^\alpha+\varepsilon^\alpha\rho^\alpha\mathbf{g}\cdot\mathbf{v}^\alpha+\mathcal{I}_\epsilon^\alpha+\mathcal{R}_\epsilon^\alpha+\mathcal{S}_\epsilon^\alpha\end{aligned} \tag{3.26}$$

where E_u is the internal energy; v is the magnitude of the velocity vector; $\mathbf{T}$ is the fluid stress tensor; $\mathbf{j}_e$ is an energy transport vector comprised of dispersive and conductive components; $\mathbf{g}$ is the gravity vector; $\mathcal{I}_e$ represents the exchange of energy across interfaces; $\mathcal{R}_e$ denotes energy produced from reactions; $\mathcal{S}_e$ represents sources of energy, such as radiative; and α is a phase qualifier.

The energy balance equation is often written as a balance equation expressed in terms of temperature for the α-phase as [*de Marsily*, 1986]:

$$\frac{\partial}{\partial t}\left(\epsilon^{\alpha}\rho^{\alpha}c^{\alpha}T^{\alpha}\right) = -\nabla\cdot\left(\epsilon^{\alpha}\rho^{\alpha}c^{\alpha}T^{\alpha}\mathbf{v}^{\alpha}\right) - \nabla\cdot\mathbf{j}_T^{\alpha} + \mathcal{I}_T^{\alpha} + R_T^{\alpha} + \mathcal{S}_T^{\alpha} \qquad (3.27)$$

where c^{α} is a specific heat, T is temperature, and the subscript T denotes that temperature is the dependent variable, which is used to qualify non-advective transport, interphase transfer, reaction, and source terms in the energy equation. With the above noted exceptions aside, the energy balance equation is usually omitted either explicitly or implicitly by assuming the system is isothermal

3.3 Alternate Approaches

The differential continuum approach outlined above represents the breadth of conventional approaches that utilize a control volume at the macroscale to write differential equations to govern multiphase flow and transport. Subsurface systems can be better approximated by including more rigorous constitutive relations and by including chemical reactions, biological degradation, and non-equilibrium interphase mass transfer. However, the differential continuum approach is limited as improvements can only be obtained through additional empirical relations. The method of formulating additional constraints and constitutive relations is unclear and does not assure thermodynamic consistency. Also, definitions of parameters in the governing macroscale equations must be averaged quantities but are not rigorously defined as such. These shortcoming of conventional approaches to describe the flow and transport of contaminants through porous media has led researchers to consider alternative approaches.

The integral approach, an alternative method to the development of governing equations for multiphase flow and transport, provides a means for changing scale while retaining important physical processes from smaller scales. The integral approach also is based directly on first principles such that the equations are thermodynamically consistent. The remainder of this report will develop integral balance formulations to describe macroscale transport of mass, momentum, energy, and entropy in porous media.

Chapter 4

Development of Macroscale Integral Continuum Equations

"Do not worry about your difficulties in mathematics. I can assure you mine are still greater." Albert Einstein

4.1 Overview of the Integral Approach

In light of discrepancies and shortcomings that exist in current control volume derivations, alternate derivations of governing balance equations for multiphase flow and transport are worthy of research. The goal of this chapter is to derive governing balance equations that incorporate physical information from smaller length-scales in order to rigorously describe MPFT.

The integral continuum approach (ICA) — which requires integration over a representative elementary region to produce balance equations that are formulated about volumes, interfacial areas between phases, and contact lines — has been explored by many researchers [*Whitaker*, 1969; *Bear*, 1972; *Hassanizadeh and Gray*, 1979a, 1979b, 1980a; *Cushman*, 1983; *Gray*, 1983; *Quintard and Whitaker*, 1988; *Gray and Hassanizadeh*, 1991a, 1991b; *Hassanizadeh and Gray*, 1993a, 1993b; *Chen et al.*, 1994;

Quintard and Whitaker, 1994]. These balance equations are supplemented with constitutive relations. The constitutive relations are constrained using entropy inequality constraints [*Coleman and Noll*, 1963; *Hassanizadeh and Gray*, 1980a]. The purpose of this chapter is to develop macroscale integral balance equations for volumes, interfaces, and contact lines that can be used systematically to change spatial scales.

Inconsistencies in the DCA have been pointed out by several researchers [*Hassanizadeh and Gray*, 1979a; *Cushman*, 1983; *Quintard and Whitaker*, 1988, 1994], especially for the cases of flow in the unsaturated zone [*Gray and Hassanizadeh*, 1991a, 1991b] and two-phase flow [*Hassanizadeh and Gray*, 1993a, 1993b]:

1. constitutive theory, used to close the traditional balance equations for multiphase, multidimensional systems, has evolved from extensions of single-phase, small-scale laboratory experiments (e.g., the extended form of Darcy's law);
2. some existing constitutive relations for macroscopic systems use microscopic thermodynamic expressions that have no meaning at the macroscale (e.g., contact angle);
3. some interfacial effects have been excluded [*Abriola and Gray*, 1985] and the related effects approximated in an *ad hoc* manner (e.g., relative permeability); and
4. the conventional constitutive relations for the dependence of saturation on capillary pressure are inconsistent in several respects.

The application of the ICA — also referred to as formal averaging — is fairly new and seen by some as arduous. Coupled with the mathematics associated with the introduction of the integral approach and the attention given to scales, additional attention is paid to the conservation of energy and the balance of entropy. Energy and entropy equations, that are not derived as part of conventional macroscale equations, are included to derive rigorous constitutive relations that do not violate thermodynamic laws. This chapter will introduce the facets of the integral approach in a logical progression so that these building blocks may be applied to MPFT.

It will be useful to establish some terminology and mathematical notation before presenting integral balance equations. The length scales that were defined in the previous chapter will be heavily utilized and additional points of the REV assumption will be highlighted. It will also be shown that simply integrating over a volume does not circumvent the discrepancies of the DCA but thoughtful application of integral equations through the ICA can produce improved balance equations.

4.2 Mathematical Notation

In order to clearly present the integral continuum approach, it is helpful to begin with the mathematical notation that will be used in equation development and manipulation. This section is intended to provide the motivation for applying integration and averaging theorems, the mechanics for defining phase and mass averages, and to note other helpful mathematical notations. A thorough review of the derivation of averaging theorems can be found in *Gray et al.* [1993]. The following formulations and identities will be referenced as used in the equation development at the end of this chapter.

4.2.1 Notation

As in Chapter 3, the following notation will be followed unless noted in specific circumstances. Scalar variables will be represented with lower-case Roman and Greek letters (e.g., t, μ). Vector variables will be represented with bold-face lower-case Roman and Greek letters (e.g., $\mathbf{v}, \boldsymbol{\psi}$). Tensor quantities will be represented with bold-face upper-case Roman letters (e.g., $\mathbf{T}$). Script capital Roman letters represent source, reaction, and production terms (e.g., $\mathcal{R}$). Phases qualifiers are denoted as a superscripted α, β, or γ unless the species are of interest in which case the species will be superscripted and the phase qualifier will be the subscript.

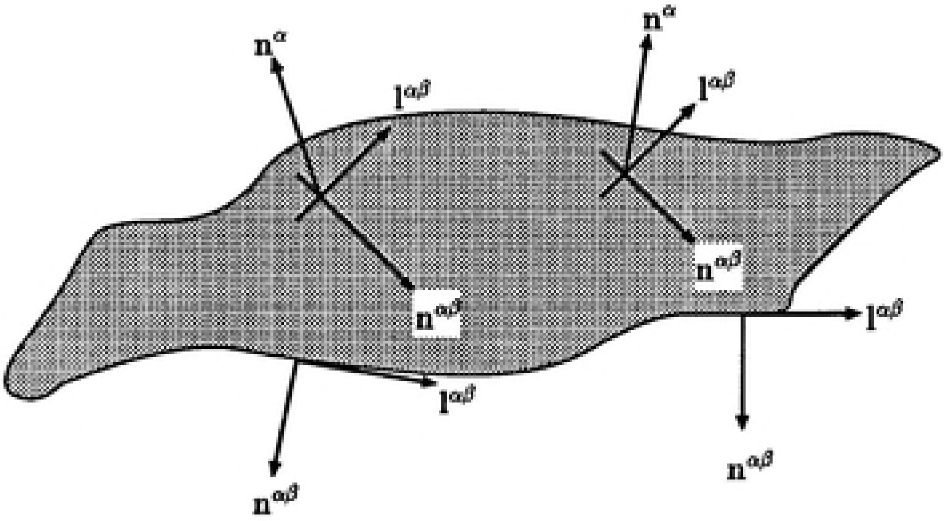
Additionally in this chapter, the symbols V and A will be used to respectively indicate volumes and areas while $\mathcal{V}$ and $\mathcal{A}$ will respectively indicate domains for integration about volumes and closed surfaces. Mass transfer terms will be indicated with hatted and slanted lower-case letters with the phase from which the mass is originating superscripted and the interface to which the mass is being transferred subscripted. For example, the transfer of mass from the α-phase to the $\alpha\beta$-interface is represented as $\hat{e}^{\alpha}_{\alpha\beta}$.

4.2.2 Integration and Averaging Theorems

The integral continuum approach is based upon integration over volumes, surfaces, and contact lines. Theorems of integration and averaging facilitate the meaningful expression of balance equations from the microscale to the macroscale. Integration theorems relate integrals over some region to integrals over the boundary of that region [*Gray et al.*, 1993, p. 90]. Averaging theorems are used to express an integral of the derivative of a microscopic function to a derivative of an integral of a macroscopic function [*Gray et al.*, 1993, p. 94].

To continue our development, we first define a coordinate system with orthogonal unit vectors. In general, the notation for normal vectors is depicted in Figure 4.1 where $\mathbf{n}^{\alpha}$ denotes a unit vector normal to the surface pointing outward, $\mathbf{n}^{\alpha\beta}$ denotes a unit vector that is tangent to the surface and directed outward normal to a curve of interest, and $\mathbf{l}^{\alpha\beta}$ denotes a unit vector that is also tangent to the surface and tangent to a curve of interest, therefore being orthogonal to $\mathbf{n}^{\alpha\beta}$.

Figure 4.2 depicts specifically the normal vectors for the volumes, interfaces, and contact lines used in this report. For the volume, $\mathbf{n}^{\alpha}$ again represents a unit vector normal to the α-phase, occurring on the $\mathcal{A}_{\alpha\beta}$ surface pointing outward from the α-phase. $\mathbf{n}^{\alpha}_{\mathrm{b}}$ represents a unit vector normal to the α-phase volume occurring at the REV boundary ($\mathcal{A}_{\alpha\alpha}$) pointing outward from the α-phase. For the interface, $\mathbf{n}^{\alpha\beta}$ represents a unit vector tangent to the surface and normal to the $\alpha\beta\gamma$-contact line ($\mathcal{C}_{\alpha\beta\gamma}$) pointing outward. $\mathbf{n}^{\alpha\beta}_{\mathrm{b}}$ represents a unit vector tangent to the surface and normal to the surface boundary line ($\mathcal{C}_{\alpha\beta}$) pointing outward. For the contact line, $\mathcal{P}_{\alpha\beta\gamma}$ represents the endpoint of $\mathcal{C}_{\alpha\beta\gamma}$ that is caused by the edge of $\mathcal{V}$. $\mathcal{P}_{\alpha\beta\gamma\lambda}$ represent the internal endpoints of $\mathcal{C}_{\alpha\beta\gamma}$. $\mathbf{n}^{\alpha\beta\gamma}$ is the unit vector tangent to the curve $\mathcal{C}_{\alpha\beta\gamma}$ at its endpoints within the REV. $\mathbf{n}^{\alpha\beta\gamma}_{\mathrm{b}}$ is the unit vector tangent to the curve $\mathcal{C}_{\alpha\beta\gamma}$ at



Othogonal Unit Vectors

$\mathbf{l}^{\alpha\beta}$	*Tangent to the surface and tangent to a curve*
$\mathbf{n}^{\alpha\beta}$	*Tangent to the surface and normal to a curve*
$\mathbf{n}^{\alpha}$	*Normal to the surface*

Figure 4.1: Notation for Orthogonal Unit Vectors

its endpoints at the boundary of the REV.

The notation for vector functions along volumes, interfaces, and contact lines is shown in Figure 4.3. Velocity, $\mathbf{v}$, is used as a representative vector. $\mathbf{v}^{\alpha}$ represents the velocity of the α-phase. $\mathbf{v}^{\alpha\beta}$ represents the velocity of the $\alpha\beta$-interface. $\mathbf{v}_b^{\alpha}$ represent the velocity of the of the REV boundary of the α-phase. $\mathbf{v}_b^{\alpha\beta}$ represent the velocity of the of the REV boundary of the $\alpha\beta$-interface. $\mathbf{v}^{\alpha\beta\gamma}$ represents the velocity of the $\alpha\beta\gamma$ contact line. $\mathbf{v}_b^{\alpha\beta\gamma}$ represents the velocity of $\mathcal{P}_{\alpha\beta\gamma}$ at the REV boundary of the $\alpha\beta$-interface. $\mathbf{v}^{\alpha\beta\gamma\lambda}$ represents the velocity of the point $\mathcal{P}_{\alpha\beta\gamma\lambda}$.

Beginning with the orthogonal unit vectors, we define a vector function in component form as [*Gray et al.*, 1993]:

$$\mathbf{f}^{\alpha} = \mathbf{l}^{\alpha\beta}\left(\mathbf{l}^{\alpha\beta}\cdot\mathbf{f}^{\alpha}\right) + \mathbf{n}^{\alpha\beta}\left(\mathbf{n}^{\alpha\beta}\cdot\mathbf{f}^{\alpha}\right) + \mathbf{n}^{\alpha}\left(\mathbf{n}^{\alpha}\cdot\mathbf{f}^{\alpha}\right) \tag{4.1}$$

where the terms $(\mathbf{l}^{\alpha\beta}\cdot\mathbf{f}^{\alpha})$, $(\mathbf{n}^{\alpha\beta}\cdot\mathbf{f}^{\alpha})$, and $(\mathbf{n}^{\alpha}\cdot\mathbf{f}^{\alpha})$ are the components of $\mathbf{f}^{\alpha}$ in the $\mathbf{l}^{\alpha\beta}$, $\mathbf{n}^{\alpha\beta}$, and $\mathbf{n}^{\alpha}$ directions, respectively. Taking advantage of the coordinate framework allows for the definition of a surface functions, $\mathbf{f}^{\alpha\beta}$, as:

$$\begin{aligned} \mathbf{f}^{\alpha\beta} &= \mathbf{l}^{\alpha\beta}(\mathbf{l}^{\alpha\beta}\cdot\mathbf{f}^{\alpha}) + \mathbf{n}^{\alpha\beta}(\mathbf{n}^{\alpha\beta}\cdot\mathbf{f}^{\alpha}) \\ &= \mathbf{f}^{\alpha} - \mathbf{n}^{\alpha}(\mathbf{n}^{\alpha}\cdot\mathbf{f}^{\alpha}) \end{aligned} \tag{4.2}$$

and similarly, for the vector component along a curve, $\mathbf{f}^{\alpha\beta\gamma}$, can be defined as:

$$\begin{aligned} \mathbf{f}^{\alpha\beta\gamma} &= \mathbf{l}^{\alpha\beta}(\mathbf{l}^{\alpha\beta}\cdot\mathbf{f}^{\alpha}) \\ &= \mathbf{f}^{\alpha} - \mathbf{n}^{\alpha}(\mathbf{n}^{\alpha}\cdot\mathbf{f}^{\alpha}) - \mathbf{n}^{\alpha\beta}(\mathbf{n}^{\alpha\beta}\cdot\mathbf{f}^{\alpha}) \end{aligned} \tag{4.3}$$

Many additional properties of this orthogonal coordinate system exist and are derived in *Gray et al.* [1993].

With the coordinate system established, we proceed to the two specific integration theorems used in this report, the divergence and transport theorems. Formally, the divergence theorem, generally attributed to Karl Gauss (1777-1855) but also independently obtained by Michel Ostrogradsky (1801-1861), states [*Greenberg*, 1988, p. 390]:

$$\int_V \nabla\cdot\mathbf{f}\,dV = \int_A \mathbf{n}\cdot\mathbf{f}\,dA \tag{4.4}$$

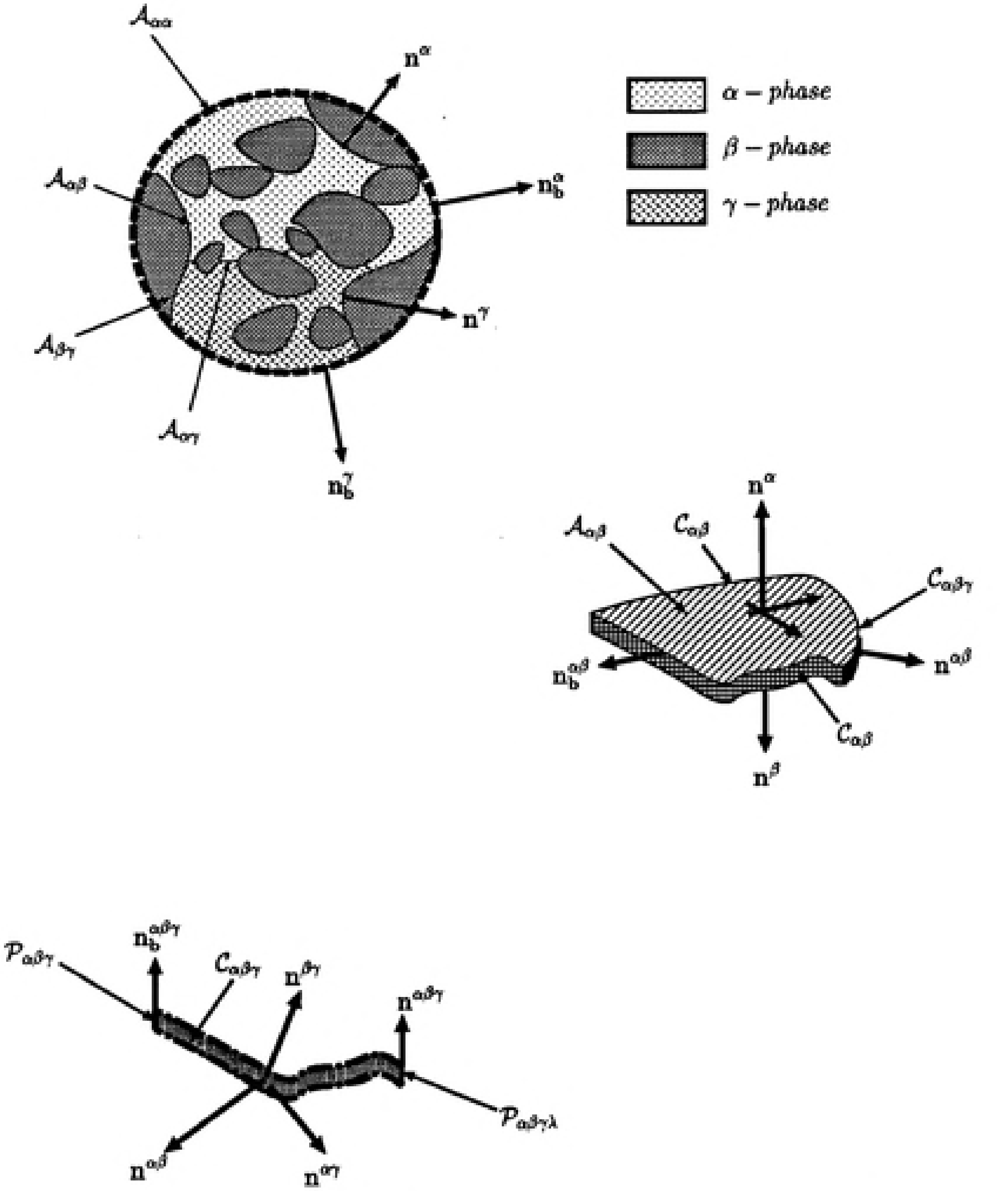


Figure 4.2: Definition of Normal Vector Notation for Volumes, Interfaces, and Contact Lines

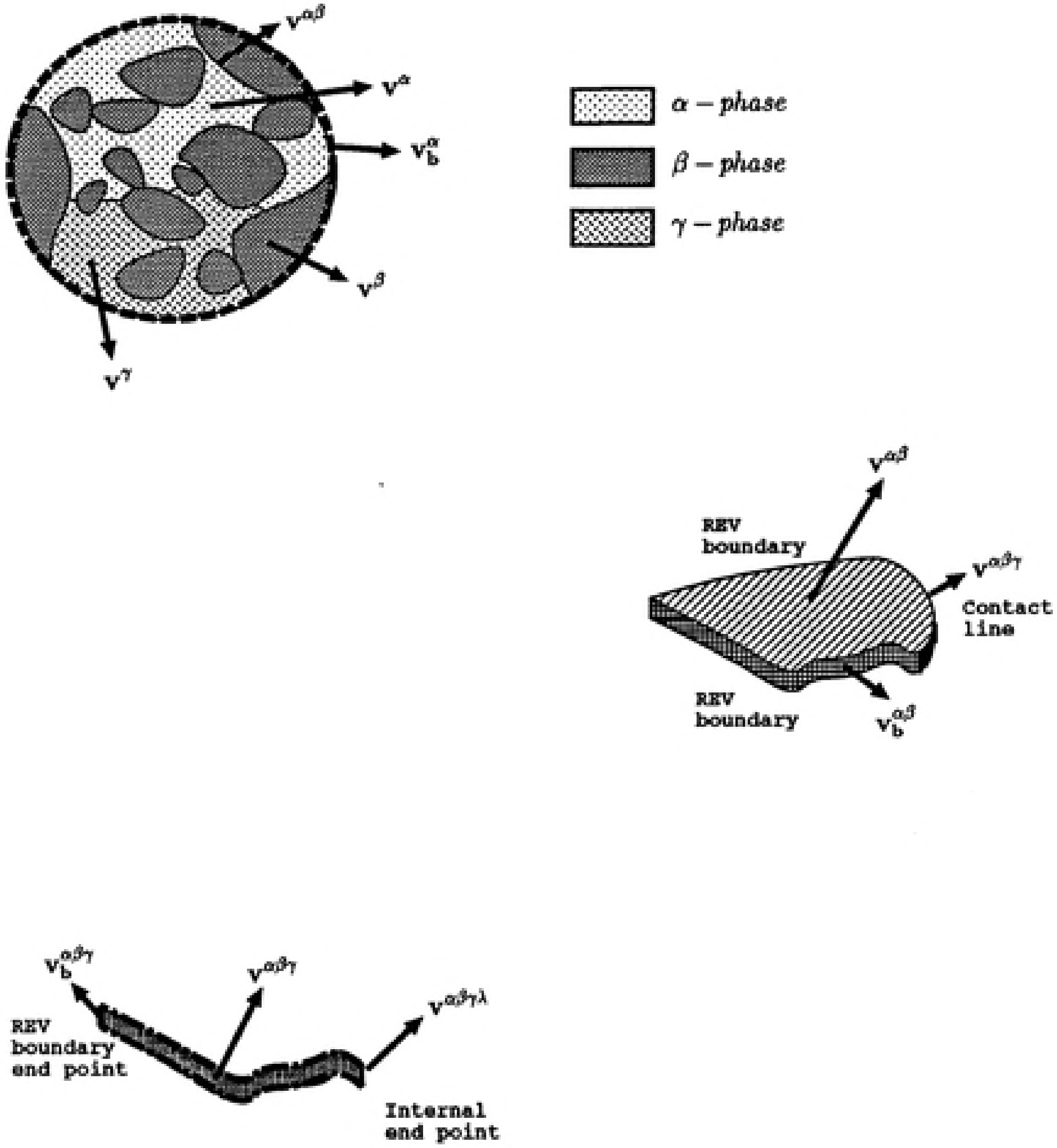


Figure 4.3: Definition of Vector Function Notation for Volumes, Interfaces, and Contact Lines

where $\mathcal{V}$ is the region enclosed by the surface $\mathcal{A}$, $\int_{\mathcal{V}}$ represents a volume integral, $\int_{\mathcal{A}}$ represents a surface integral, $\mathbf{n}$ is the unit normal vector pointing out of the surface, and $\mathbf{f}$ is a vector function of interest. Proofs of the divergence theorem can be found in advanced calculus [*Schey*, 1992, p. 37], physics [*Halliday and Resnick*, 1988, p. 573], and fluid mechanics books [*Whitaker*, 1981, p. 84]. The divergence theorem is a tool of convenience and practicality used for converting fluxes through surfaces into volume integrals which may, in turn, be more easily evaluated.

The transport theorem is another helpful tool used to express the rate of change of the integral of a function [*Whitaker*, 1981]. In general, the transport theorem states:

$$\frac{d}{dt}\int_{\mathcal{V}} h\,dV = \int_{\mathcal{V}} \frac{\partial h}{\partial t}\,dV - \int_{\mathcal{A}} \mathbf{n}\cdot\mathbf{v}^{\alpha\beta} h\,dA \qquad (4.5)$$

where h is some scalar or vector function of interest that varies in space and time and $\mathbf{v}^{\alpha\beta}$ is the velocity of surface of the volume. The transport theorem transforms a total time derivative of a function to a partial derivative of that function by accounting for the relative movement of the surface.

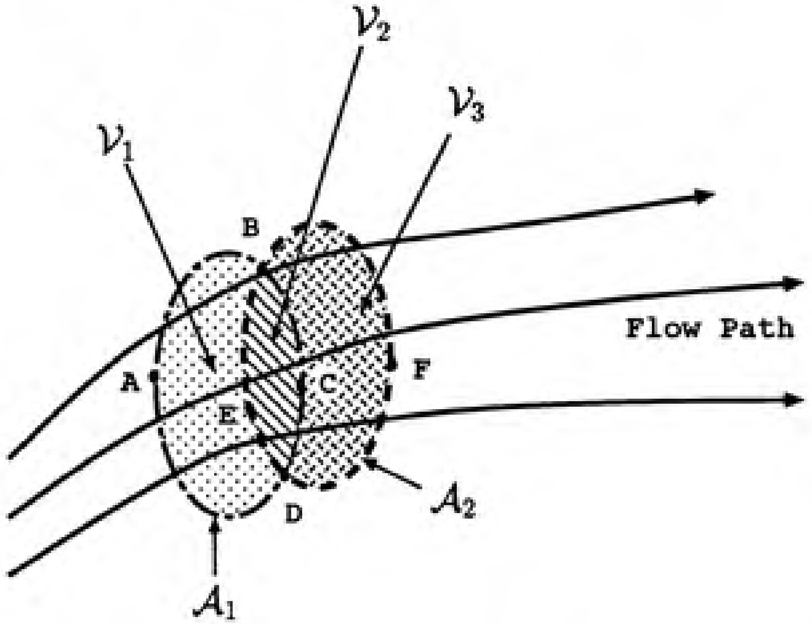


Figure 4.4: Rate of Change of a Function for Flow Through a Fixed Volume

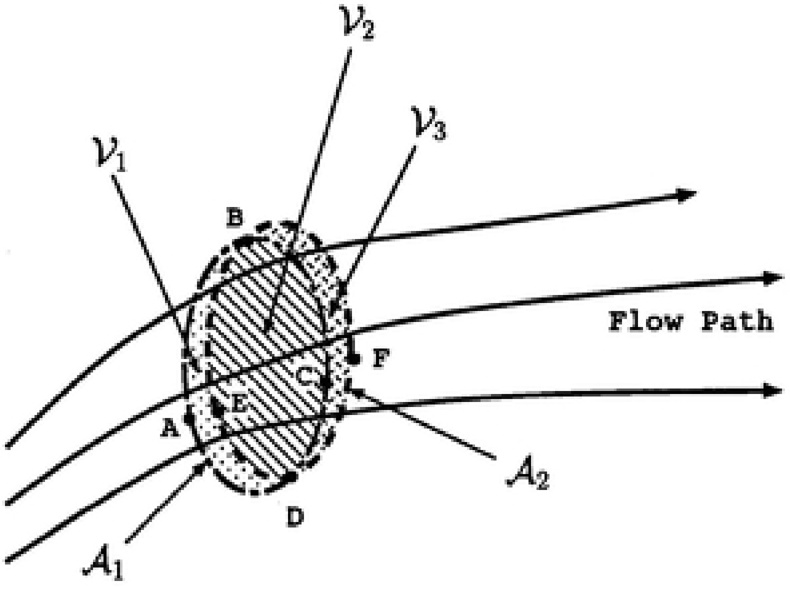


Figure 4.5: Rate of Change of a Function for Flow Through a Fixed Volume as Change in Time Decreases

The transport theorem can be described by stepping through Figures 4.4 and 4.5 [*Bear*, 1972; *Olson and Wright*, 1990]. In reference to Figure 4.4, at time t let the bounding surface which goes through points A, B, C, and D be denoted as $\mathcal{A}1$. $\mathcal{A}1$ will enclose the initial amount of h which occupies the volumes $\mathcal{V}1$ and $\mathcal{V}2$. Let the functions $h_{\mathcal{V}1}$, $h_{\mathcal{V}2}$, and $h_{\mathcal{V}3}$ represent an extensive fluid property such as mass, momentum, energy, or entropy within the volumes $\mathcal{V}1$, $\mathcal{V}2$, and $\mathcal{V}3$ respectively. After an incremental time, Δt, the initial amount of h will move to an area which can then be bounded by the closed surface denoted by points B, F, D, and E which we will call $\mathcal{A}2$. The bounding surface $\mathcal{A}2$ now encloses the property h which now occupies the volumes $\mathcal{V}2$ and $\mathcal{V}3$. The value of h as a function of time can then be stated as:

$$h(t) = h_{\mathcal{V}1}(t) + h_{\mathcal{V}2}(t) \tag{4.6}$$

and at $t = t + \Delta t$:

$$h(t + \Delta t) = h_{\mathcal{V}2}(t + \Delta t) + h_{\mathcal{V}3}(t + \Delta t) \tag{4.7}$$

Therefore, the temporal change in the property h in the system over a time step of Δt can be found through subtraction as:

$$\begin{aligned} \Delta h &= h(t + \Delta t) - h(t) \\ &= h_{\mathcal{V}2}(t + \Delta t) - h_{\mathcal{V}2}(t) + h_{\mathcal{V}3}(t + \Delta t) - h_{\mathcal{V}1}(t) \end{aligned} \tag{4.8}$$

or equivalently

$$\frac{\Delta h}{\Delta t} = \frac{\Delta h_{\mathcal{V}2}}{\Delta t} + \frac{h_{\mathcal{V}3}(t + \Delta t)}{\Delta t} - \frac{h_{\mathcal{V}1}(t)}{\Delta t} \tag{4.9}$$

As $\Delta t \to 0$, as shown in Figure 4.5, the volumes $\mathcal{V}1$ and $\mathcal{V}3$ will approach zero. Consequently, the volume $\mathcal{V}2$ will will approach the volume of initial control volume, such that the first term on the RHS of Eq. (4.9) can be written as:

$$\lim_{\Delta t \to 0} \frac{\Delta h_{\mathcal{V}2}}{\Delta t} = \frac{\partial h_{\mathcal{V}}}{\partial t} = \int_{\mathcal{V}} \frac{\partial}{\partial t} h \, dV \tag{4.10}$$

As $\Delta t \to 0$, the volumes $\mathcal{V}1$ and $\mathcal{V}3$ will in effect shrink to be the surfaces of the initial control volume. $\mathcal{V}1$ will effectively become the line represented by the points D, A, and B. Also, $\mathcal{V}3$ will effectively become the line represented by the points B, F and D. Therefore, the second term on the RHS of Eq. (4.9) will account for the rate of efflux of h through the surface. The third term on the RHS account for the rate of influx of h through the surface. Combining these terms will represent the net flux of h out of the control volume across the entire surface that encloses V at time t. For a surface velocity of $\mathbf{v}^{\alpha\beta}$, the net flux through the surface is written as:

$$\lim_{\Delta t \to 0} \left(\frac{h_{V3}(t+\Delta t) - h_{V1}(t)}{\Delta t} \right) = \int_{A} \mathbf{n} \cdot h \, \mathbf{v}^{\alpha\beta} \, dA \tag{4.11}$$

Therefore, as $\Delta t \to 0$, Eq. (4.9) can be written as:

$$\frac{d}{dt} \int_{V} h \, dV = \int_{V} \frac{\partial h}{\partial t} \, dV - \int_{A} \mathbf{n} \cdot \mathbf{v}^{\alpha\beta} h \, dA \tag{4.12}$$

which is exactly the general transport theorem as stated in Eq. (4.5).

If the volume of interest is fixed in space, then $\mathbf{v}^{\alpha\beta} = 0$ and

$$\frac{d}{dt} \int_{V} h \, dV = \int_{V} \frac{\partial h}{\partial t} \, dV \tag{4.13}$$

The divergence and transport theorems ease the formulation of balance equations which consider interfacial effects between phases, allowing the interfacial terms to be written in terms of volume integrals which are more readily measured. The specific application of these theorems for multiphase systems, such as the systems pictured in Figure 4.2, have been described with generalized functions for volumes, interfaces, and contact lines [*Gray et al.*, 1993]. The strength of generalized functions lies in the ability for equation manipulations that involve the integrand with minimal concern for the limits of integration [*Kanwal*, 1983]. More conventional and complicated methods exist that track the moving and deforming interfaces [*Slattery*, 1972; *Whitaker*, 1981] but this report will focus on the application of generalized functions to more readily derive balance equations.

To apply the integration and averaging theorems that we have described in general, we will first define the terminology. We will also develop the specific integration and averaging theorems used in multiphase systems for volumes, surfaces, and contact lines.

Integration and Averaging Theorems for Volumes

In the case of a volume that represents the α-phase which is averaged from the microscale to the macroscale, the methodology of *Gray et al.* [1993] may be used to facilitate equation development. The averaging theorem for the divergence of a vector field occurring in a volume can be written as [*Gray et al.*, 1993]:

$$\int_{V_\alpha} \nabla \cdot \mathbf{f}^\alpha \, dV = \nabla \cdot \int_{V_\alpha} \mathbf{f}^\alpha \, dV + \int_{A_{\alpha\beta}} \mathbf{n}^\alpha \cdot \mathbf{f}^\alpha \, dA + \int_{A_{\alpha\gamma}} \mathbf{n}^\alpha \cdot \mathbf{f}^\alpha \, dA \tag{4.14}$$

where These surfaces are highlighted in Figures 4.6 and 4.7.

The integration theorem for divergence, Eq. (4.4), can be rewritten for the α-phase which is in contact with the β- and γ-phases as:

$$\int_{V_\alpha} \nabla \cdot \mathbf{f}^\alpha \, dV = \int_{A_{\alpha\alpha}} \mathbf{n}^\alpha_\mathrm{b} \cdot \mathbf{f}^\alpha \, dA + \int_{A_{\alpha\beta}} \mathbf{n}^\alpha \cdot \mathbf{f}^\alpha \, dA + \int_{A_{\alpha\gamma}} \mathbf{n}^\alpha \cdot \mathbf{f}^\alpha \, dA \tag{4.15}$$

where $\int_{A_{\alpha\alpha}}$ represents a surface integral over the external boundary of V_α that coincides with the α-phase. Again, this surface is depicted in Figure 4.6 and in Figure 4.7.

Combining the above integration theorem, Eq. (4.15), with the averaging theorem stated in Eq. (4.14) yields:

$$\nabla \cdot \int_{V_\alpha} \mathbf{f}^\alpha \, dV = \int_{A_{\alpha\alpha}} \mathbf{n}^\alpha_\mathrm{b} \cdot \mathbf{f}^\alpha \, dA \tag{4.16}$$

For the volume of interest that fixed in space, the transport equation stated in Eq. (4.13) can be applied and restated as:

$$\frac{d}{dt} \int_{V_\alpha} h \, dV = \int_{V_\alpha} \frac{\partial h}{\partial t} \, dV \tag{4.17}$$

Integration and Averaging Theorems for Interfaces

At the interfaces, integration and averaging the theorems can be applied to transform line integrals to surface integrals. Figure 4.8 again shows a portion of a multiphase system, in a three-dimensional perspective, and highlights the interfacial areas. Now consider the interface between the α- and β-phases, shown in Figure 4.8 and highlighted in Figure 4.9. The interface is bounded above and below by the two

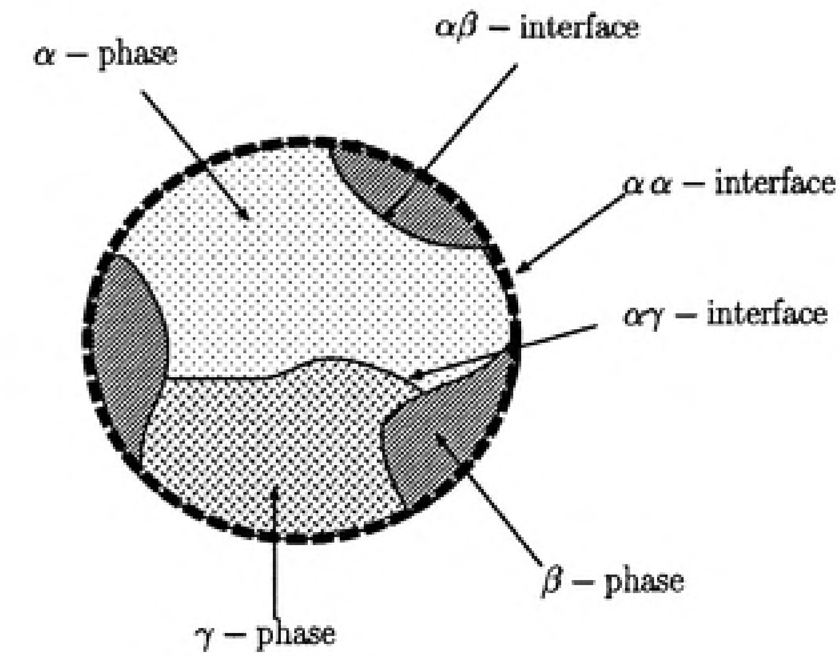


Figure 4.6: A Simplified Multiphase Volume Showing Phases and Interfaces

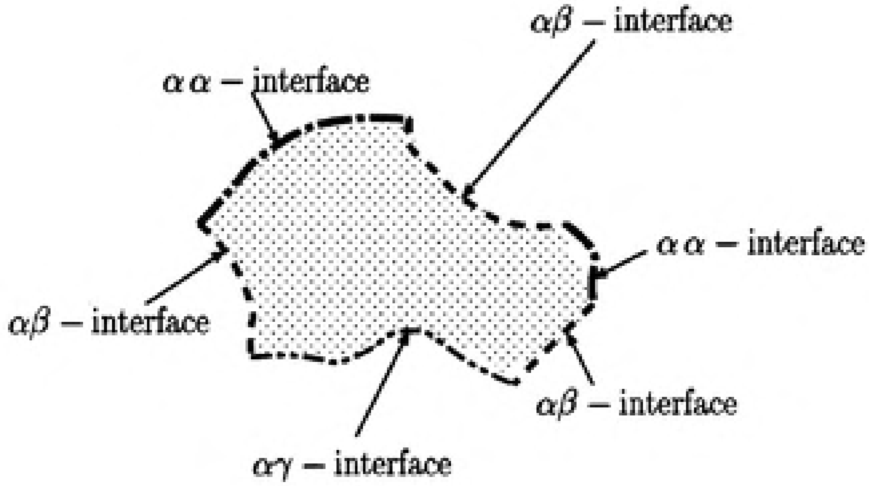


Figure 4.7: Highlighting the α-phase and Associated Interfaces

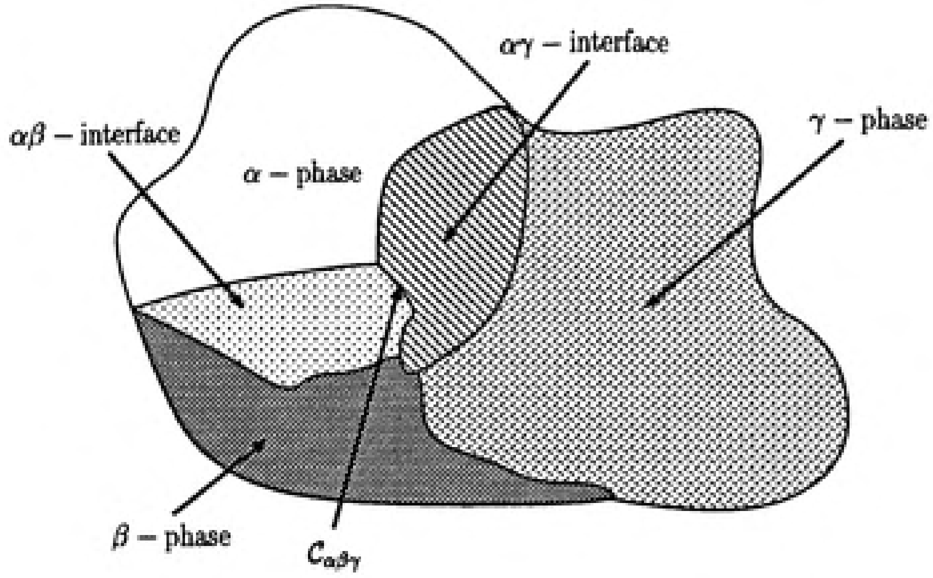


Figure 4.8: Three Phase Representative Figure

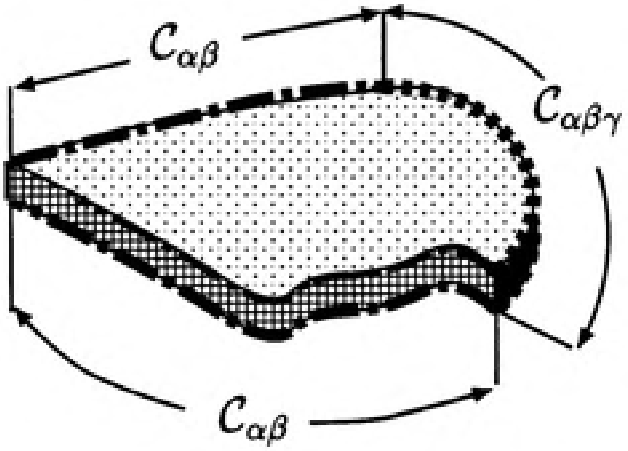


Figure 4.9: The $\alpha\beta$-interface

phases, on one edge by the $\alpha\beta\gamma$-contact line, and on the remaining edges by the boundary of the REV.

The motivation for use of the divergence theorem applied to surficial areas is to express the integral of the fluxes out of the sides and boundaries of the surface as the divergence of a vector field over the surface. Following the methodology previously applied to volumes in Eq. (4.4), the divergence for a surface will be formulated in terms of fluxes on the boundary of the surface, taking into consideration the top and bottom of the surface as well as the boundaries. This can be written as [*Gray and Hassanizadeh*, 1989]:

$$\int_{A_{\alpha\beta}} \nabla \cdot \mathbf{f}^{\alpha}\, dA = \int_{A_{\alpha\beta}} \mathbf{n}^{\alpha} \cdot \mathbf{f}^{\alpha}\, dA + \int_{C_{\alpha\beta}} \mathbf{n}_{\mathrm{b}}^{\alpha\beta} \cdot \mathbf{f}^{\alpha\beta}\, dC + \int_{C_{\alpha\beta\gamma}} \mathbf{n}^{\alpha\beta} \cdot \mathbf{f}^{\alpha\beta}\, dC \tag{4.18}$$

where the term on the LHS represents divergence directed outward normal to the surface, the first term on the RHS represents the flux out of the $A_{\alpha\beta}$ interface into the phases, the second term on the RHS represents the flux out of the boundary of the $A_{\alpha\beta}$ interface caused by the REV boundary and the third term on the RHS represents the flux out of the boundary of the $A_{\alpha\beta}$ interface into the $C_{\alpha\beta\gamma}$ contact line.

The averaging theorem for the divergence of a vector field occurring on a surface, converting microscopic derivatives to macroscopic derivatives, can be written as [*Gray et al.*, 1993, p. 163]:

$$\int_{A_{\alpha\beta}} \nabla \cdot \mathbf{f}^{\alpha}\, dA = \nabla \cdot \int_{A_{\alpha\beta}} \mathbf{f}^{\alpha\beta}\, dA + \int_{A_{\alpha\beta}} \mathbf{n}^{\alpha} \cdot \mathbf{f}^{\alpha}\, dA + \int_{C_{\alpha\beta\gamma}} \mathbf{n}^{\alpha\beta} \cdot \mathbf{f}^{\alpha\beta}\, dC \tag{4.19}$$

Combining Eq. (4.18) and Eq. (4.19) yields:

$$\nabla \cdot \int_{A_{\alpha\beta}} \mathbf{f}^{\alpha\beta}\, dA = \int_{C_{\alpha\beta}} \mathbf{n}_{\mathrm{b}}^{\alpha\beta} \cdot \mathbf{f}^{\alpha\beta}\, dC \tag{4.20}$$

where $\mathbf{f}^{\alpha\beta}$ has been defined in Eq. (4.2).

The transport theorem for surfaces uses the integration theorem presented at the beginning of this subsection for a volume. Assuming the volumes in Figures 4.4 and 4.5 were instead surfaces with sides and bounding edges, the equivalent transport theorem is stated as [*Gray et al.*, 1993, p. 143]:

$$\frac{d}{dt}\int_{\mathcal{A}_{\alpha\beta}} h\,dA = \int_{\mathcal{A}_{\alpha\beta}} \frac{\partial h}{\partial t}\,dA + \int_{\mathcal{A}_{\alpha\beta}} \mathbf{n}^{\alpha}\cdot\mathbf{v}^{\alpha\beta} h\,dA + \int_{\mathcal{C}_{\alpha\beta}} \mathbf{n}_{\mathrm{b}}^{\alpha\beta}\cdot\mathbf{v}^{\alpha\beta} h\,dC + \int_{\mathcal{C}_{\alpha\beta\gamma}} \mathbf{n}^{\alpha\beta}\cdot\mathbf{v}^{\alpha\beta} h\,dC \tag{4.21}$$

which relates the surface to the moving surface plus flux out normal to the surface plus flux out the bounding edges. The term on the LHS represents the temporal change of a quantity of interest, h, within the interface. The first term on the RHS represents the integral of a partial temporal change of quantity of interest within the interface. The second term on the RHS represents the flux out of the surfaces of the $\mathcal{A}_{\alpha\beta}$ interface. The third term on the RHS represents the flux out of the line caused by the REV boundary and the fourth term on the RHS represents the flux out of the boundary of the $\mathcal{A}_{\alpha\beta}$ interface into the $\mathcal{C}_{\alpha\beta\gamma}$ contact line.

The averaging theorem that converts microscopic surface derivatives to three-dimensional macroscopic derivatives is stated as [*Gray et al.*, 1993, p. 164]:

$$\int_{\mathcal{A}_{\alpha\beta}} \frac{\partial h}{\partial t}\,dA = \frac{\partial}{\partial t}\int_{\mathcal{A}_{\alpha\beta}} h\,dA + \nabla\cdot\int_{\mathcal{A}_{\alpha\beta}} \mathbf{v}^{\alpha\beta} h\,dA - \int_{\mathcal{A}_{\alpha\beta}} \mathbf{n}^{\alpha}\cdot\mathbf{v}^{\alpha\beta} h\,dA - \int_{\mathcal{C}_{\alpha\beta\gamma}} \mathbf{n}^{\alpha\beta}\cdot\mathbf{v}^{\alpha\beta} h\,dC \tag{4.22}$$

Combining Eq. (4.21) and Eq. (4.22) yields the transport theorem for an interface as:

$$\frac{d}{dt}\int_{\mathcal{A}_{\alpha\beta}} h\,dA = \frac{\partial}{\partial t}\int_{\mathcal{A}_{\alpha\beta}} h\,dA + \nabla\cdot\int_{\mathcal{A}_{\alpha\beta}} \mathbf{v}^{\alpha\beta} h\,dA + \int_{\mathcal{C}_{\alpha\beta}} \mathbf{n}^{\alpha\beta}\cdot\mathbf{v}^{\alpha\beta} h\,dC \tag{4.23}$$

For a fixed interface, $\mathbf{v}^{\alpha\beta} = 0$, the transport equation reduces to:

$$\frac{d}{dt}\int_{\mathcal{A}_{\alpha\beta}} h\,dA = \frac{\partial}{\partial t}\int_{\mathcal{A}_{\alpha\beta}} h\,dA \tag{4.24}$$

Integration and Averaging Theorems for Contact Lines

At the contact line, shown in Figure 4.10, integration and averaging the theorems can be applied. Following the methodology previously applied to volumes in Eq.

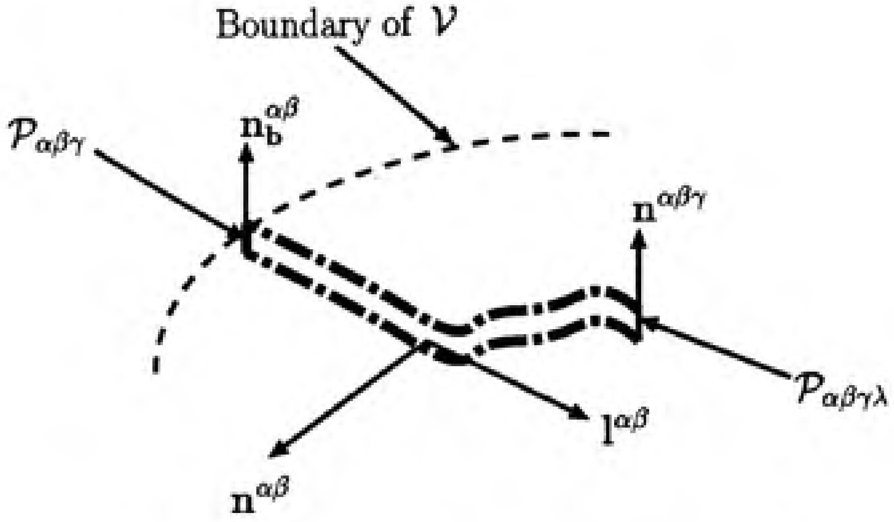


Figure 4.10: A Contact Line Showing Internal and External Endpoints

(4.4), the divergence for a contact line can be written as [*Gray et al.*, 1993, p. 168]:

$$\int_{C_{\alpha\beta\gamma}} \nabla \cdot \mathbf{f}^{\alpha}\, dC = -\int_{C_{\alpha\beta\gamma}} \mathbf{l}^{\alpha\beta} \cdot \mathbf{f}^{\alpha\beta}\, dC + \sum_{\mathcal{P}_{\alpha\beta\gamma}} \mathbf{n}_{\mathbf{b}}^{\alpha\beta\gamma} \cdot \mathbf{f}^{\alpha\beta\gamma}\, dC + \sum_{\mathcal{P}_{\alpha\beta\gamma\lambda}} \mathbf{n}^{\alpha\beta\gamma} \cdot \mathbf{f}^{\alpha\beta\gamma}\, dC \quad (4.25)$$

where the term on the LHS represents divergence directed outward normal to the contact line, $\mathcal{P}_{\alpha\beta\gamma}$ represents the endpoint of $C_{\alpha\beta\gamma}$ that is caused by the edge of $\mathcal{V}$, $\mathcal{P}_{\alpha\beta\gamma\lambda}$ represent the internal endpoints of $C_{\alpha\beta\gamma}$, and $\mathbf{n}^{\alpha\beta\gamma}$ is the unit vector tangent to the curve $C_{\alpha\beta\gamma}$ at its endpoints within the REV positive in the direction out from the curve such that $\mathbf{l}^{\alpha\beta} \cdot \mathbf{n}^{\alpha\beta\gamma} = \pm 1$. The first term on the RHS represents the flux out of the $C_{\alpha\beta\gamma}$ contact line into the adjacent $\alpha\beta$-interfaces, the second term on the RHS represents the flux out of the line into the point $\mathcal{P}_{\alpha\beta\gamma}$, and the third term on the RHS represents the flux out of the line into the point $\mathcal{P}_{\alpha\beta\gamma\lambda}$.

The averaging theorem for the divergence of a vector field occurring on a surface, converting microscopic derivatives to macroscopic derivatives, can be written as [*Gray et al.*, 1993, p. 164]:

$$\int_{C_{\alpha\beta\gamma}} \nabla \cdot \mathbf{f}^{\alpha}\, dC = \nabla \cdot \int_{C_{\alpha\beta\gamma}} \mathbf{f}^{\alpha\beta\gamma}\, dC - \int_{C_{\alpha\beta\gamma}} \mathbf{l}^{\alpha\beta} \cdot \mathbf{f}^{\alpha\beta}\, dC + \sum_{\mathcal{P}_{\alpha\beta\gamma\lambda}} \mathbf{n}^{\alpha\beta\gamma} \cdot \mathbf{f}^{\alpha\beta\gamma}\, dC \quad (4.26)$$

Combining Eq. (4.25) and Eq. (4.26) yields:

$$\nabla \cdot \int_{C_{\alpha\beta\gamma}} \mathbf{f}^{\alpha\beta\gamma}\, dC = \sum_{\mathcal{P}_{\alpha\beta\gamma}} \mathbf{n}_{\mathrm{b}}^{\alpha\beta\gamma} \cdot \mathbf{f}^{\alpha\beta\gamma}\, dC \tag{4.27}$$

stating that the divergence of the integral of a vector function along a line will be equal to the flux out of the boundary endpoints. $\mathbf{f}^{\alpha\beta\gamma}$ was previously defined in Eq. (4.3).

The transport theorem for surfaces uses the integration theorem presented at the beginning of this subsection for a volume. If the volumes in Figure 4.4 were instead a line, the equivalent transport theorem could be stated as [*Gray et al.*, 1993, p. 154]:

$$\begin{aligned} \frac{d}{dt} \int_{C_{\alpha\beta\gamma}} h\, dA &= \int_{C_{\alpha\beta\gamma}} \frac{\partial h}{\partial t}\, dC \\ &+ \int_{C_{\alpha\beta\gamma}} \mathbf{l}^{\alpha\beta} \cdot \mathbf{v}^{\alpha\beta\gamma} h\, dA + \sum_{\mathcal{P}_{\alpha\beta\gamma}} \mathbf{n}_{\mathrm{b}}^{\alpha\beta\gamma} \cdot \mathbf{v}^{\alpha\beta\gamma} h\, dC + \sum_{\mathcal{P}_{\alpha\beta\gamma\lambda}} \mathbf{n}^{\alpha\beta\gamma} \cdot \mathbf{v}^{\alpha\beta\gamma} h\, dC \end{aligned} \tag{4.28}$$

which relates the contact line to the moving line plus flux out of the ends of the line. The term on the LHS represents the temporal change of a quantity of interest, h, within the contact line. The first term on the RHS represents the integral of a partial temporal change of quantity of interest within the contact line. The second term on the RHS represents transport out of the contact line, the third term on the RHS represents the transport out of the line at the boundary point, and the fourth term on the RHS represents the transport out of the line at the internal endpoint.

The averaging theorem to convert microscopic derivatives to macroscopic derivatives is stated as [*Gray et al.*, 1993, p. 165]:

$$\begin{aligned} \int_{C_{\alpha\beta\gamma}} \frac{\partial h}{\partial t}\, dC &= \frac{\partial}{\partial t} \int_{C_{\alpha\beta\gamma}} h\, dC \\ &+ \nabla \cdot \int_{C_{\alpha\beta\gamma}} \mathbf{v}^{\alpha\beta\gamma} h\, dA - \int_{C_{\alpha\beta\gamma}} \mathbf{l}^{\alpha\beta} \cdot \mathbf{v}^{\alpha\beta\gamma} h\, dA - \sum_{\mathcal{P}_{\alpha\beta\gamma\lambda}} \mathbf{n}^{\alpha\beta\gamma} \cdot \mathbf{v}^{\alpha\beta\gamma} h\, dC \end{aligned} \tag{4.29}$$

Combining Eq. (4.28) and Eq. (4.29) produces:

$$\frac{d}{dt} \int_{C_{\alpha\beta\gamma}} h\, dA = \frac{\partial}{\partial t} \int_{C_{\alpha\beta\gamma}} h\, dC + \nabla \cdot \int_{C_{\alpha\beta\gamma}} \mathbf{v}^{\alpha\beta\gamma} h\, dA + \sum_{\mathcal{P}_{\alpha\beta\gamma}} \mathbf{n}_{\mathrm{b}}^{\alpha\beta} \cdot \mathbf{v}^{\alpha\beta\gamma} h\, dC \tag{4.30}$$

For a fixed contact line, $\mathbf{v}^{\alpha\beta\gamma} = 0$ and Eq. (4.30) reduces to:

$$\frac{d}{dt} \int\limits_{C_{\alpha\beta\gamma}} h\,dA = \frac{\partial}{\partial t} \int\limits_{C_{\alpha\beta\gamma}} h\,dC \tag{4.31}$$

4.2.3 Intrinsic Phase- and Mass-Averages

In the previous chapter, we discussed length scales and the assumption that at the macroscale a representative elementary volume (REV) existed. Intrinsic phase-averages and mass-weighted averages are defined by integrating microscale quantities over macroscale volumes, surfaces, and contact lines under the premise that an average value can be stated and is representative. Additional implications of the REV assumption for the integral approach will be mentioned at the end of this subsection.

To develop a macroscale balance equation, we propose that variables such as density, porosity, velocity, internal energy, etc. can be described with average values [*Whitaker*, 1967; *Slattery*, 1967; *Bear*, 1972]. Quantities such as mass, momentum, and stress are assumed continuously distributed. In this subsection, we define the formulation of averaged values for volumes, surfaces, and contact lines.

In Figure 4.12, a macroscopic volume is shown which has a total volume of V. The volume of the α-phase is V_α. The intrinsic macroscopic value for a microscopic property, h, will be defined as [*Hassanizadeh and Gray*, 1979a]:

$$\langle h \rangle^{\alpha} = \frac{1}{V_\alpha} \int\limits_{V_\alpha} h\,dV \tag{4.32}$$

Figures 4.12 and 4.13 show two different perspective of an interface between phases. The area of the $\alpha\beta$-interface is $A_{\alpha\beta}$. The specific surface, $\langle a \rangle^{\alpha\beta}$, is the amount of the $\alpha\beta$-interface per unit volume and is defined as:

$$\langle a \rangle^{\alpha\beta} = \frac{1}{V} \int\limits_{A_{\alpha\beta}} dA = \frac{A_{\alpha\beta}}{V} \tag{4.33}$$

which facilitates the definition of the intrinsic surface-average as:

$$\langle h \rangle^{\alpha\beta} = \frac{1}{A_{\alpha\beta}} \int\limits_{A_{\alpha\beta}} h\,dA \tag{4.34}$$

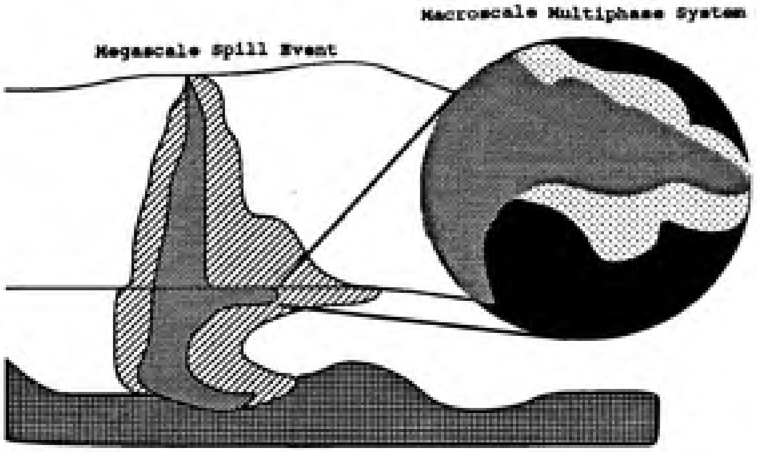


Figure 4.11: A Volume at the Macroscale

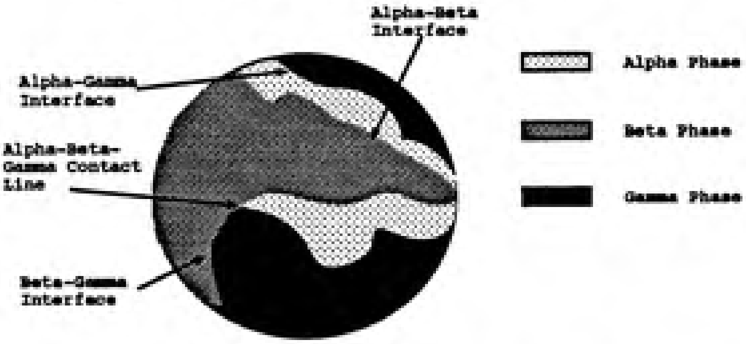


Figure 4.12: Highlighted Volumes, Surfaces, and a Contact Line

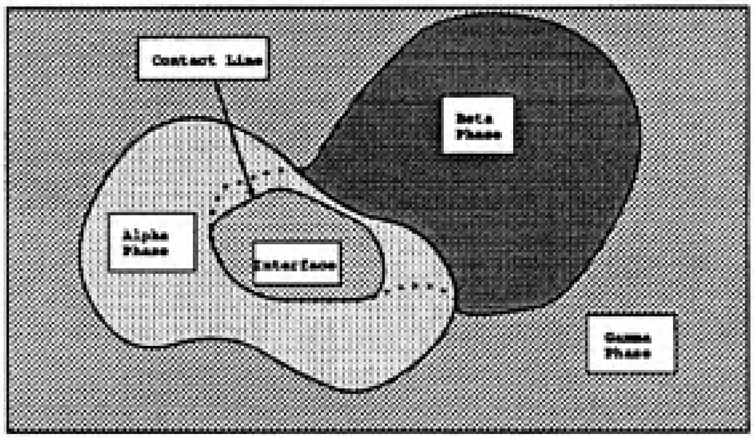


Figure 4.13: Another Perspective of A Three Phase System

For contact lines, $\langle l\rangle^{\alpha\beta\gamma}$ is the specific length representing the length of the $\alpha\beta\gamma$-contact line, $C_{\alpha\beta\gamma}$, per averaging volume and is defined as:

$$\langle l\rangle^{\alpha\beta\gamma} = \frac{1}{V}\int_{C_{\alpha\beta\gamma}} dC = \frac{C_{\alpha\beta\gamma}}{V} \tag{4.35}$$

which allows the contact line intrinsic phase-average to be defined as:

$$\langle h\rangle^{\alpha\beta\gamma} = \frac{1}{C_{\alpha\beta\gamma}}\int_{C_{\alpha\beta\gamma}} h\, dC \tag{4.36}$$

The mass-weighted average of a microscale property h, for a volume, a surface, and a contact line is defined respectively as [*Hassanizadeh and Gray*, 1979a]:

$$\overline{h^{\alpha}} = \frac{\int_{V_\alpha} \rho\, h\, dV}{\int_{V_\alpha} \rho\, dV} = \frac{1}{\langle\rho\rangle^{\alpha} V_\alpha}\int_{V_\alpha} \rho\, h\, dV = \frac{\langle\rho\, h\rangle^{\alpha}}{\langle\rho\rangle^{\alpha}} \tag{4.37}$$

$$\overline{h^{\alpha\beta}} = \frac{1}{\langle\rho\rangle^{\alpha\beta} A_{\alpha\beta}}\int_{A_{\alpha\beta}} \rho\, h\, dA = \frac{\langle\rho\, h\rangle^{\alpha\beta}}{\langle\rho\rangle^{\alpha\beta}} \tag{4.38}$$

$$\overline{h^{\alpha\beta\gamma}} = \frac{1}{\langle\rho\rangle^{\alpha\beta\gamma} C_{\alpha\beta\gamma}}\int_{C_{\alpha\beta\gamma}} \rho\, h\, dC = \frac{\langle\rho\, h\rangle^{\alpha\beta\gamma}}{\langle\rho\rangle^{\alpha\beta\gamma}} \tag{4.39}$$

where $\langle\rho\rangle^{\alpha}$ is the density of the α-phase in units of mass per volume, $\langle\rho\rangle^{\alpha\beta}$ is the density of the $\alpha\beta$-interface in units of mass per area, $\langle\rho\rangle^{\alpha\beta\gamma}$ is the density of the $\alpha\beta\gamma$-contact line in units of mass per length.

The REV assumption states that at a macroscopic length scale average values exist that do not change significantly with small change is length, however trends and fluctuations are expected in environmental systems. Properties can therefore be considered as a macroscopic average of microscopic quantities plus a fluctuation term. This allows for the examination of the ramifications of trends and fluctuations as the governing balance equations are developed. For a volume, a surface, or a contact line, we can write respectively:

$$h^{\alpha} = \overline{h}^{\alpha} + \tilde{h}^{\alpha} \tag{4.40}$$

$$h^{\alpha\beta} = \overline{h}^{\alpha\beta} + \tilde{h}^{\alpha\beta} \tag{4.41}$$

$$h^{\alpha\beta\gamma} = \overline{h}^{\alpha\beta\gamma} + \tilde{h}^{\alpha\beta\gamma} \tag{4.42}$$

where $\tilde{h}$ is the fluctuation of h about some mean value.

Additionally, the following identities for mass-averages of means and fluctuations will be used in the derivation of conservation equations where h and g are microscopic properties of interest [*Hassanizadeh and Gray*, 1979a; *Tompson*, 1985]:

1.
$$\overline{\overline{g^\alpha}}^\alpha = \frac{1}{\langle\rho\rangle^\alpha\, V_\alpha} \int\limits_{V_\alpha} \rho\overline{g^\alpha}\, dV = \overline{g^\alpha} \tag{4.43}$$
by the ergodic assumption, stating that the mean of the system is exactly the calculated mean at a point [*Christakos*, 1992].

2.
$$\overline{\tilde{g}^\alpha}^\alpha = \frac{1}{\langle\rho\rangle^\alpha\, V_\alpha} \int\limits_{V_\alpha} \rho(g - \overline{g^\alpha})\, dV = \overline{g^\alpha} - \overline{g^\alpha} = 0 \tag{4.44}$$
also by the ergodic assumption, stating that the mean of the fluctuations will be zero.

3.
$$\begin{aligned}\overline{\tilde{g}^\alpha \overline{h^\alpha}}^\alpha &= \frac{1}{\langle\rho\rangle^\alpha\, V_\alpha} \int\limits_{V_\alpha} \rho(\tilde{g}^\alpha \overline{h^\alpha})\, dV \\ &= \frac{\overline{h^\alpha}}{\langle\rho\rangle^\alpha\, V_\alpha} \int\limits_{V_\alpha} \rho\tilde{g}^\alpha\, dV = \overline{h^\alpha}\,\overline{\tilde{g}^\alpha}^\alpha = 0\end{aligned} \tag{4.45}$$
stating that the mean of a mean fluctuation multiplied by an overall mean will, assuming that the correlation between the fluctuation and the mean is negligible, reduce to multiplication by zero and hence be equal to zero.

4.
$$\begin{aligned}\overline{gh}^\alpha &= \overline{(\overline{g^\alpha} + \tilde{g}^\alpha)(\overline{h^\alpha} + \tilde{h}^\alpha)}^\alpha = \overline{\overline{g^\alpha}\,\overline{h^\alpha}}^\alpha + \overline{\overline{g^\alpha}\tilde{h}^\alpha}^\alpha \\ &+ \overline{\tilde{g}^\alpha \overline{h^\alpha}}^\alpha + \overline{\tilde{g}^\alpha \tilde{h}^\alpha}^\alpha = \overline{g^\alpha}\,\overline{h^\alpha} + \overline{\tilde{g}^\alpha \tilde{h}^\alpha}^\alpha\end{aligned} \tag{4.46}$$
stating that the mean of the product of two properties that both have independent fluctuations will be the product of the two means plus the mean of

the product of the two fluctuations. The mean of the product of the two fluctuations is many times assumed to very small, this assumption will be stated as applied. Cross terms will be equal to zero as they include the mean of a fluctuation.

4.2.4 Definitions and Identities

Certain mathematical relations are used frequently in the manipulation of the following balance equations and will be specified a priori for convenience. Standard vector calculus will be used. As a refresher, the following notation represents the indicated operation and results for general scalars, vectors, and tensors of interest [*Whitaker*, 1981; *Greenberg*, 1988]

Operation		Result
$\mathbf{f} \cdot \mathbf{g}$	→	scalar
$\mathbf{F} : \mathbf{G}$	→	scalar
$\text{div}\ \mathbf{f} \equiv \nabla \cdot \mathbf{f}$	→	scalar
$\text{div}\ \mathbf{F} \equiv \nabla \cdot \mathbf{F}$	→	vector
$\text{grad}\ f \equiv \nabla f$	→	vector
$\text{grad}\ \mathbf{f} \equiv \nabla \mathbf{f}$	→	tensor

Specifically, to multiply a tensor by a tensor to yield a scalar as indicated above, the tensor dot product, :, is defined as [*Whitaker*, 1981]:

$$\mathbf{F} : \mathbf{G} = \sum_{i,j} (\mathbf{F})_{ij} (\mathbf{G})_{ij} \tag{4.47}$$

It is helpful to define the variables used to describe flow and transport through a porous media system relative to a fixed coordinate system. Therefore, a material derivative is defined as the time rate of change of a property of interest relative to a fixed position. This is defined for an α-phase volume with a velocity $\mathbf{v}^{\alpha}$ as [*Eringen*, 1980]:

$$\frac{D^{\alpha} f}{Dt} = \frac{\partial f}{\partial t} + \mathbf{v}^{\alpha} \cdot \nabla f \tag{4.48}$$

where f is a property of interest which may be a scalar or vector quantity.

Similarly, for motion relative to an $\alpha\beta$-interface and an $\alpha\beta\gamma$- contact line, we respectively define:

$$\frac{D^{\alpha\beta} f}{Dt} = \frac{\partial f}{\partial t} + \mathbf{v}^{\alpha\beta} \cdot \nabla f \tag{4.49}$$

$$\frac{D^{\alpha\beta\gamma} f}{Dt} = \frac{\partial f}{\partial t} + \mathbf{v}^{\alpha\beta\gamma} \cdot \nabla f \tag{4.50}$$

where $\mathbf{v}^{\alpha\beta}$ is the velocity of the $\alpha\beta$-interface and $\mathbf{v}^{\alpha\beta\gamma}$ is the velocity of the $\alpha\beta\gamma$-contact line.

The definition of the scalar product below serves to simplify forthcoming equations stated as [*Whitaker*, 1981, p. 222]:

$$\begin{aligned} h\mathbf{f} \cdot \frac{D\mathbf{f}}{Dt} &= hf_x \frac{Df_x}{Dt} + hf_y \frac{Df_y}{Dt} + hf_z \frac{Df_z}{Dt} \\ &= \frac{D\left(\frac{hf_x^2}{2}\right)}{Dt} + \frac{D\left(\frac{hf_y^2}{2}\right)}{Dt} + \frac{D\left(\frac{hf_z^2}{2}\right)}{Dt} \\ &= h\frac{D\left(\frac{f^2}{2}\right)}{Dt} \end{aligned} \tag{4.51}$$

where $f^2 = f_x^2 + f_y^2 + f_z^2$ and represents the magnitude of the vector in the respective directions.

As in Chapter 3, the following mathematical identities will also lend clarity to equation manipulations [*Greenberg*, 1988]:

$$\frac{\partial (gh)}{\partial t} = g\frac{\partial h}{\partial t} + h\frac{\partial g}{\partial t} \tag{4.52}$$

$$\nabla \cdot (\mathbf{f}g) = \mathbf{f} \cdot \nabla g + g \nabla \cdot \mathbf{f} \tag{4.53}$$

With these tools in hand, we will proceed to the development of integral balance equations first at the microscale and then at the macroscale.

4.3 Microscale Formulations for Integral Balance Equations

Naturally occurring multiphase subsurface systems conserve mass, momentum, and energy throughout time. The total entropy of these systems will increase over time due to processes such as dispersion and diffusion. To quantify these conservation statements and the entropy inequality, a general integral balance equation for a property of interest will be developed, first about a microscale point, then at a macroscale point, and finally at the macroscale using the ICA.

4.3.1 Microscale Integral Point Formulation

The microscale integral balance equation is integrated about a microscale point at the length-scale d, as shown in Figure 4.14. By definition, each phase will be treated individually at the microscale. The general integral balance equation for a given scalar or vector property, ψ, of a single-phase fluid in a fixed microscale volume,

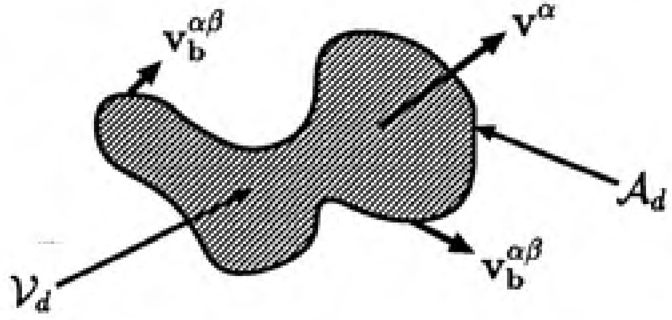


Figure 4.14: Microscale Point Volume for a Single Phase

$\mathcal{V}_d$, with a determined surface boundary, $\mathcal{A}_d$, is stated as [*Bear and Bachmat*, 1986]:

$$\overbrace{\frac{d}{dt}\int_{\mathcal{V}_d} \rho\psi \, dV}^{\text{Accumulation}} = \underbrace{-\int_{\mathcal{A}_d} \mathbf{n}^\alpha \cdot \rho(\mathbf{v}^\alpha - \mathbf{v}_\mathbf{b}^{\alpha\beta})\psi \, dA}_{\text{Advective Flux}} - \overbrace{\int_{\mathcal{A}_d} \mathbf{n}^\alpha \cdot \mathbf{j}_\psi \, dA}^{\text{Non-Advective Flux}} + \underbrace{\int_{\mathcal{V}_d} \rho(\mathcal{S} + \mathcal{P}) \, dV}_{\text{Sources and Production}} \tag{4.54}$$

where $\mathbf{n}^\alpha$ is a unit vector normal to the surface and pointing outward from the volume, ρ is the fluid density, $\mathbf{v}^\alpha$ is the fluid velocity, $\mathbf{v}_\mathbf{b}^{\alpha\beta}$ is the velocity of the boundary of the volume, $\mathbf{j}_\psi$ is the non-advective flux of ψ, $\mathcal{S}$ is an external source of ψ, and $\mathcal{P}$ represents any production of ψ within the volume. Stating that the accumulation of a property in a microscale volume over time is equal to the opposite of the net advective and non-advective fluxes directed out through the surface plus source terms plus any production of the property within the volume.

If we assume that $\mathbf{v}_\mathbf{b}^{\alpha\beta} = 0$, the application of the general transport theorem for a fixed volume, Eq. (4.13), to Eq. (4.54) brings the ordinary time derivative inside the integral as a partial time derivative. Application of the divergence theorem, Eq. (4.4), to Eq. (4.54) converts the advective and non-advective surfaces fluxes to volume integrals. The equivalent equation is restated as:

$$\int_{\mathcal{V}_d} \frac{\partial(\rho\psi)}{\partial t} \, dV = \int_{\mathcal{V}_d} \left[-\nabla \cdot (\rho\mathbf{v}^\alpha\psi) - \nabla \cdot \mathbf{j}_\psi + \rho(\mathcal{S} + \mathcal{P})\right] dV \tag{4.55}$$

Noting the equivalence of the integrands yields a microscopic continuity equation which is commonly stated in fluid and continuum mechanics as [*Bird et al.*, 1960; *Eringen*, 1980; *Whitaker*, 1981]:

$$\frac{\partial(\rho\psi)}{\partial t} = -\nabla \cdot (\rho\mathbf{v}^\alpha\psi) - \nabla \cdot \mathbf{j}_\psi + \rho(\mathcal{S} + \mathcal{P}) \tag{4.56}$$

Applications of the microscale balance equations, through network and pore scale modeling, have been used to examine relative permeability – capillary pressure relationships [*Jerauld and Salter*, 1990; *Ferrand and Celia*, 1992] and to examine residual NAPL distributions [*Mayer and Miller*, 1992a; *Lowry and Miller*, 1995]. Microscale multiphase balance equations will require the description of both the complex geometry associated with the domain $(\mathcal{V}_d)$ and the complex geometry associated with the boundary conditions $(\mathcal{A}_d)$, their changes with time, and the exchange of properties across these boundaries. This is a hopeless task for aquifer systems. There exists no easy way to verify the microscale solutions as no instruments are available for measuring values of dependent variables at the microscale. Also, the resulting system of equations with such detailed information would be prohibitive in size; therefore, equations must be formulated at a larger scale with quantities that can be measured and/or approximated [*Bachmat and Bear*, 1986].

4.3.2 Macroscale Point Formulation

The above difficulties associated with the microscale point formulation motivates a coarser description of the multiple phases present in groundwater systems. Figure 4.15 depicts a macroscopic volume with multiple phases. The macroscale describes the different phases in the porous medium as overlapping continua [*Gray et al.*, 1993], each occupying a fraction of the macroscale volume. Therefore, the extensive properties that are averaged over the macroscopic volume avoid describing the complex geometry associated with the single-fluid phase-boundaries that was necessary with the microscale balance equations. The advantages and the remaining limitations of

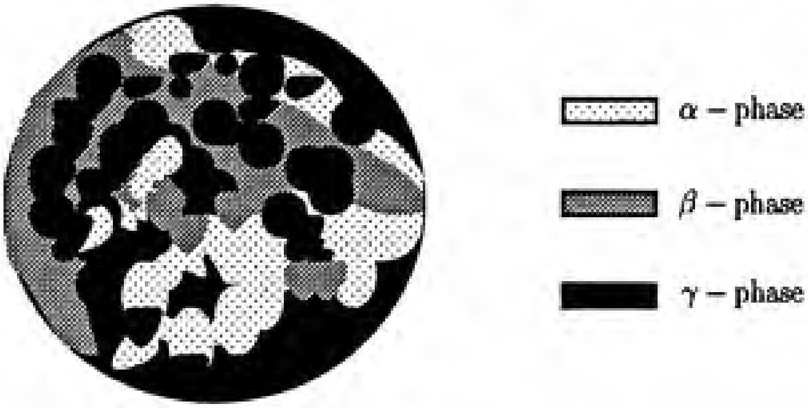


Figure 4.15: Macroscale Point Volume Showing Three Phases

writing integral balance equations at the macroscale will be highlighted after the balance equation itself is presented.

The macroscale integral balance equation is integrated about a macroscopic mathematical point, at the length-scale l, which will result in averaging over volumes containing multiple phases. The general integral balance equation for a given scalar or vector property, ψ, of the α-phase in a macroscopic volume, $\mathcal{V}_l$, with a surface boundary, $\mathcal{A}_l$, is stated as [*Bear and Bachmat*, 1986, p. 244]:

$$\overbrace{\frac{d}{dt}\int_{\mathcal{V}_l} \varepsilon^\alpha \rho^\alpha \psi^\alpha \, dV}^{\text{Accumulation}} = - \overbrace{\int_{\mathcal{A}_l} \mathbf{n}^\alpha \cdot \left[\varepsilon^\alpha \rho^\alpha (\mathbf{v}^\alpha - \mathbf{v}_\mathbf{b}^{\alpha\beta})\psi^\alpha + \varepsilon^\alpha \mathbf{j}_\psi^\alpha\right] dA}^{\substack{\text{Advective and} \\ \text{Non-Advective Fluxes}}} + \underbrace{\int_{\mathcal{V}_l} \varepsilon^\alpha \rho^\alpha \left(\mathcal{S}^\alpha + \mathcal{P}^\alpha\right) dV}_{\substack{\text{Sources and} \\ \text{Production}}} \tag{4.57}$$

where the α-phase is one of the phases in the volume under consideration, $\mathcal{S}^\alpha$ is an external source of ψ into the α-phase and $\mathcal{P}^\alpha$ represents production of ψ into the α-phase.

If we assume that $\mathbf{v}_\mathbf{b}^{\alpha\beta} = 0$, applying the transport theorem for a fixed volume, Eq. (4.13), and the general divergence theorem, Eq. (4.4), to Eq. (4.57) produces:

$$\int_{\mathcal{V}_l} \frac{\partial(\varepsilon^\alpha \rho^\alpha \psi^\alpha)}{\partial t} \, dV = \int_{\mathcal{V}_l} \left[-\nabla \cdot (\varepsilon^\alpha \rho^\alpha \mathbf{v}^\alpha \psi^\alpha) - \nabla \cdot (\varepsilon^\alpha \mathbf{j}_\psi^\alpha) + \varepsilon^\alpha \rho^\alpha \left(\mathcal{S}^\alpha + \mathcal{P}^\alpha\right)\right] dV \tag{4.58}$$

Noting the equivalence of the integrands yields a macroscopic balance equation commonly stated as [*Bear*, 1972; *Peaceman*, 1977; *Corey*, 1994]:

$$\frac{\partial(\varepsilon^\alpha \rho^\alpha \psi^\alpha)}{\partial t} = -\nabla \cdot (\varepsilon^\alpha \rho^\alpha \mathbf{v}^\alpha \psi^\alpha) - \nabla \cdot (\varepsilon^\alpha \mathbf{j}_\psi^\alpha) + \varepsilon^\alpha \rho^\alpha \left(\mathcal{S}^\alpha + \mathcal{P}^\alpha\right) \tag{4.59}$$

The macroscale point balance equation circumvents the need to define unspecifiable interphase boundaries and allows for the measurement or parameterization of variable of interest at the macroscopic scale. Mass transfer across interfaces, when included in the above equation, is commonly described with a first-order rate model, which is scalar and independent of flow direction. Models generally assume local equilibrium, are empirical in nature, and are based upon data that only covers a portion of the domain of interest [*Miller et al.*, 1996]. Theoretically, macroscale coefficients can now be calculated from information supplied from the microscale. In practice, however, this is not usually possible and the macroscale coefficients must be deduced from experiments in which the various phenomena related to these parameters are observed. Also, the relations that are empirically based on these experiments are not thermodynamically constrained and do not provide a consistent means for describing the system.

The simplicity of the macroscale point formulation soon becomes a disadvantage as more complicated systems are encountered. The interaction between multiple phases must be incorporated empirically. Also, the incomplete parameterization of variables over domains of interest and lack of experimental data quickly becomes a disadvantage in applying the macroscale point balance equations to systems of interest.

Eq. (4.59) parallels the differential continuum approach's starting point, Eq. (3.6). The shortcomings that have been highlighted in the development of equations beginning with Eq. (3.6) will also remain true for equations developed from Eq. (4.59).

4.4 Macroscale Integral Continuum Approach

Use of the aforementioned microscale and macroscale balance equations leaves unresolved issues. Table 4.1 outlines advantages and disadvantages associated with existing modeling approaches. The inability to make microscale measurements for porous media systems severely limits microscale applications. For macroscale formulations, as more complex systems such as surfactant, cosolvent, or non-isothermal systems are of increasing importance, existing differential balance equations must be supplemented. The current differential continuum framework does not allow for the systematic incorporation of additional balance equations often resulting in *ad hoc* constitutive theories to describe unforeseen issues [*Brown et al.*, 1994].

In contrast to the above point derivations, an integral continuum approach, fol-

Table 4.1: Modeling approaches for multiphase flow and transport in porous media

Modeling Approach	Length-Scale	Advantages	Limitations
Integral Point Continuum	Micro-scale	Theoretically rigorous, physically descriptive and complete	Complex geometry of boundaries difficult to describe, parameters not possible to measure for verification
Differential Continuum and Integral Point Continuum	Macro-scale	Avoids specification of interphase boundaries, defined physical properties can be measured, describes physical processes in terms of differential equations allowing solution	Ad hoc constitutive theory which may violate laws of thermodynamics, parameters must be represented empirically, lack of consistent framework for changing scales
Integral Continuum	Macro-scale	Systematic description of averaged quantities, includes description of interfaces and contact lines, thermodynamically consistent	Leads to large systems of equations, non-traditional constitutive relations may be needed

lowing the methodology presented by *Hassanizadeh and Gray* [1979a, 1979b, 1980a], can be used to develop macroscale integral equations such that processes occurring at interfaces can be represented as precisely defined averaged processes rather than cumbersome boundary conditions that require descriptions of boundaries and their changes with time. The ICA method retains the advantage of describing physical processes in terms of differential equations allowing for potential solution. The ICA method also provides a systematic approach for changing scales.

Figure 4.16 is a simplified two-dimensional depiction of a multiphase system so that notation can be clearly defined. The REV, $\mathcal{V}$, contains multiple phases with respective volumes, $\mathcal{V}_\alpha$, $\mathcal{V}_\beta$, and $\mathcal{V}_\gamma$. The bounding surfaces of each subvolume can further be subdivided; for example, the boundary of $\mathcal{V}_\alpha$ will be divided into three parts, $\mathcal{A}_{\alpha\alpha}$, $\mathcal{A}_{\alpha\beta}$ and $\mathcal{A}_{\alpha\gamma}$. The surface $\mathcal{A}_{\alpha\alpha}$ represents portions of the surface that intersect the α-phase and are coincident with the boundary of $\mathcal{V}$. $\mathcal{A}_{\alpha\beta}$ represent portions of the boundary that are interfaces between the α- and β-phases and part of the interior of $\mathcal{V}$. Likewise, $\mathcal{A}_{\alpha\gamma}$ represent portions of the bounding surface that are interfaces between the α- and γ-phases and part of the interior of $\mathcal{V}$. The physical volume of the REV is V and the physical volume of $\mathcal{V}_\alpha$ is V_α.

To then write a macroscale integral continuum approach for a scalar or vector property, ψ, we begin with a balance equation for that property, ψ, written about the volume $\mathcal{V}_\alpha$. Quantities within the integrands are microscale quantities that will be assumed to reach continuous, average values when integrated about the macroscopic volume. The interfaces and boundary of $\mathcal{V}_\alpha$ are partitioned as noted in Figure 4.16 to allow for processes occurring at these interfaces to be represented as precisely defined averaged processes. The resulting balance equation for a fixed volume is written as [*Hassanizadeh and Gray*, 1979a, 1979b]:

$$\overbrace{\frac{d}{dt}\int\limits_{V_\alpha} \rho\psi\, dV}^{\text{Accumulation}} \;=\; - \;\overbrace{\int\limits_{A_{\alpha\alpha}} \mathbf{n}_b^{\alpha}\cdot\left(\rho\mathbf{v}^{\alpha}\psi + \mathbf{j}_\psi\right) dA}^{\substack{\text{Advective and}\\ \text{Non-Advective Fluxes}\\ \text{through volume boundary}}}$$

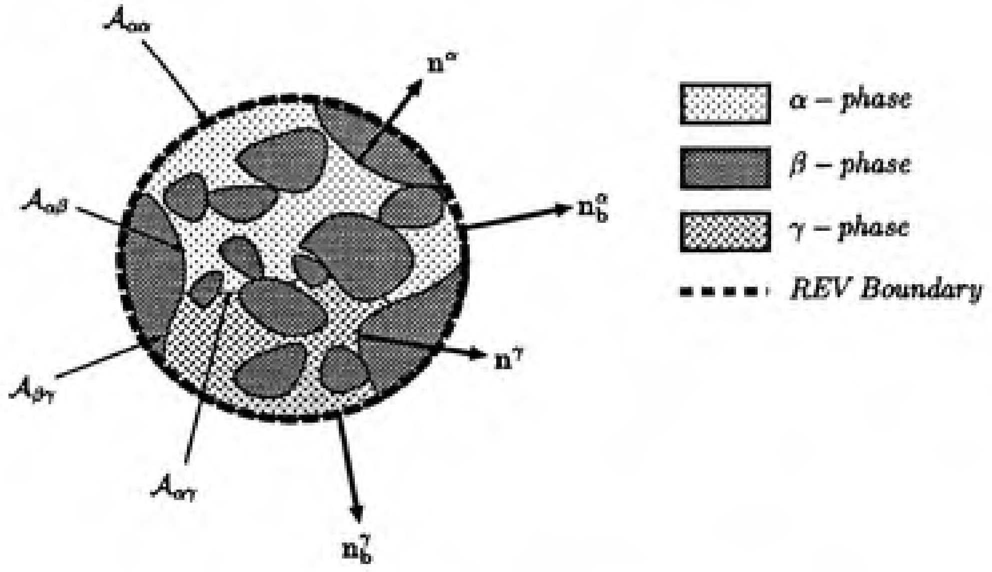


Figure 4.16: Simplified Macroscale REV

$$- \underbrace{\sum_{\beta\neq\alpha}\int\limits_{\mathcal{A}_{\alpha\beta}} \mathbf{n}^\alpha\cdot\left[\rho(\mathbf{v}^\alpha-\mathbf{v}^{\alpha\beta})\psi+\mathbf{j}_\psi\right]dA}_{\substack{\text{Advective and}\\ \text{Non-Advective Fluxes}\\ \text{into interfaces}}} + \underbrace{\int\limits_{\mathcal{V}_\alpha}\rho\left(\mathcal{S}+\mathcal{P}\right)\,dV}_{\substack{\text{Sources and}\\ \text{Production}}} \quad (4.60)$$

where $\mathbf{v}^{\alpha\beta}$ is the velocity of the $\alpha\beta$-interface, the quantity $\rho\mathbf{v}^\alpha\psi$ represents advection that can be out through either the $\mathcal{A}_{\alpha\alpha}$ surface as in the first term on the RHS or through the $\mathcal{A}_{\alpha\beta}$ surface as in the second term on the RHS, $\mathbf{j}_\psi$ represents non-advective fluxes out through also the $\mathcal{A}_{\alpha\alpha}$ and $\mathcal{A}_{\alpha\beta}$ surfaces, and the notation in the second term on the RHS, $\sum_{\beta\neq\alpha}\int\limits_{\mathcal{A}_{\alpha\beta}}$ is used to indicates that all of the $\mathcal{A}_{\alpha\beta}$ surfaces are collectively considered.

The transport theorem for a fixed volume, Eq. (4.13), is used to express the total time derivative in the term on the LHS of Eq. (4.60) as a partial time derivative. The divergence theorem, Eq. (4.16), is used to transform the integral of the surface flux [the first term on the RHS of Eq. (4.60)] into the divergence of an integral over the volume $\mathcal{V}_\alpha$ [*Gray and Lee*, 1977]. Combined, this allows the macroscale balance equation, still containing microscopic quantities inside integrals, to be stated as:

$$\frac{\partial}{\partial t}\int\limits_{V_\alpha} \rho\psi \, dV = -\nabla \cdot \int\limits_{V_\alpha} (\rho \mathbf{v}^\alpha \psi + \mathbf{j}_\psi) \, dV - \sum_{\beta \neq \alpha} \int\limits_{A_{\alpha\beta}} \mathbf{n}^\alpha \cdot [\rho(\mathbf{v}^\alpha - \mathbf{v}^{\alpha\beta})\psi + \mathbf{j}_\psi] \, dA + \int\limits_{V_\alpha} \rho\,(\mathcal{S} + \mathcal{P}) \; dV \tag{4.61}$$

Dividing Eq. (4.61) by the macroscopic volume ($V = V^\alpha / \varepsilon^\alpha$), which is assumed to be a constant, yields:

$$\frac{\langle \varepsilon \rangle^\alpha}{V^\alpha}\left(\frac{\partial}{\partial t}\int\limits_{V^\alpha} \rho\psi \, dV\right) = -\frac{\langle \varepsilon \rangle^\alpha}{V^\alpha}\left(\nabla \cdot \int\limits_{V^\alpha} (\rho \mathbf{v}^\alpha \psi + \mathbf{j}_\psi) \, dV\right) - \frac{\langle \varepsilon \rangle^\alpha}{V^\alpha} \sum_{\beta \neq \alpha} \int\limits_{A_{\alpha\beta}} \mathbf{n}^\alpha \cdot [\rho(\mathbf{v}^\alpha - \mathbf{v}^{\alpha\beta})\psi + \mathbf{j}_\psi] \, dA + \frac{\langle \varepsilon \rangle^\alpha}{V^\alpha} \int\limits_{V^\alpha} \rho\,(\mathcal{S} + \mathcal{P}) \; dV \tag{4.62}$$

Using the previously defined volume average, Eq. (4.32), the mass average for a volume, Eq. (4.37), and defining fluctuation terms as described in Eq. (4.40) allows us to write Eq. (4.62) in terms of macroscopic quantities as:

$$\frac{\partial\left[\langle \varepsilon \rangle^\alpha \; \langle \rho \rangle^\alpha \; \left(\overline{\psi}^\alpha + \tilde{\psi}^\alpha\right)\right]}{\partial t} = -\nabla \cdot \left[\langle \varepsilon \rangle^\alpha \; \langle \rho \rangle^\alpha \; \left(\overline{\mathbf{v}\psi}^\alpha\right)\right] - \nabla \cdot \langle \varepsilon \rangle^\alpha \; \langle \mathbf{j}_\psi \rangle^\alpha - \sum_{\beta \neq \alpha}\left[\left(\int\limits_{A_{\alpha\beta}} \mathbf{n}^\alpha \cdot \left[\rho\left(\mathbf{v}^\alpha - \mathbf{v}^{\alpha\beta}\right)\right] dA\right)\left(\overline{\psi}^\alpha + \tilde{\psi}^\alpha\right)\right] - \sum_{\beta \neq \alpha} \int\limits_{A_{\alpha\beta}} \mathbf{n}^\alpha \cdot \mathbf{j}_\psi \, dA + \langle \varepsilon \rangle^\alpha \; \langle \rho \rangle^\alpha \; \left(\overline{\mathcal{S}}^\alpha + \overline{\mathcal{P}}^\alpha\right) \tag{4.63}$$

Simplifying Eq. (4.63) with identities (4.43) through (4.46) yields:

$$\frac{\partial\left[\langle \varepsilon \rangle^\alpha \; \langle \rho \rangle^\alpha \; \left(\overline{\psi}^\alpha + \tilde{\psi}^\alpha\right)\right]}{\partial t} = -\nabla \cdot \left[\langle \varepsilon \rangle^\alpha \; \langle \rho \rangle^\alpha \; \left(\left(\overline{\mathbf{v}}^\alpha \; \overline{\psi}^\alpha\right) + \left(\overline{\tilde{\mathbf{v}}^\alpha \tilde{\psi}^\alpha}^\alpha\right)\right)\right] - \nabla \cdot \langle \varepsilon \rangle^\alpha \; \langle \mathbf{j}_\psi \rangle^\alpha - \sum_{\beta \neq \alpha}\left[\left(\int\limits_{A_{\alpha\beta}} \mathbf{n}^\alpha \cdot \left[\rho\left(\mathbf{v}^\alpha - \mathbf{v}^{\alpha\beta}\right)\right] dA\right)\left(\overline{\psi}^\alpha + \tilde{\psi}^\alpha\right)\right] - \sum_{\beta \neq \alpha} \int\limits_{A_{\alpha\beta}} \mathbf{n}^\alpha \cdot \mathbf{j}_\psi \, dA + \langle \varepsilon \rangle^\alpha \; \langle \rho \rangle^\alpha \; \left(\overline{\mathcal{S}}^\alpha + \overline{\mathcal{P}}^\alpha\right) \tag{4.64}$$

Assuming that macroscopic deviations from the mean accumulation of a property will be observed as part of the non-advective flux term and deviations from mean velocity yields the intrinsic macroscale balance equation as:

$$\frac{\partial\left(\langle\epsilon\rangle^{\alpha}\ \langle\rho\rangle^{\alpha}\ \overline{\psi}^{\alpha}\right)}{\partial t} = -\nabla\cdot\left[\langle\epsilon\rangle^{\alpha}\ \langle\rho\rangle^{\alpha}\ \left(\left(\overline{\mathbf{v}}^{\alpha}\ \overline{\psi}^{\alpha}\right)+\left(\overline{\tilde{\mathbf{v}}^{\alpha}\tilde{\psi}^{\alpha}}^{\alpha}\right)\right)\right]-\nabla\cdot\langle\epsilon\rangle^{\alpha}\ \langle\mathbf{j}_{\psi}\rangle^{\alpha}$$
$$-\sum_{\beta\neq\alpha}\left[\hat{e}^{\alpha}_{\alpha\beta}\left(\overline{\psi}^{\alpha}+\tilde{\psi}^{\alpha}\right)+\hat{i}^{\alpha}_{\alpha\beta}\right]+\langle\epsilon\rangle^{\alpha}\ \langle\rho\rangle^{\alpha}\ \left(\overline{\mathcal{S}}^{\alpha}+\overline{\mathcal{P}}^{\alpha}\right) \tag{4.65}$$

where

$$\hat{e}^{\alpha}_{\alpha\beta}=\frac{\langle\epsilon\rangle^{\alpha}}{V^{\alpha}}\int\limits_{\mathcal{A}_{\alpha\beta}}\mathbf{n}^{\alpha}\cdot\left[\rho\left(\mathbf{v}^{\alpha}-\mathbf{v}^{\alpha\beta}\right)\right]dA \tag{4.66}$$

and

$$\hat{i}^{\alpha}_{\alpha\beta}=\frac{\langle\epsilon\rangle^{\alpha}}{V^{\alpha}}\int\limits_{\mathcal{A}_{\alpha\beta}}\mathbf{n}^{\alpha}\cdot\mathbf{j}_{\psi}\,dA \tag{4.67}$$

where $\hat{e}^{\alpha}_{\alpha\beta}$ represents the advective transfer of ψ from the α-phase into the $\alpha\beta$-interface by integrating over $\alpha\beta$-interface interface. The quantity $\hat{i}^{\alpha}_{\alpha\beta}$ accounts the non-advective flux from the α-phase into the $\alpha\beta$-interface.

The above equation is a continuum macroscale equation that specifies the conservation of a quantity of interest in terms of mathematically defined averages within the volume and at all interfaces. The formulation allows for the measurement or parameterization of variables of interest within the REV and at interfaces. The differential equations can be systematically applied to aquifer-scale problems. The rigorous equation development allows for the incorporation of more complex systems with the interaction between multiple phases explicitly defined. The additional detail can also be used to develop energy and entropy balance equations that can be used to constrain constitutive relationships in concurrence with the second law of thermodynamics.

Eq. (4.65) can now be compared to the previously developed macroscale point conservation equation, Eq. (4.59). The following comparisons are noted:

$$\varepsilon = \langle\epsilon\rangle^{\alpha} \tag{4.68}$$

$$\rho^{\alpha} = \langle\rho\rangle^{\alpha} \tag{4.69}$$

$$\mathbf{v}^{\alpha} = \overline{\mathbf{v}}^{\alpha} \tag{4.70}$$

$$\psi^{\alpha} = \overline{\psi}^{\alpha} \tag{4.71}$$

$$\mathcal{S}^\alpha = \overline{\mathcal{S}}^\alpha \tag{4.72}$$

$$\mathbf{j}_\psi{}^\alpha = \langle \mathbf{j}_\psi \rangle^\alpha + \langle \rho \rangle^\alpha \left(\overline{\tilde{\mathbf{v}}^\alpha \tilde{\psi}^\alpha}^\alpha \right) \tag{4.73}$$

$$\mathcal{P}^\alpha = \overline{\mathcal{P}}^\alpha - \frac{1}{\langle \varepsilon \rangle^\alpha \langle \rho \rangle^\alpha} \sum_{\beta \neq \alpha} \left[\hat{e}^\alpha_{\alpha\beta} \left(\overline{\psi}^\alpha + \tilde{\psi}^\alpha \right) + \hat{i}^\alpha_{\alpha\beta} \right] \tag{4.74}$$

The above comparison highlights the initial differences between the ICA and both the DCA or integral macroscale point approach. Significant differences can be noted in the representation of the non-advective flux term and the production term. First, deviations from mean behavior add to the non-advective flux in the ICA formulation. While intuitive, it is not considered in the other approaches. Second, production terms are specifically defined including clearly stated interfacial averages in the ICA formulation. The interfacial mass transfer processes occurring at interfaces must be incorporated in an *ad hoc* manner to the DCA and integral macroscale point approach. The precise definition of interfacial processes and the type of averages produced is a clear advantage of the ICA in the description of the complex multiphase systems that are routinely encountered in environmental remediation efforts.

4.5 Macroscopic Conservation Equations applied to Mass, Momentum, Engery, and Entropy

The macroscopic balance equation, Eq. (4.65), is formulated in a general form that allows the substitution of any conservation law. Averaged quantities must be additive quantities [*Narasimhan*, 1980]. Intensive quantities such as pressure and temperature must first be transformed to a quantity with additive properties before integration and averaging [*Hassanizadeh and Gray*, 1980b]. Equations will now be generated for conservation of mass, momentum, energy, and entropy.

4.5.1 Conservation of Mass

For the conservation of mass for the α-phase, $\psi = 1$, $\mathbf{j}_\psi = 0$ stating that the non-advective movement of mass when summed over all species in a phase will be zero, $\mathcal{S} = 0$ assuming that there are no sources of mass, and $\mathcal{P} = 0$ stating there are no mass producing processes. Substitution into Eq. (4.65) yields:

$$\overbrace{\frac{\partial(\langle\epsilon\rangle^{\alpha}\ \langle\rho\rangle^{\alpha}\ )}{\partial t}}^{\text{Accumulation}} = \underbrace{-\nabla\cdot(\langle\epsilon\rangle^{\alpha}\ \langle\rho\rangle^{\alpha}\ \mathbf{v}^{\alpha}\ )}_{\substack{\text{Advective flux}\\ \text{out of volume}}} - \overbrace{\sum_{\beta\neq\alpha}\hat{e}^{\alpha}_{\alpha\beta}}^{\substack{\text{Mass transfer out}\\ \text{through interfaces}}} \tag{4.75}$$

where $\hat{e}^{\alpha}_{\alpha\beta}$ is defined in Eq. (4.66). The term on the LHS represents the accumulation of mass in the REV. The first term on the RHS represents the mass-averaged advective transport. The second term on the RHS represents the advective mass transfer from the α-phase to all $\alpha\beta$-interfaces.

It is helpful to describe the governing equations for a porous media system in terms of the material derivative, Eq. (4.48), defined in the mathematical notation section. This allows restatement of Eq. (4.75) as:

$$\frac{D^{\alpha}(\langle\epsilon\rangle^{\alpha}\ \langle\rho\rangle^{\alpha}\ )}{Dt} = -\langle\epsilon\rangle^{\alpha}\ \langle\rho\rangle^{\alpha}\ \nabla\cdot\mathbf{v}^{\alpha}\ - \sum_{\beta\neq\alpha}\hat{e}^{\alpha}_{\alpha\beta} \tag{4.76}$$

4.5.2 Conservation of Momentum

The momentum of a particle is a vector defined as the product of mass and the velocity vector of the particle. By Newton's second law, the time rate of change of momentum will be equal to the sum of forces acting on the system. For the conservation of momentum of the α-phase, $\psi = \mathbf{v}^{\alpha}$ such that the accumulation term is the product of mass per volume and velocity representing the momentum per volume.

The terms on the RHS of the equation now represent the sum of forces acting on the α-phase per volume. The forces that act on an REV are surface forces and body forces [*Slattery*, 1972; *Whitaker*, 1981]. Surface forces, such as stress with normal and tangential components, represent forces exerted on the surface of the REV. Body forces, such as gravity, magnetic, and electrostatic forces, arise from actions that occur at a distance from the REV without physical connection. These forces, with their normal and tangential components, must be represented by tensors.

The expression of surface forces requires explanation and clear definition. To account for surface forces, we define $\mathbf{j}^\alpha_\psi = \mathbf{T}^\alpha$ where the stress tensor is assumed to be a continuous function with the three following properties:

1. A stress vector, $\mathbf{t}^\alpha$, may be written in terms of the divergence of the stress tensor, $\mathbf{T}^\alpha$, as [*Slattery*, 1972; *Truesdell*, 1977]:

$$\mathbf{t}^\alpha = \nabla \cdot \mathbf{T}^\alpha \tag{4.77}$$

2. The stress tensor is symmetric [*Hassanizadeh and Gray*, 1979b] as all portions of the medium are assumed non-polar [*Truesdell and Toupin*, 1960];

3. The stress vectors acting upon opposite sides of the same surface at a given point are equal in magnitude and opposite in direction (e.g., $\mathbf{t}^\alpha_n = -\mathbf{t}^\alpha_{-n}$ where n indicates that the stress is acting in the normal outward direction) [*Whitaker*, 1981];

Traditionally, the momentum balance and the stress tensor are not explicitly considered. Rather the extended form of Darcy's law as a constitutive relation describing the velocity in terms of pressures [*Bear*, 1972] is utilized as a momentum balance. Momentum flux and momentum dissipation are neglected through this approach.

The application of body forces is straightforward. $\mathcal{S} = \mathbf{g}$ where gravity is the only body force per unit mass considered. Additionally, $\mathcal{P} = 0$ as there are no velocity producing processes. Substitution of the quantities described above into Eq. (4.65) yields:

$$\begin{aligned}
\overbrace{\frac{\partial(\langle\varepsilon\rangle^\alpha \langle\rho\rangle^\alpha \overline{\mathbf{v}}^\alpha)}{\partial t}}^{\substack{\text{Accumulation}\\ \text{of momentum}}} &= -\overbrace{\nabla \cdot (\langle\varepsilon\rangle^\alpha \langle\rho\rangle^\alpha \overline{\mathbf{v}}^\alpha \overline{\mathbf{v}}^\alpha)}^{\substack{\text{Advection out}\\ \text{of volume}}} - \overbrace{\nabla \cdot (\langle\varepsilon\rangle^\alpha \mathbf{T}^\alpha)}^{\substack{\text{Non-advective}\\ \text{surface force}}} \\
&+ \underbrace{\langle\varepsilon\rangle^\alpha \langle\rho\rangle^\alpha \mathbf{g}}_{\text{Body force}} - \underbrace{\sum_{\beta\neq\alpha} \hat{e}^\alpha_{\alpha\beta}(\overline{\mathbf{v}}^\alpha + \tilde{\mathbf{v}}^\alpha)}_{\substack{\text{Advective transfer}\\ \text{into interfaces}}} - \underbrace{\sum_{\beta\neq\alpha} \hat{\mathbf{t}}^\alpha_{\alpha\beta}}_{\substack{\text{Non-advective transfer}\\ \text{into interfaces}}}
\end{aligned} \tag{4.78}$$

where

$$\mathbf{T}^\alpha = \langle\mathbf{T}\rangle^\alpha + \langle\rho\rangle^\alpha \left(\overline{\tilde{\mathbf{v}}^\alpha \tilde{\mathbf{v}}^\alpha}^\alpha\right) \tag{4.79}$$

$$\hat{\mathbf{t}}^{\alpha}_{\alpha\beta} = \frac{\langle\epsilon\rangle^{\alpha}}{V^{\alpha}} \int\limits_{A_{\alpha\beta}} \mathbf{n}^{\alpha} \cdot \mathbf{T}\, dA \tag{4.80}$$

where $\hat{\mathbf{t}}^{\alpha}_{\alpha\beta}$ accounts for the dissipation of momentum from the α-phase to the $\alpha\beta$-interfaces.

Eq. (4.78) may be simplified by subtraction of the macroscale mass conservation equation, Eq. (4.75), multiplied by the velocity of the α-phase from Eq. (4.78). This yields the following form of the momentum balance equation:

$$\begin{aligned} \frac{\partial(\langle\varepsilon\rangle^{\alpha}\ \langle\rho\rangle^{\alpha}\ \overline{\mathbf{v}}^{\alpha}\ )}{\partial t} - \overline{\mathbf{v}}^{\alpha}\ \frac{\partial(\langle\varepsilon\rangle^{\alpha}\ \langle\rho\rangle^{\alpha}\ )}{\partial t} = \\ -\nabla\cdot(\langle\varepsilon\rangle^{\alpha}\ \langle\rho\rangle^{\alpha}\ \overline{\mathbf{v}}^{\alpha}\ \overline{\mathbf{v}}^{\alpha}\ ) + \overline{\mathbf{v}}^{\alpha}\ \nabla\cdot(\langle\varepsilon\rangle^{\alpha}\ \langle\rho\rangle^{\alpha}\ \overline{\mathbf{v}}^{\alpha}\ ) - \nabla\cdot(\langle\varepsilon\rangle^{\alpha}\ \mathbf{T}^{\alpha}) \\ +\langle\varepsilon\rangle^{\alpha}\ \langle\rho\rangle^{\alpha}\ \mathbf{g} - \sum_{\beta\neq\alpha} \hat{e}^{\alpha}_{\alpha\beta}(\overline{\mathbf{v}}^{\alpha}\ + \tilde{\mathbf{v}}^{\alpha}) + \overline{\mathbf{v}}^{\alpha}\ \sum_{\beta\neq\alpha}\hat{e}^{\alpha}_{\alpha\beta} - \sum_{\beta\neq\alpha}\hat{\mathbf{t}}^{\alpha}_{\alpha\beta} \end{aligned} \tag{4.81}$$

Using the mathematical identities Eq. (4.52) and Eq. (4.53) and the definition of a material derivative as stated in Eq. (4.48), Eq. (4.81) can be simplified and rewritten as [*Hassanizadeh and Gray*, 1979b]:

$$\langle\varepsilon\rangle^{\alpha}\ \langle\rho\rangle^{\alpha}\ \frac{D^{\alpha}\overline{\mathbf{v}}^{\alpha}}{Dt} = -\nabla\cdot(\langle\varepsilon\rangle^{\alpha}\ \mathbf{T}^{\alpha}) + \langle\varepsilon\rangle^{\alpha}\ \langle\rho\rangle^{\alpha}\ \mathbf{g} - \sum_{\beta\neq\alpha}\left(\hat{e}^{\alpha}_{\alpha\beta}\tilde{\mathbf{v}}^{\alpha} + \hat{\mathbf{t}}^{\alpha}_{\alpha\beta}\right) \tag{4.82}$$

4.5.3 Conservation of Energy

The conservation of energy for a system follows from the first law of thermodynamics stating that the accumulation of energy (the sum of all internal and kinetic energies) in a volume is equal to the rate of surface work done by the volume plus the rate at which work is done on the body by body forces such as gravity plus the rate that heat, magnetic, electrical, and chemical energies are transferred out of the volume [*Whitaker*, 1981; *Chung*, 1996].

The averaged potential energy in the system will be represented as $\overline{E}$, written in terms of energy per unit mass. Kinetic energy per mass will be equal to the square of the magnitude of velocity over two. With the decision that the velocity will consist of a mean and a fluctuation, the energy balance for a volume can then be written as [*Hassanizadeh and Gray*, 1979b]:

$$\psi = \overline{E} + \frac{\tilde{v}^2}{2} + \frac{\overline{v^2}}{2} \tag{4.83}$$

where E is the internal energy density function and $\overline{v}$ and $\tilde{v}$ are the mean and fluctuation in the magnitude of the velocity, respectively. Fluctuations in the magnitude of velocity are due to the diffusion velocity [*Achanta et al.*, 1994]. These fluctuations will be detected as part of the internal energy measurement when all species in a phase are considered collectively.

Two methods in which energy can be exchanged between the volume and its surroundings are the surface work done by the volume and the heat that is transferred out of the volume. The work done on the surface can be represented by the dot product of the stress tensor and the velocity vector [*Slattery*, 1972]. Combined with the outward movement of heat, the energy dissipated out of $\mathcal{V}_\alpha$ is defined as $\mathbf{j}_\psi = \mathbf{T} \cdot \mathbf{v} + \mathbf{q}$ where $\mathbf{q}$ is a heat flux vector. This intrinsic flux is written as [*Hassanizadeh and Gray*, 1979b]:

$$\langle \mathbf{T} \cdot \mathbf{v} + \mathbf{q} \rangle^\alpha = \frac{\langle \epsilon \rangle^\alpha}{V^\alpha} \int\limits_{\mathcal{V}_\alpha} \mathbf{n}^\alpha \cdot \left[\mathbf{T} \cdot \mathbf{v} + \mathbf{q} - \rho \tilde{\mathbf{v}}^\alpha \tilde{E}_\psi^\alpha \right] dV \tag{4.84}$$

Setting $\mathbf{v} = \overline{\mathbf{v}} + \tilde{\mathbf{v}}$ and rearrangement yields:

$$\langle \mathbf{j}_\psi \rangle^\alpha = \langle \mathbf{T} \rangle^\alpha \cdot \overline{\mathbf{v}^\alpha} + \langle \mathbf{q} \rangle^\alpha \tag{4.85}$$

where

$$\langle \mathbf{q} \rangle^\alpha = \frac{\langle \epsilon \rangle^\alpha}{V^\alpha} \int\limits_{\mathcal{V}_\alpha} \mathbf{n}^\alpha \cdot \left[\mathbf{T} \cdot \tilde{\mathbf{v}} + \mathbf{q} + \rho \tilde{\mathbf{v}}^\alpha \tilde{E}_\psi^\alpha \right] dV \tag{4.86}$$

Energy is supplied to $\mathcal{V}_\alpha$ from both body forces acting on the volume and external supplies [*Whitaker*, 1981]. This is defined as $\mathcal{S} = \mathbf{g} \cdot \mathbf{v} + h$ where h represents the external supply of energy. $\mathcal{P} = 0$ assuming that mass is not converted to energy and there are no nuclear reactions.

Substitution into Eq. (4.65) yields:

$$\overbrace{\frac{\partial\left(\langle \epsilon \rangle^\alpha \langle \rho \rangle^\alpha \overline{E}_\psi^\alpha \right)}{\partial t}}^{\substack{\text{Accumulation} \\ \text{of energy}}} = \overbrace{-\nabla \cdot \left(\langle \epsilon \rangle^\alpha \langle \rho \rangle^\alpha \overline{\mathbf{v}}^\alpha \overline{E}_\psi^\alpha \right)}^{\substack{\text{Advection out} \\ \text{of volume}}} - \overbrace{\nabla \cdot \langle \epsilon \rangle^\alpha \left[\langle \mathbf{T} \rangle^\alpha \cdot \overline{\mathbf{v}^\alpha} + \langle \mathbf{q} \rangle^\alpha \right]}^{\substack{\text{Non-advective} \\ \text{transfer of} \\ \text{energy to surfaces}}}$$
$$+ \underbrace{\langle \epsilon \rangle^\alpha \langle \rho \rangle^\alpha \overline{\mathbf{g} \cdot \mathbf{v} + h}^\alpha}_{\substack{\text{Supply of} \\ \text{energy}}} - \underbrace{\sum_{\beta \neq \alpha} \hat{e}_{\alpha\beta}^\alpha \left(\overline{E}_\psi^\alpha + \tilde{E}_\psi^\alpha \right)}_{\substack{\text{Advective transfer} \\ \text{into interfaces}}} - \underbrace{\sum_{\beta \neq \alpha} \hat{q}^{*\,\alpha}_{\alpha\beta}}_{\substack{\text{Non-advective} \\ \text{transfer} \\ \text{into interfaces}}} \tag{4.87}$$

where

$$\overline{E}_{\psi}^{\alpha} = \overline{E^{\alpha}} + \frac{\overline{v^2}^{\alpha}}{2} \tag{4.88}$$

and

$$\begin{aligned} \hat{q^*}_{\alpha\beta}^{\alpha} &= \frac{\langle\varepsilon\rangle^{\alpha}}{V^{\alpha}} \int_{A_{\alpha\beta}} \mathbf{n}^{\alpha} \cdot \left[\mathbf{T} \cdot (\overline{\mathbf{v}} + \tilde{\mathbf{v}}) + \mathbf{q} + \rho \tilde{\mathbf{v}}^{\alpha} \tilde{E}_{\psi}^{\alpha} \right] dA \\ &= \hat{\mathbf{t}}_{\alpha\beta}^{\alpha} \cdot \overline{\mathbf{v}} + \hat{q}_{\alpha\beta}^{\alpha} \end{aligned} \tag{4.89}$$

such that

$$\hat{q}_{\alpha\beta}^{\alpha} = \frac{\langle\varepsilon\rangle^{\alpha}}{V^{\alpha}} \int_{A_{\alpha\beta}} \mathbf{n}^{\alpha} \cdot \left[\mathbf{T} \cdot \tilde{\mathbf{v}} + \mathbf{q} + \rho \tilde{\mathbf{v}}^{\alpha} \tilde{E}_{\psi}^{\alpha} \right] dA \tag{4.90}$$

Eq. (4.87) is simplified first by subtracting the continuity equation, Eq. (4.75), multiplied by E_{ψ} to yield:

$$\begin{aligned} &\frac{\partial\left(\langle\varepsilon\rangle^{\alpha} \langle\rho\rangle^{\alpha} \overline{E}_{\psi}^{\alpha}\right)}{\partial t} - \left(\overline{E^{\alpha}} + \frac{\overline{v^2}^{\alpha}}{2}\right) \frac{\partial(\langle\varepsilon\rangle^{\alpha} \langle\rho\rangle^{\alpha})}{\partial t} \\ &= -\nabla \cdot \left(\langle\varepsilon\rangle^{\alpha} \langle\rho\rangle^{\alpha} \overline{\mathbf{v}}^{\alpha} \overline{E}_{\psi}^{\alpha}\right) + \nabla \cdot \left(\overline{E^{\alpha}} + \frac{\overline{v^2}^{\alpha}}{2}\right) (\langle\varepsilon\rangle^{\alpha} \langle\rho\rangle^{\alpha} \overline{\mathbf{v}}^{\alpha}) \\ &\quad - \nabla \cdot \langle\varepsilon\rangle^{\alpha} \left[\langle\mathbf{T}\rangle^{\alpha} \cdot \overline{\mathbf{v}^{\alpha}} + \langle\mathbf{q}\rangle^{\alpha}\right] + \langle\varepsilon\rangle^{\alpha} \langle\rho\rangle^{\alpha} \overline{\mathbf{g} \cdot \mathbf{v} + h}^{\alpha} \\ &\quad - \sum_{\beta \neq \alpha} \hat{e}_{\alpha\beta}^{\alpha} \left(\overline{E}_{\psi}^{\alpha} + \tilde{E}_{\psi}^{\alpha}\right) + \left(\overline{E^{\alpha}} + \frac{\overline{v^2}^{\alpha}}{2}\right) \sum_{\beta \neq \alpha} \hat{e}_{\alpha\beta}^{\alpha} - \sum_{\beta \neq \alpha} \hat{q^*}_{\alpha\beta}^{\alpha} \end{aligned} \tag{4.91}$$

Using the mathematical identities Eq. (4.52) and Eq. (4.53) and the definition of a material derivative as stated in Eq. (4.48), Eq. (4.91) can be simplified and rewritten as:

$$\begin{aligned} \langle\varepsilon\rangle^{\alpha} \langle\rho\rangle^{\alpha} \frac{D(\overline{E^{\alpha}} + \frac{\overline{v^2}^{\alpha}}{2})}{Dt} &= -\nabla \cdot \langle\varepsilon\rangle^{\alpha} \left[\langle\mathbf{T}\rangle^{\alpha} \cdot \overline{\mathbf{v}^{\alpha}} + \langle\mathbf{q}\rangle^{\alpha}\right] \\ &\quad + \langle\varepsilon\rangle^{\alpha} \langle\rho\rangle^{\alpha} \overline{\mathbf{g} \cdot \mathbf{v} + h}^{\alpha} - \sum_{\beta \neq \alpha} \left(\hat{e}_{\alpha\beta}^{\alpha} \tilde{E}_{\psi}^{\alpha} + \hat{q^*}_{\alpha\beta}^{\alpha}\right) \end{aligned} \tag{4.92}$$

Further simplification is attained by subtraction of the scalar product of $\mathbf{v}^{\alpha}$ and the momentum equation, Eq. (4.82) eliminating the magnitude of velocity terms

[*Whitaker*, 1981]. This is first stated as:

$$\begin{aligned}\langle\epsilon\rangle^\alpha\,\langle\rho\rangle^\alpha\,\frac{D(\overline{E^\alpha}+\overline{\frac{v^2}{2}}^\alpha)}{Dt}-\mathbf{v}^\alpha\cdot\langle\epsilon\rangle^\alpha\,\langle\rho\rangle^\alpha\,\frac{D^\alpha\mathbf{v}^\alpha}{Dt}=\\ -\nabla\cdot\langle\epsilon\rangle^\alpha\,\left[\langle\mathbf{T}\rangle^\alpha\cdot\overline{\mathbf{v}^\alpha}+\langle\mathbf{q}\rangle^\alpha\right]+\mathbf{v}^\alpha\cdot\nabla\cdot(\langle\epsilon\rangle^\alpha\,\mathbf{T}^\alpha)\\ +\langle\epsilon\rangle^\alpha\,\langle\rho\rangle^\alpha\,\overline{\mathbf{g}\cdot\mathbf{v}+h}^\alpha-\mathbf{v}^\alpha\cdot\langle\epsilon\rangle^\alpha\,\langle\rho\rangle^\alpha\,\mathbf{g}\\ -\sum_{\beta\neq\alpha}\left(\hat{e}^\alpha_{\alpha\beta}\tilde{E}^\alpha_\psi+\hat{q}^{*\alpha}_{\alpha\beta}\right)+\mathbf{v}^\alpha\cdot\sum_{\beta\neq\alpha}\left(\hat{e}^\alpha_{\alpha\beta}\tilde{\mathbf{v}}^\alpha\right)+\mathbf{v}^\alpha\cdot\sum_{\beta\neq\alpha}\left(\hat{\mathbf{t}}^\alpha_{\alpha\beta}\right)\end{aligned}\qquad(4.93)$$

Rearrangement using identities (4.47) and (4.51), assuming that the term $\mathbf{v}^\alpha\cdot\tilde{\mathbf{v}}^\alpha$ is negligible, and subtraction yields the macroscopic integral energy equation as [*Hassanizadeh and Gray*, 1990]:

$$\begin{aligned}\langle\epsilon\rangle^\alpha\,\langle\rho\rangle^\alpha\,\frac{D\overline{E^\alpha}}{Dt}=-\langle\epsilon\rangle^\alpha\,\mathbf{T}^\alpha:\nabla\mathbf{v}^\alpha\;-\nabla\cdot(\langle\epsilon\rangle^\alpha\,\langle\mathbf{q}\rangle^\alpha\,)\\ +\langle\epsilon\rangle^\alpha\,\langle\rho\rangle^\alpha\,\overline{h}^\alpha\;-\sum_{\beta\neq\alpha}\left(\hat{e}^\alpha_{\alpha\beta}\tilde{E}^\alpha_\psi+\hat{q}^\alpha_{\alpha\beta}\right)\end{aligned}\qquad(4.94)$$

4.5.4 Balance Equation for Entropy

In addition to conserving energy, systems will converge toward an equilibrium state in which entropy reaches a maximum value and no longer changes with time [*Greiner et al.*, 1994]. As a thought experiment, consider a perfume which is sprayed into a room. The perfume will disperse throughout the room. A spontaneous gathering of the perfume in one corner of the room, however, defies common sense and has never been observed, although this would not violate the conservation of energy. This illustrates that additional information about a porous media system is gained by quantifying the specific production of entropy that must be greater than or equal to zero [*Coleman and Noll*, 1963; *Hassanizadeh and Gray*, 1990, 1993a].

For the α-phase, η will be used to represent the specific entropy per unit mass. Utilizing the framework of the macroscopic balance equation, Eq. (4.65), we will set $\psi=\eta$ [*Hassanizadeh and Gray*, 1979b].

Entropy can be exchanged between the volume and its surroundings. The outward advective movement of entropy is represented by the divergence of the product of η and the mean velocity. The non-advective movement of entropy out of $\mathcal{V}_\alpha$ is represented as $\mathbf{j}_\psi = \phi^\alpha$ where ϕ^α is a entropy flux vector for the α-phase [*Hassanizadeh and Gray*, 1979b].

Entropy is the only conserved quantity in which production, as defined, is permissible. Therefore, $\mathcal{P} = \Lambda$ where Λ is the specific production of entropy. $\mathcal{S} = b$ where b represents the external supply of entropy.

Substitution into Eq. (4.65) yields:

$$\begin{aligned}\overbrace{\frac{\partial(\langle\varepsilon\rangle^\alpha \langle\rho\rangle^\alpha \overline{\eta^\alpha})}{\partial t}}^{\substack{\text{Accumulation}\\ \text{of entropy}}} &= -\overbrace{\nabla\cdot(\langle\varepsilon\rangle^\alpha \langle\rho\rangle^\alpha \overline{\mathbf{v}}^\alpha \overline{\eta^\alpha})}^{\substack{\text{Advection out}\\ \text{of volume}}} - \overbrace{\nabla\cdot(\langle\varepsilon\rangle^\alpha \phi^\alpha)}^{\substack{\text{Non-advective}\\ \text{transfer out}\\ \text{of volume}}}\\ &+ \underbrace{\langle\varepsilon\rangle^\alpha \langle\rho\rangle^\alpha \overline{b^\alpha}}_{\substack{\text{Supply of}\\ \text{entropy}}} + \underbrace{\langle\varepsilon\rangle^\alpha \langle\rho\rangle^\alpha \overline{\Lambda^\alpha}}_{\substack{\text{Production of}\\ \text{entropy}}} - \underbrace{\sum_{\beta\neq\alpha} \hat{e}^\alpha_{\alpha\beta}(\overline{\eta}^\alpha + \tilde{\eta}^\alpha)}_{\substack{\text{Advective transfer}\\ \text{into interfaces}}} - \underbrace{\sum_{\beta\neq\alpha} \hat{\mathbf{n}}^\alpha_{\alpha\beta}}_{\substack{\text{Non-advective}\\ \text{transfer}\\ \text{into interfaces}}}\end{aligned} \tag{4.95}$$

where

$$\phi^\alpha = \langle\phi\rangle^\alpha + \langle\rho\rangle^\alpha \left(\overline{\tilde{\mathbf{v}}^\alpha \tilde{\eta}^\alpha}\right) \tag{4.96}$$

$$\hat{\mathbf{n}}^\alpha_{\alpha\beta} = \frac{1}{V}\int_{A_{\alpha\beta}} \mathbf{n}^\alpha \cdot \phi \, dA \tag{4.97}$$

Eq. (4.95) is simplified by subtraction of the continuity equation, Eq. (4.75), multiplied by $\overline{\eta}^\alpha$ to yield:

$$\begin{aligned}\frac{\partial(\langle\varepsilon\rangle^\alpha \langle\rho\rangle^\alpha \overline{\eta}^\alpha)}{\partial t} - \overline{\eta}^\alpha \frac{\partial(\langle\varepsilon\rangle^\alpha \langle\rho\rangle^\alpha)}{\partial t} &=\\ &-\nabla\cdot(\langle\varepsilon\rangle^\alpha \langle\rho\rangle^\alpha \overline{\mathbf{v}}^\alpha \overline{\eta}^\alpha) + \overline{\eta}^\alpha \nabla\cdot(\langle\varepsilon\rangle^\alpha \langle\rho\rangle^\alpha \overline{\mathbf{v}}^\alpha)\\ &-\nabla\cdot(\langle\varepsilon\rangle^\alpha \phi^\alpha) + \langle\varepsilon\rangle^\alpha \langle\rho\rangle^\alpha \overline{b^\alpha} + \langle\varepsilon\rangle^\alpha \langle\rho\rangle^\alpha \overline{\Lambda^\alpha}\\ &-\sum_{\beta\neq\alpha} \hat{e}^\alpha_{\alpha\beta}(\overline{\eta}^\alpha + \tilde{\eta}^\alpha) + \overline{\eta}^\alpha \sum_{\beta\neq\alpha} \hat{e}^\alpha_{\alpha\beta} - \sum_{\beta\neq\alpha} \hat{\mathbf{n}}^\alpha_{\alpha\beta}\end{aligned} \tag{4.98}$$

Using the mathematical identities Eq. (4.52) and Eq. (4.53) and the definition of a material derivative as stated in Eq. (4.48), Eq. (4.98) can be simplified and rewritten as [*Hassanizadeh and Gray*, 1979b]:

$$\begin{aligned}\langle\varepsilon\rangle^\alpha \langle\rho\rangle^\alpha \frac{D\overline{\eta^\alpha}}{Dt} &= -\nabla\cdot\langle\varepsilon\rangle^\alpha \phi^\alpha + \langle\varepsilon\rangle^\alpha \langle\rho\rangle^\alpha \overline{b^\alpha}\\ &+\langle\varepsilon\rangle^\alpha \langle\rho\rangle^\alpha \overline{\Lambda^\alpha} - \sum_{\beta\neq\alpha}\left(\hat{e}^\alpha_{\alpha\beta}\tilde{\eta}^\alpha + \hat{\mathbf{n}}^\alpha_{\alpha\beta}\right)\end{aligned} \tag{4.99}$$

The rigorous development of the entropy inequality is important in determining thermodynamically feasible constitutive relations for a coherent and systematic application of multiphase flow and transport equations. Existing mathematical theories of multiphase flow have been lacking in rigor, consisting primarily of heuristic constitutive theory which appear to have physically unrealistic properties [*Gray and Hassanizadeh*, 1991a; *Hassanizadeh and Gray*, 1993b]. With the quantification of entropy, two related approaches have been applied for the development of thermodynamically constrained constitutive theories. Non-equilibrium thermodynamics [*Marle*, 1982; *Kalaydjian*, 1987; *Pavone*, 1992] and the methodology of *Coleman and Noll* [1963], applied by [*Hassanizadeh and Gray*, 1980a; *Gray and Hassanizadeh*, 1991b; *Hassanizadeh and Gray*, 1993b], have served to formulate constitutive relationships describing the behavior of multiphase systems at the macroscale. Much work is still needed in the development of constitutive relationships and will be discussed in more detail in Chapter 5.

4.5.5 Summary of Conservation Equations

To summarize, a systematic description of averaged quantities including the description of interfaces has been derived from the microscale. Physical information from the microscale is filtered and utilized at the macroscale. Processes occurring at interfaces are represented as precisely defined averaged quantities. Admittedly, many equations are presented in an effort to clearly describe the integral macroscopic conservation equation, Eq. (4.65), and its application to mass, momentum, energy, and entropy balances. Table 4.2 summarizes the quantities that are substituted into Eq. (4.65) to obtain independent conservation equations for mass [Eq. (4.76)], momentum [Eq. (4.82)], energy [Eq. (4.94)], and entropy [Eq. (4.99)].

4.6 Interface Equations

In multiphase fluid flow, there will be multiple fluid-solid interfaces and fluid-fluid interfaces. Interfacial effects have been largely ignored by conventional approaches

Table 4.2: Quantities for macroscopic volume balance equations

Quantity	ψ	$\mathbf{j}_\psi$	$\mathcal{S}$	$\mathcal{P}$
Mass	1	0	0	0
Momentum	$\mathbf{v}^\alpha$	$\mathbf{T}^\alpha$	$\mathbf{g}$	0
Energy	$E^\alpha + \frac{1}{2}v^2$	$\mathbf{T}^\alpha \cdot \mathbf{v}^\alpha + \mathbf{q}^\alpha$	$\mathbf{g} \cdot \mathbf{v}^\alpha + h^\alpha$	0
Entropy	η^α	ϕ^α	b^α	Λ^α

to the solution of flow and transport, however, these interfaces have significant consequences [*Slattery*, 1980; *Abriola and Gray*, 1985; *Gray and Hassanizadeh*, 1989, 1991b]. In order to represent the interfacial effects, mass, momentum, energy, and entropy balance equations will be written for the interfaces.

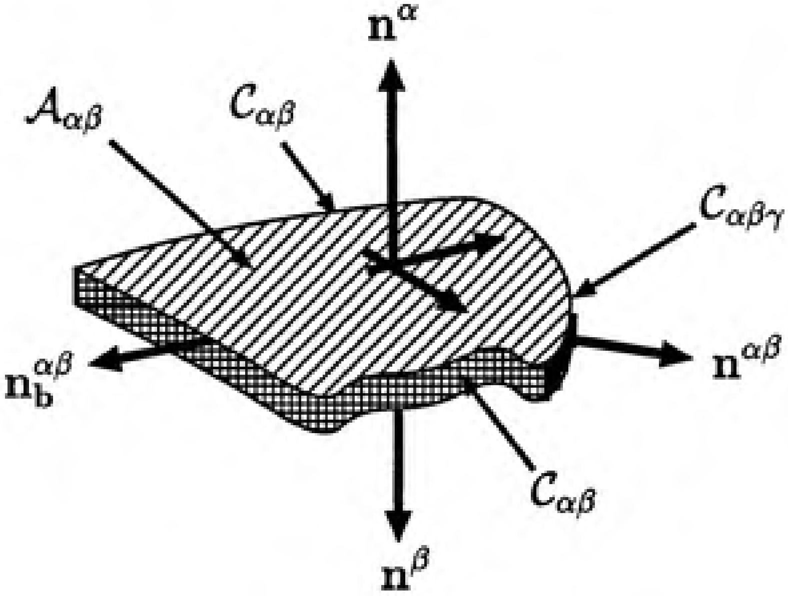


Figure 4.17: The $\alpha\beta$-interface

The representative interface, $\mathcal{A}_{\alpha\beta}$, shown previously in Figure 4.8 and highlighted above in Figure 4.17, is bounded on either side by the α- and β-phases. The bounding lines surrounding the interface can be subdivided into the two types, $\mathcal{C}_{\alpha\beta}$ and $\mathcal{C}_{\alpha\beta\gamma}$.

$C_{\alpha\beta}$ represents the line caused by the intersection of the interface and the boundary of $\mathcal{V}$. $C_{\alpha\beta\gamma}$ represents the edges caused by the $\alpha\beta\gamma$-contact line.

To then write a macroscale integral continuum balance equation for a scalar or vector property, ψ, we follow the methodology presented in the previous section for balance equations about volumes. Quantities within the integrands are microscale quantities that will be assumed to reach continuous, average values when integrated about the macroscopic interface. For the bounding edges of the $\alpha\beta$-interface defined as noted above, the conservation equation for the $\alpha\beta$-interface can be stated as [*Hassanizadeh and Gray*, 1990]:

$$\overbrace{\frac{d}{dt}\int_{A_{\alpha\beta}} \rho^{\alpha\beta}\psi\, dA}^{\text{Accumulation}} = \overbrace{\int_{A_{\alpha\beta}} \rho^{\alpha\beta}(\mathcal{S}+\mathcal{P})\, dA}^{\substack{\text{Sources and}\\ \text{Production}}} - \overbrace{\sum_{\gamma\neq\alpha,\beta}\int_{C_{\alpha\beta\gamma}} \mathbf{n}^{\alpha\beta}\cdot\left[\rho^{\alpha\beta}(\mathbf{v}^{\alpha\beta}-\mathbf{v}^{\alpha\beta\gamma})\psi+\mathbf{j}_{\psi}\right] dC}^{\substack{\text{Advective and}\\ \text{Non-Advective Fluxes}\\ \text{Through Contact Lines}}}$$
$$\underbrace{-\int_{C_{\alpha\beta}} \mathbf{n}_{b}^{\alpha\beta}\cdot\left[\rho^{\alpha\beta}\mathbf{v}^{\alpha\beta}\psi+\mathbf{j}_{\psi}^{\alpha\beta}\right] dC}_{\substack{\text{Advective and}\\ \text{Non-Advective Fluxes}\\ \text{Through Bounding Edges}}} - \underbrace{\sum_{i=\alpha,\beta}\int_{A_{\alpha\beta}} \mathbf{n}^{i}\cdot\left[\rho^{i}(\mathbf{v}^{i}-\mathbf{v}^{\alpha\beta})\psi+\mathbf{j}_{\psi}\right] dA}_{\substack{\text{Advective and}\\ \text{Non-Advective Fluxes}\\ \text{Through Bounding Surfaces}}} \quad (4.100)$$

where $\rho^{\alpha\beta}$ is the mass density of the $\alpha\beta$-interface; $\mathbf{v}^{\alpha\beta}$ is the velocity of the $\alpha\beta$-interface; $\mathbf{v}_{b}^{\alpha\beta}$ is the velocity of $\mathcal{C}^{\alpha\beta}$; $\mathbf{v}^{\alpha\beta\gamma}$ is the velocity of $\mathcal{C}^{\alpha\beta\gamma}$; and $\mathbf{j}_{\psi}$ represents non-advective flux terms. The term on the LHS represents the accumulation of the scalar or vector property, ψ, within $A_{\alpha\beta}$; the first term on the RHS represents sources and production within the $\alpha\beta$-interface; the second term on the RHS represents advective and non-advective fluxes out of the $\alpha\beta$-interface and into the contact line; the third term on the RHS represents advective and non-advective fluxes out of one representative area into an adjacent representative area; the fourth term on the RHS represents advective and non-advective fluxes out of the $\alpha\beta$-interface and into either the α- or β-phases. In the second term on the RHS, the notation, $\sum_{\gamma\neq\alpha,\beta}\int_{C_{\alpha\beta\gamma}}$ is used to indicates that all of the $C_{\alpha\beta\gamma}$ lines are collectively considered.

The transport theorem for a fixed interface, Eq. (4.24), is used to express the total time derivative in the term on the LHS of Eq. (4.100) as a partial time derivative. The divergence theorem, Eq. (4.20), is used to transform the integral of the flux out through bounding edges into the divergence of an integral over the surface $\mathcal{A}_{\alpha\beta}$. Combined, this allows the macroscale balance equation, still containing microscopic quantities within the integrals, to be stated as:

$$\begin{aligned}\frac{\partial}{\partial t}\int_{\mathcal{A}_{\alpha\beta}} \rho^{\alpha\beta}\psi\, dA &= \int_{\mathcal{A}_{\alpha\beta}} \rho^{\alpha\beta}(\mathcal{S}+\mathcal{P})\, dA - \sum_{\gamma\neq\alpha,\beta}\int_{C_{\alpha\beta\gamma}} \mathbf{n}^{\alpha\beta}\cdot\left[\rho^{\alpha\beta}(\mathbf{v}^{\alpha\beta}-\mathbf{v}^{\alpha\beta\gamma})\psi+\mathbf{j}_{\psi}\right] dC \\ &\quad -\nabla\cdot\int_{\mathcal{A}_{\alpha\beta}}\left(\rho^{\alpha\beta}\mathbf{v}^{\alpha\beta}\psi+\mathbf{j}_{\psi}^{\alpha\beta}\right) dA - \sum_{i=\alpha,\beta}\int_{\mathcal{A}_{\alpha\beta}} \mathbf{n}^{i}\cdot\left[\rho^{i}(\mathbf{v}^{i}-\mathbf{v}^{\alpha\beta})\psi+\mathbf{j}_{\psi}\right] dA \qquad (4.101)\end{aligned}$$

Noting that the specific surface, $\langle a\rangle^{\alpha\beta}$, from Eq. (4.33) can be stated as:

$$\frac{1}{V}=\frac{\langle a\rangle^{\alpha\beta}}{A_{\alpha\beta}} \qquad (4.102)$$

Therefore dividing Eq. (4.101) by the macroscopic volume, V, yields:

$$\begin{aligned}\left(\frac{\langle a\rangle^{\alpha\beta}}{A_{\alpha\beta}}\right)\frac{\partial}{\partial t}\int_{\mathcal{A}_{\alpha\beta}} \rho^{\alpha\beta}\psi\, dA &= -\left(\frac{\langle a\rangle^{\alpha\beta}}{A_{\alpha\beta}}\right)\nabla\cdot\int_{\mathcal{A}_{\alpha\beta}}\left(\rho^{\alpha\beta}\mathbf{v}^{\alpha\beta}\psi+\mathbf{j}_{\psi}^{\alpha\beta}\right) dA \\ &\quad -\left(\frac{\langle a\rangle^{\alpha\beta}}{A_{\alpha\beta}}\right)\sum_{\gamma\neq\alpha,\beta}\int_{C_{\alpha\beta\gamma}} \mathbf{n}^{\alpha\beta}\cdot\left[\rho^{\alpha\beta}(\mathbf{v}^{\alpha\beta}-\mathbf{v}^{\alpha\beta\gamma})\psi+\mathbf{j}_{\psi}\right] dC \\ -\left(\frac{\langle a\rangle^{\alpha\beta}}{A_{\alpha\beta}}\right)\sum_{i=\alpha,\beta}\int_{\mathcal{A}_{\alpha\beta}} \mathbf{n}^{i}\cdot\left[\rho^{i}(\mathbf{v}^{i}-\mathbf{v}^{\alpha\beta})\psi+\mathbf{j}_{\psi}\right] dA &+\left(\frac{\langle a\rangle^{\alpha\beta}}{A_{\alpha\beta}}\right)\int_{\mathcal{A}_{\alpha\beta}} \rho^{\alpha\beta}(\mathcal{S}+\mathcal{P})\, dA \qquad (4.103)\end{aligned}$$

Applying the volume-averaging technique for surfaces, Eq. (4.34) yields:

$$\begin{aligned}\frac{\partial(\langle a\rangle^{\alpha\beta}\ \langle\rho^{\alpha\beta}\psi\rangle^{\alpha\beta}\ )}{\partial t} &= -\nabla\cdot\left(\langle a\rangle^{\alpha\beta}\ \langle\rho^{\alpha\beta}\mathbf{v}^{\alpha\beta}\psi\rangle^{\alpha\beta}\ \right)-\nabla\cdot\left(\langle a\rangle^{\alpha\beta}\ \langle\mathbf{j}_{\psi}\rangle^{\alpha\beta}\ \right) \\ &\quad -\left(\frac{\langle a\rangle^{\alpha\beta}}{A_{\alpha\beta}}\right)\sum_{\gamma\neq\alpha,\beta}\int_{C_{\alpha\beta\gamma}} \mathbf{n}^{\alpha\beta}\cdot\left[\rho^{\alpha\beta}(\mathbf{v}^{\alpha\beta}-\mathbf{v}^{\alpha\beta\gamma})\psi+\mathbf{j}_{\psi}\right] dC \\ +\left(\frac{\langle a\rangle^{\alpha\beta}}{A_{\alpha\beta}}\right)\sum_{i=\alpha,\beta}\int_{\mathcal{A}_{\alpha\beta}} \mathbf{n}^{i}\cdot\left[\rho^{i}(\mathbf{v}^{i}-\mathbf{v}^{\alpha\beta})\psi+\mathbf{j}_{\psi}\right] dA &+ \langle a\rangle^{\alpha\beta}\ \langle\rho^{\alpha\beta}(\mathcal{S}+\mathcal{P})\rangle^{\alpha\beta} \qquad (4.104)\end{aligned}$$

Applying the definition of the mass average, Eq. (4.38) to Eq. (4.104) and describing the expected fluctuations as in Eq. (4.41) yields:

$$\frac{\partial(\langle a\rangle^{\alpha\beta}\ \langle\rho\rangle^{\alpha\beta}\ \overline{\psi}^{\alpha\beta}\ )}{\partial t} = -\nabla\cdot\left[\langle a\rangle^{\alpha\beta}\ \langle\rho\rangle^{\alpha\beta}\ \left(\overline{\mathbf{v}^{\alpha\beta\gamma}\psi}^{\alpha\beta}\ \right)\right]-\nabla\cdot\langle a\rangle^{\alpha\beta}\ \langle\mathbf{j}_{\psi}\rangle^{\alpha\beta}$$

$$- \sum_{\gamma \neq \alpha,\beta} \left\{ \frac{1}{V} \int_{\mathcal{C}_{\alpha\beta\gamma}} \mathbf{n}^{\alpha\beta} \cdot \left[\rho^{\alpha\beta} (\mathbf{v}^{\alpha\beta\gamma} - \mathbf{v}^{\alpha\beta_\gamma}) \left(\overline{\psi}^{\alpha\beta} + \tilde{\psi}^{\alpha\beta} \right) \right] dC + \frac{1}{V} \int_{\mathcal{C}_{\alpha\beta\gamma}} \mathbf{n}^{\alpha\beta} \cdot \mathbf{j}_\psi \, dC \right\}$$

$$- \sum_{i=\alpha,\beta} \left\{ \frac{1}{V} \int_{\mathcal{A}_{\alpha\beta}} \mathbf{n}^{\mathbf{i}} \cdot \left[\rho^{i} (\mathbf{v}^{\mathbf{i}} - \mathbf{v}^{\alpha\beta}) \left(\overline{\psi}^{\,i} + \tilde{\psi}^{i} \right) \right] dA + \frac{1}{V} \int_{\mathcal{A}_{\alpha\beta}} \mathbf{n}^{\mathbf{i}} \cdot \mathbf{j}_\psi \, dA \right\}$$

$$+ \langle a \rangle^{\alpha\beta} \, \langle \rho \rangle^{\alpha\beta} \, \left(\overline{\mathcal{S}^{\alpha\beta}} + \overline{\mathcal{P}^{\alpha\beta}} \right) \qquad (4.105)$$

Simplifying Eq. (4.105) with identities (4.43) through (4.46) yields the macroscale interface balance equation in terms of averaged microscale quantities as:

$$\frac{\partial (\langle a \rangle^{\alpha\beta} \, \langle \rho \rangle^{\alpha\beta} \, \overline{\psi}^{\alpha\beta})}{\partial t} = - \nabla \cdot \left(\langle a \rangle^{\alpha\beta} \, \langle \rho \rangle^{\alpha\beta} \, \overline{\mathbf{v}}^{\alpha\beta} \, \overline{\psi}^{\alpha\beta} \right)$$

$$- \nabla \cdot \left\{ \langle a \rangle^{\alpha\beta} \, \left[\langle \mathbf{j}_\psi \rangle^{\alpha\beta} - \langle \rho \rangle^{\alpha\beta} \, \overline{\tilde{\mathbf{v}}^{\alpha\beta} \tilde{\psi}^{\alpha\beta}}^{\alpha\beta} \right] \right\} + \langle a \rangle^{\alpha\beta} \, \langle \rho \rangle^{\alpha\beta} \, \left(\overline{\mathcal{S}^{\alpha\beta}} + \overline{\mathcal{P}^{\alpha\beta}} \right)$$

$$+ \sum_{i=\alpha,\beta} \left[\hat{e}^{i}_{\alpha\beta} \left(\overline{\psi}^{\,i} + \tilde{\psi}^{i} \right) + \overset{\rightharpoonup}{i}{}^{i}_{\alpha\beta} \right] - \sum_{\gamma \neq \alpha,\beta} \left[\hat{e}^{\alpha\beta}_{\alpha\beta\gamma} \left(\overline{\psi}^{\alpha\beta} + \tilde{\psi}^{\alpha\beta} \right) + \overset{\rightharpoonup}{i}{}^{\alpha\beta}_{\alpha\beta\gamma} \right] \qquad (4.106)$$

where

$$\hat{e}^{\alpha\beta}_{\alpha\beta\gamma} = \frac{1}{V} \int_{\mathcal{C}_{\alpha\beta\gamma}} \mathbf{n}^{\alpha\beta} \cdot \left[\rho^{\alpha\beta} (\mathbf{v}^{\alpha\beta} - \mathbf{v}^{\alpha\beta\gamma}) \right] dC \qquad (4.107)$$

and

$$\overset{\rightharpoonup}{i}{}^{\alpha\beta}_{\alpha\beta\gamma} = \frac{1}{V} \int_{\mathcal{C}_{\alpha\beta\gamma}} \mathbf{n}^{\alpha\beta} \cdot \mathbf{j}_\psi \, dC \qquad (4.108)$$

and $\hat{e}^{i}_{\alpha\beta}$ and $\overset{\rightharpoonup}{i}{}^{\alpha}_{\alpha\beta}$ are defined in Eq. (4.66) and Eq. (4.67), respectively.

The above equation is a continuum macroscale equation that specifies the conservation of a quantity of interest in terms of mathematically defined averages within the volume and at all interfaces. The formulation allows for the measurement or parameterization of variables of interest within the REV and at interfaces. The differential equations can be systematically applied to aquifer-scale problems. The rigorous equation development allows for the incorporation of more complex systems with the interaction between multiple phases explicitly defined. The additional detail can also be used to develop energy and entropy balance equations that can be used to constrain constitutive relationships in concurrence with the second law of thermodynamics.

The last two terms of Eq. (4.106), as defined above, account for interactions of an $\alpha\beta$-interface with a bounding contact line.

4.6.1 Conservation of Mass

For the conservation of mass for the $\alpha\beta$-interface, $\psi = 1$, $\mathbf{j}_{\psi}^{\alpha\beta} = 0$ assuming that the net diffusive flux is zero, $\mathcal{S}^{\alpha\beta} = 0$ assuming that there are no sources of mass, and $\mathcal{P}^{\alpha\beta} = 0$ assuming that there is no production of mass.

Substitution into Eq. (4.106) yields:

$$\overbrace{\frac{\partial(\langle a\rangle^{\alpha\beta}\ \langle\rho\rangle^{\alpha\beta}\ )}{\partial t}}^{\substack{\text{Accumulation}\\ \text{of mass}}} = -\underbrace{\nabla\cdot(\langle a\rangle^{\alpha\beta}\ \langle\rho\rangle^{\alpha\beta}\ \mathbf{v}^{\alpha\beta}\ )}_{\substack{\text{Advection out}\\ \text{of interface}}} + \overbrace{\hat{e}_{\alpha\beta}^{\alpha} + \hat{e}_{\alpha\beta}^{\beta}}^{\substack{\text{Advective transfer}\\ \text{from volumes}}} - \underbrace{\sum_{\gamma\neq\alpha,\beta} \hat{e}_{\alpha\beta\gamma}^{\alpha\beta}}_{\substack{\text{Advective transfer}\\ \text{to contact lines}}} \qquad (4.109)$$

where the term on the LHS represents any accumulation of mass on the interface due to changes in the specific area or the density. The first term on the RHS represents the average advection of mass in all spatial dimensions. The second and third terms on the RHS account for mass transferred from the α- and β-phases, respectively, into the $\alpha\beta$-interface, therefore representing an addition of mass. The fourth term on the RHS accounts for transfer of mass from the $\alpha\beta$-interface to the the $\alpha\beta\gamma$-contact line.

It is helpful to describe the governing equations for a porous media system in terms the material derivative, Eq. (4.49), defined in the mathematical notation section. This allows restatement of Eq. (4.109) as:

$$\frac{D(\langle a\rangle^{\alpha\beta}\ \langle\rho\rangle^{\alpha\beta}\ )}{Dt} = -\langle a\rangle^{\alpha\beta}\ \langle\rho\rangle^{\alpha\beta}\ \nabla\cdot\mathbf{v}^{\alpha\beta}\ + \hat{e}_{\alpha\beta}^{\alpha} + \hat{e}_{\alpha\beta}^{\beta} - \sum_{\gamma\neq\alpha,\beta} \hat{e}_{\alpha\beta\gamma}^{\alpha\beta} \qquad (4.110)$$

4.6.2 Conservation of Momentum

An interface must conserve momentum in the same manner as the volume [*Hassanizadeh and Gray*, 1993a]. For the conservation of momentum of the $\alpha\beta$-interface, $\psi = \mathbf{v}^{\alpha\beta}$ such that the accumulation term is the product of mass per area and velocity representing the momentum per area.

The terms on the RHS of the equation now represent the sum of forces acting on the $\alpha\beta$-interface per area. The forces that act on an interface are surface forces and body forces [*Slattery*, 1972; *Whitaker*, 1981]. Surface forces, such as stress with normal and tangential components, represent forces exerted on the surface of the interface. Body forces, such as gravity, magnetic, and electrostatic forces, arise from actions that occur at a distance from the interface without physical connection.

The expression of surface forces requires explanation and clear definition. To account for surface forces, we define $\mathbf{j}_{\psi}^{\alpha\beta} = \mathbf{T}^{\alpha\beta}$ where the stress tensor is assumed to be a continuous function with the three following properties:

1. A stress vector, $\mathbf{t}^{\alpha\beta}$, may be written in terms of the divergence of the stress tensor, $\mathbf{T}^{\alpha\beta}$, as [*Slattery*, 1990]:

$$\mathbf{t}^{\alpha\beta} = \nabla \cdot \mathbf{T}^{\alpha\beta} \tag{4.111}$$

2. The interfacial stress tensor is symmetric [*Hassanizadeh and Gray*, 1993a] as all portions of the medium are assumed non-polar [*Slattery*, 1990];

3. The stress vectors acting upon opposite sides of the same edge of the interface at a given point are equal in magnitude and opposite in direction (e.g., $\mathbf{t}_{n}^{\alpha\beta} = -\mathbf{t}_{-n}^{\alpha\beta}$ where n indicates that the stress is acting in the normal outward direction) [*Whitaker*, 1981];

$\mathcal{S} = \mathbf{g}$ where gravity is the only body force per unit mass considered. Additionally, $\mathcal{P} = 0$ as there are no velocity producing processes occurring on the interface. Substitution into Eq. (4.106) yields:

$$\begin{aligned}\overbrace{\frac{\partial\left(\langle a\rangle^{\alpha\beta}\ \langle\rho\rangle^{\alpha\beta}\ \overline{\mathbf{v}}^{\alpha\beta}\right)}{\partial t}}^{\substack{\text{Accumulation}\\ \text{of momentum}}} = &-\overbrace{\nabla\cdot\left(\langle a\rangle^{\alpha\beta}\ \langle\rho\rangle^{\alpha\beta}\ \overline{\mathbf{v}}^{\alpha\beta}\ \overline{\mathbf{v}}^{\alpha\beta}\right)}^{\substack{\text{Advection out}\\ \text{of interface}}} - \overbrace{\nabla\cdot\left(\langle a\rangle^{\alpha\beta}\ \mathbf{T}^{\alpha\beta}\right)}^{\substack{\text{Non-advective}\\ \text{surface forces}}} + \overbrace{\langle a\rangle^{\alpha\beta}\ \langle\rho\rangle^{\alpha\beta}\ \mathbf{g}}^{\text{Body forces}}\\ &+ \underbrace{\sum_{i=\alpha,\beta}\left[\hat{e}_{\alpha\beta}^{i}\left(\overline{\mathbf{v}}^{\,i}+\tilde{\mathbf{v}}^{i}\right)+\hat{\mathbf{t}}_{\alpha\beta}^{i}\right]}_{\substack{\text{Advective and}\\ \text{Non-advective transfer}\\ \text{from volumes}}} - \underbrace{\sum_{\gamma\neq\alpha,\beta}\left[\hat{e}_{\alpha\beta\gamma}^{\alpha\beta}\left(\overline{\mathbf{v}}^{\alpha\beta}+\tilde{\mathbf{v}}^{\alpha\beta}\right)+\hat{\mathbf{t}}_{\alpha\beta\gamma}^{\alpha\beta}\right]}_{\substack{\text{Advective and}\\ \text{Non-advective transfer}\\ \text{into contact lines}}}\end{aligned} \tag{4.112}$$

where

$$\mathbf{T}^{\alpha\beta} = \langle \mathbf{T} \rangle^{\alpha\beta} + \langle \rho \rangle^{\alpha\beta} \, \overline{\tilde{\mathbf{v}}^{\alpha\beta} \tilde{\mathbf{v}}^{\alpha\beta}}^{\alpha\beta} \tag{4.113}$$

$$\hat{\mathbf{t}}^{\alpha\beta}_{\alpha\beta\gamma} = \frac{1}{V} \int_{C_{\alpha\beta\gamma}} \mathbf{n}^{\alpha\beta} \cdot \mathbf{T} \, dC \tag{4.114}$$

Multiplication of Eq. (4.109) by $\mathbf{v}^{\alpha\beta}$ and subtraction from Eq. (4.112) yields the momentum equation in the following form:

$$\begin{aligned} \langle a \rangle^{\alpha\beta} \, \langle \rho \rangle^{\alpha\beta} \, \frac{D\mathbf{v}^{\alpha\beta}}{Dt} &= -\nabla \cdot \left(\langle a \rangle^{\alpha\beta} \, \mathbf{T}^{\alpha\beta} \right) + \langle a \rangle^{\alpha\beta} \, \langle \rho \rangle^{\alpha\beta} \, \mathbf{g} \\ &+ \sum_{i=\alpha,\beta} \left[\hat{e}^{i}_{\alpha\beta} \left(\mathbf{v}^{\,i,\alpha\beta} + \tilde{\mathbf{v}}^{i,\alpha\beta} \right) + \hat{\mathbf{t}}^{i}_{\alpha\beta} \right] - \sum_{\gamma \neq \alpha,\beta} \left(\hat{e}^{\alpha\beta}_{\alpha\beta\gamma} \tilde{\mathbf{v}}^{\alpha\beta} + \hat{\mathbf{t}}^{\alpha\beta}_{\alpha\beta\gamma} \right) \end{aligned} \tag{4.115}$$

where

$$\mathbf{v}^{\mathrm{i},\alpha\beta} = \mathbf{v}^{\mathrm{i}} - \mathbf{v}^{\alpha\beta} \tag{4.116}$$

4.6.3 Conservation of Energy

The conservation of energy follows from the first law of thermodynamics stating that the accumulation of energy (the sum of internal and kinetic) in the interface is equal to the rate of surface work done by the interface plus the net rate that heat, magnetic, electrical, and chemical energies are transferred out of the interface plus the rate at which work is done on the interface by body forces such as gravity [*Whitaker*, 1981; *Chung*, 1996].

With the understanding that fluctuations will exist in the macroscopic velocity field, the energy for the interface is written as:

$$\psi = \overline{E}^{\alpha\beta} + \frac{(\tilde{v}^{\alpha\beta})^2}{2} + \frac{\overline{(v^{\alpha\beta})^2}}{2} \tag{4.117}$$

where $E^{\alpha\beta}$ is the internal energy density function for the interface and $\overline{v^{\alpha\beta}}$ and $\tilde{v}^{\alpha\beta}$ are the mean and fluctuation in the magnitude of the interfacial velocity, respectively. Fluctuations in the magnitude of velocity are due to the diffusion velocity [*Achanta et al.*, 1994]. These fluctuations will be detected as part of the internal energy measurement when all species in a phase are considered collectively.

Two methods in which energy can be exchanged between the interface and its surroundings are the surface work done by the interface and the heat that is transferred out of the interface. The work done on the boundary of the interface can be represented as the dot product of the stress tensor and the velocity vector [*Slattery*, 1972]. Combined with the outward movement of heat, the energy dissipated out of the interface is defined as [*Hassanizadeh and Gray*, 1990]:

$$\langle \mathbf{T}\cdot\mathbf{v}^{\alpha\beta}+\mathbf{q}\rangle^{\alpha\beta} = \frac{1}{A_{\alpha\beta}}\int_{A_{\alpha\beta}} \mathbf{n}^{\alpha}\cdot\left[\mathbf{T}\cdot\mathbf{v}^{\alpha\beta}+\mathbf{q}-\rho^{\alpha\beta}\tilde{\mathbf{v}}^{\alpha\beta}\tilde{E}_{\psi}^{\alpha\beta}\right]dA \tag{4.118}$$

Setting $\mathbf{v}^{\alpha\beta}=\overline{\mathbf{v}}+\tilde{\mathbf{v}}$ and rearrangement yields:

$$\langle \mathbf{j}_{\psi}\rangle^{\alpha\beta} = \langle \mathbf{T}\rangle^{\alpha\beta}\cdot\overline{\mathbf{v}}^{\alpha\beta}+\langle \mathbf{q}\rangle^{\alpha\beta} \tag{4.119}$$

where

$$\langle \mathbf{q}\rangle^{\alpha\beta} = \frac{1}{A_{\alpha\beta}}\int_{A_{\alpha\beta}} \mathbf{n}^{\alpha}\cdot\left[\mathbf{T}\cdot\tilde{\mathbf{v}}^{\alpha\beta}+\mathbf{q}+\rho^{\alpha\beta}\tilde{\mathbf{v}}^{\alpha\beta}\tilde{E}_{\psi}^{\alpha\beta}\right]dA \tag{4.120}$$

Energy supply is described by $\mathcal{S}=\mathbf{g}\cdot\mathbf{v}^{\alpha\beta}+h$ where h is the external supply of energy, and $\mathcal{P}=0$ assuming that there are no energy producing processes. Substitution into Eq. (4.106) yields:

$$\overbrace{\frac{\partial\left(\langle a\rangle^{\alpha\beta}\,\langle\rho\rangle^{\alpha\beta}\,\overline{E}_{\psi}{}^{\alpha\beta}\right)}{\partial t}}^{\substack{\text{Accumulation}\\ \text{of energy}}} = -\overbrace{\nabla\cdot\left(\langle a\rangle^{\alpha\beta}\,\langle\rho\rangle^{\alpha\beta}\,\overline{\mathbf{v}}^{\alpha\beta}\,\overline{E}_{\psi}{}^{\alpha\beta}\right)}^{\substack{\text{Advection}\\ \text{of energy}}} - \overbrace{\nabla\cdot\left(\langle a\rangle^{\alpha\beta}\,\mathbf{T}^{\alpha\beta}\right)}^{\substack{\text{Non-advective}\\ \text{flux of energy}}} + \overbrace{\langle a\rangle^{\alpha\beta}\,\langle\rho\rangle^{\alpha\beta}\,\breve{h}^{\alpha\beta}}^{\substack{\text{Supply}\\ \text{of energy}}}$$

$$+\underbrace{\sum_{i=\alpha,\beta}\left[\hat{e}^{i}_{\alpha\beta}(\overline{E}^{i}_{\psi}-\tilde{E}^{i}_{\psi})+\hat{q}^{*i}_{\alpha\beta}\right]}_{\substack{\text{Advective and}\\ \text{non-advective transfer}\\ \text{from volumes}}} - \underbrace{\sum_{\gamma\neq\alpha,\beta}\left[\hat{e}^{\alpha\beta}_{\alpha\beta\gamma}(\overline{E}_{\psi}{}^{\alpha\beta}-\tilde{E}^{\alpha\beta}_{\psi})+\hat{q}^{*\alpha\beta}_{\alpha\beta\gamma}\right]}_{\substack{\text{Advective and}\\ \text{non-advective transfer}\\ \text{into contact lines}}} \tag{4.121}$$

where

$$\overline{E}_{\psi}{}^{\alpha\beta} = \overline{E}^{\alpha\beta} + \frac{\overline{(v^{\alpha\beta})^{2}}^{\alpha\beta}}{2} \tag{4.122}$$

$$\mathbf{T}^{\alpha\beta} = \langle\mathbf{T}\rangle^{\alpha\beta}\cdot\overline{\mathbf{v}}^{\alpha\beta}+\langle\mathbf{q}\rangle^{\alpha\beta} \tag{4.123}$$

$$\breve{h}^{\alpha\beta} = \overline{\mathbf{g}\cdot\mathbf{v}^{\alpha\beta}+h}^{\alpha\beta} \tag{4.124}$$

and

$$\begin{aligned}\hat{q}^{*\alpha\beta}_{\alpha\beta\gamma} &= \frac{1}{V}\int\limits_{C_{\alpha\beta\gamma}} \mathbf{n}^{\alpha\beta}\cdot\left[\mathbf{T}\cdot(\overline{\mathbf{v}}+\tilde{\mathbf{v}})+\mathbf{q}+\rho^{\alpha\beta}\tilde{\mathbf{v}}^{\alpha\beta}\tilde{E}_{\psi}^{\alpha\beta}\right]dC \\ &= \hat{\mathbf{t}}^{\alpha\beta}_{\alpha\beta\gamma}\cdot\overline{\mathbf{v}}^{\alpha\beta}+\hat{q}^{\alpha\beta}_{\alpha\beta\gamma} \qquad (4.125)\end{aligned}$$

such that

$$\hat{q}^{\alpha\beta}_{\alpha\beta\gamma} = \frac{1}{V}\int\limits_{C_{\alpha\beta\gamma}} \mathbf{n}^{\alpha\beta}\cdot\left[\mathbf{T}\cdot\tilde{\mathbf{v}}+\mathbf{q}+\rho^{\alpha\beta}\tilde{\mathbf{v}}^{\alpha\beta}\tilde{E}_{\psi}^{\alpha\beta}\right]dC \qquad (4.126)$$

Eq. (4.121) is first simplified by subtracting the product of $\overline{E}_{\psi}^{\alpha\beta}$ and the mass conservation equation for an interface, Eq. (4.109), giving:

$$\begin{aligned}&\frac{\partial\left(\langle a\rangle^{\alpha\beta}\,\langle\rho\rangle^{\alpha\beta}\,\overline{E}_{\psi}^{\alpha\beta}\right)}{\partial t}-\left(\overline{E}^{\alpha\beta}+\frac{\overline{(v^{\alpha\beta})^2}^{\alpha\beta}}{2}\right)\frac{\partial(\langle a\rangle^{\alpha\beta}\,\langle\rho\rangle^{\alpha\beta})}{\partial t}= \\ &-\nabla\cdot(\langle a\rangle^{\alpha\beta}\,\langle\rho\rangle^{\alpha\beta}\,\overline{\mathbf{v}}^{\alpha\beta}\,\overline{E}_{\psi}^{\alpha\beta})+\left(\overline{E}^{\alpha\beta}+\frac{\overline{(v^{\alpha\beta})^2}^{\alpha\beta}}{2}\right)\nabla\cdot(\langle a\rangle^{\alpha\beta}\,\langle\rho\rangle^{\alpha\beta}\,\overline{\mathbf{v}}^{\alpha\beta}) \\ &-\nabla\cdot\left[\langle a\rangle^{\alpha\beta}\,\left(\langle\mathbf{T}\rangle^{\alpha\beta}\cdot\overline{\mathbf{v}}^{\alpha\beta}+\langle\mathbf{q}\rangle^{\alpha\beta}\right)\right]+\langle a\rangle^{\alpha\beta}\,\langle\rho\rangle^{\alpha\beta}\,\overline{\mathbf{g}\cdot\mathbf{v}^{\alpha\beta}+h}^{\alpha\beta} \\ &+\sum_{i=\alpha,\beta}\left[\hat{e}^{i}_{\alpha\beta}(\overline{E}_{\psi}^{i}-\tilde{E}_{\psi}^{i})+\hat{q}^{*i}_{\alpha\beta}\right]-\left(\overline{E}^{\alpha\beta}+\frac{\overline{(v^{\alpha\beta})^2}^{\alpha\beta}}{2}\right)\hat{e}^{\alpha}_{\alpha\beta}-\left(\overline{E}^{\alpha\beta}+\frac{\overline{(v^{\alpha\beta})^2}^{\alpha\beta}}{2}\right)\hat{e}^{\beta}_{\alpha\beta} \\ &-\sum_{\gamma\neq\alpha,\beta}\left[\hat{e}^{\alpha\beta}_{\alpha\beta\gamma}(\overline{E}_{\psi}^{\alpha\beta}-\tilde{E}_{\psi}^{\alpha\beta})+\hat{q}^{*\alpha\beta}_{\alpha\beta\gamma}\right]+\left(\overline{E}^{\alpha\beta}+\frac{\overline{(v^{\alpha\beta})^2}^{\alpha\beta}}{2}\right)\sum_{\gamma\neq\alpha,\beta}\hat{e}^{\alpha\beta}_{\alpha\beta\gamma} \qquad (4.127)\end{aligned}$$

Simplification gives:

$$\begin{aligned}\langle a\rangle^{\alpha\beta}\,\langle\rho\rangle^{\alpha\beta}\,\frac{D\left(\overline{E}^{\alpha\beta}+\frac{\overline{(v^{\alpha\beta})^2}^{\alpha\beta}}{2}\right)}{Dt} &= -\nabla\cdot\left[\langle a\rangle^{\alpha\beta}\,\left(\langle\mathbf{T}\rangle^{\alpha\beta}\cdot\overline{\mathbf{v}}^{\alpha\beta}+\langle\mathbf{q}\rangle^{\alpha\beta}\right)\right] \\ &+\langle a\rangle^{\alpha\beta}\,\langle\rho\rangle^{\alpha\beta}\,\overline{\mathbf{g}\cdot\mathbf{v}^{\alpha\beta}+h}^{\alpha\beta}+\sum_{i=\alpha,\beta}\left[\hat{e}^{i}_{\alpha\beta}(\overline{E}_{\psi}^{i,\alpha\beta}-\tilde{E}_{\psi}^{i,\alpha\beta})+\hat{q}^{*i}_{\alpha\beta}\right] \\ &-\sum_{\gamma\neq\alpha,\beta}\left(\hat{e}^{\alpha\beta}_{\alpha\beta\gamma}\tilde{E}_{\psi}^{\alpha\beta}+\hat{q}^{*\alpha\beta}_{\alpha\beta\gamma}\right) \qquad (4.128)\end{aligned}$$

where

$$E_{\psi}^{i,\alpha\beta}=E_{\psi}^{i}-E_{\psi}^{\alpha\beta} \qquad (4.129)$$

Eq. (4.128) is further simplified by subtracting the scalar product of $\mathbf{v}^{\alpha\beta}$ and the momentum equation, Eq. (4.112), yielding:

$$
\begin{aligned}
\langle a\rangle^{\alpha\beta}\,\langle\rho\rangle^{\alpha\beta}\,\frac{D\left(\overline{E}^{\alpha\beta}+\overline{\frac{(v^{\alpha\beta})^2}{2}}^{\alpha\beta}\right)}{Dt}-\mathbf{v}^{\alpha\beta}\cdot\langle a\rangle^{\alpha\beta}\,\langle\rho\rangle^{\alpha\beta}\,\frac{D\overline{\mathbf{v}}^{\alpha\beta}}{Dt} \\
=-\nabla\cdot\left[\langle a\rangle^{\alpha\beta}\,\left(\langle\mathbf{T}\rangle^{\alpha\beta}\cdot\overline{\mathbf{v}}^{\alpha\beta}+\langle\mathbf{q}\rangle^{\alpha\beta}\right)\right]+\mathbf{v}^{\alpha\beta}\cdot\nabla\cdot\left(\langle a\rangle^{\alpha\beta}\,\mathbf{T}^{\alpha\beta}\right) \\
+\langle a\rangle^{\alpha\beta}\,\langle\rho\rangle^{\alpha\beta}\,\overline{\mathbf{g}\cdot\mathbf{v}^{\alpha\beta}+h}^{\alpha\beta}-\mathbf{v}^{\alpha\beta}\cdot\langle a\rangle^{\alpha\beta}\,\langle\rho\rangle^{\alpha\beta}\,\mathbf{g} \\
+\sum_{i=\alpha,\beta}\left[\hat{e}^{i}_{\alpha\beta}(\overline{E}^{i,\alpha\beta}_{\psi}-\tilde{E}^{i,\alpha\beta}_{\psi})+\hat{\mathbf{t}}^{i}_{\alpha\beta}\cdot\overline{\mathbf{v}}^{i}+\hat{q}^{i}_{\alpha\beta}\right]-\mathbf{v}^{\alpha\beta}\cdot\sum_{i=\alpha,\beta}\left[\hat{e}^{i}_{\alpha\beta}\left(\overline{\mathbf{v}}^{\,i}+\tilde{\mathbf{v}}^{i}\right)+\hat{\mathbf{t}}^{i}_{\alpha\beta}\right] \\
-\sum_{\gamma\neq\alpha,\beta}\left(\hat{e}^{\alpha\beta}_{\alpha\beta\gamma}\tilde{E}^{\alpha\beta}_{\psi}+\hat{\mathbf{t}}^{\alpha\beta}_{\alpha\beta\gamma}\cdot\overline{\mathbf{v}}^{\alpha\beta}+\hat{q}^{\alpha\beta}_{\alpha\beta\gamma}\right)+\mathbf{v}^{\alpha\beta}\cdot\sum_{\gamma\neq\alpha,\beta}\left[\hat{e}^{\alpha\beta}_{\alpha\beta\gamma}\left(\overline{\mathbf{v}}^{\alpha\beta}+\tilde{\mathbf{v}}^{\alpha\beta}\right)+\hat{\mathbf{t}}^{\alpha\beta}_{\alpha\beta\gamma}\right] \quad (4.130)
\end{aligned}
$$

Rearrangement using identities (4.47) and (4.51) and subtraction yields the macroscopic integral energy equation as:

$$
\begin{aligned}
\langle a\rangle^{\alpha\beta}\,\langle\rho\rangle^{\alpha\beta}\,\frac{D\overline{E}^{\alpha\beta}}{Dt}=-\langle a\rangle^{\alpha\beta}\,\mathbf{T}^{\alpha\beta}:\nabla\overline{\mathbf{v}}^{\alpha\beta}-\nabla\cdot\left(\langle a\rangle^{\alpha\beta}\,\langle\mathbf{q}\rangle^{\alpha\beta}\right)+\langle a\rangle^{\alpha\beta}\,\langle\rho\rangle^{\alpha\beta}\,\overline{h}^{\alpha\beta} \\
+\sum_{i=\alpha,\beta}\left[\hat{e}^{i}_{\alpha\beta}(\overline{E}^{i,\alpha\beta}_{\psi}-\tilde{E}^{i,\alpha\beta}_{\psi})+\hat{\mathbf{t}}^{i}_{\alpha\beta}\cdot\overline{\mathbf{v}}^{i,\alpha\beta}+\hat{q}^{i}_{\alpha\beta}+\hat{q}^{i}_{\alpha\beta}\right]-\mathbf{v}^{\alpha\beta}\cdot\sum_{i=\alpha,\beta}\left[\hat{e}^{i}_{\alpha\beta}\left(\overline{\mathbf{v}}^{\,i}+\tilde{\mathbf{v}}^{i}\right)\right] \\
-\sum_{\gamma\neq\alpha,\beta}\left(\hat{e}^{\alpha\beta}_{\alpha\beta\gamma}\tilde{E}^{\alpha\beta}_{\psi}+\hat{\mathbf{t}}^{\alpha\beta}_{\alpha\beta\gamma}\cdot\overline{\mathbf{v}}^{\alpha\beta}+\hat{q}^{\alpha\beta}_{\alpha\beta\gamma}\right)+\mathbf{v}^{\alpha\beta}\cdot\sum_{\gamma\neq\alpha,\beta}\left[\hat{e}^{\alpha\beta}_{\alpha\beta\gamma}\left(\overline{\mathbf{v}}^{\alpha\beta}+\tilde{\mathbf{v}}^{\alpha\beta}\right)\right] \quad (4.131)
\end{aligned}
$$

Simplification assuming that fluctuations in the total energy and the scalar product of interfacial velocities at the interface boundary and the contact line will be observed as a part of the total energy gives [*Hassanizadeh and Gray*, 1990]:

$$
\begin{aligned}
\langle a\rangle^{\alpha\beta}\,\langle\rho\rangle^{\alpha\beta}\,\frac{D\overline{E}^{\alpha\beta}}{Dt}=-\langle a\rangle^{\alpha\beta}\,\mathbf{T}^{\alpha\beta}:\nabla\overline{\mathbf{v}}^{\alpha\beta}-\nabla\cdot\left(\langle a\rangle^{\alpha\beta}\,\langle\mathbf{q}\rangle^{\alpha\beta}\right)+\langle a\rangle^{\alpha\beta}\,\langle\rho\rangle^{\alpha\beta}\,\overline{h}^{\alpha\beta} \\
+\sum_{i=\alpha,\beta}\left[\hat{e}^{i}_{\alpha\beta}\overline{E}^{i,\alpha\beta}_{\psi}+\hat{\mathbf{t}}^{i}_{\alpha\beta}\cdot\overline{\mathbf{v}}^{\,i,\alpha\beta}+\hat{q}^{i}_{\alpha\beta}\right]-\sum_{\gamma\neq\alpha,\beta}\left(\hat{\mathbf{t}}^{\alpha\beta}_{\alpha\beta\gamma}\cdot\overline{\mathbf{v}}^{\alpha\beta}+\hat{q}^{\alpha\beta}_{\alpha\beta\gamma}\right)(4.132)
\end{aligned}
$$

4.6.4 Balance of Entropy

Systems will converge toward an equilibrium state in which entropy reaches a maximum value [*Greiner et al.*, 1994]. Additional information is gained by quantifying the specific production of entropy at the interface [*Coleman and Noll*, 1963; *Hassanizadeh and Gray*, 1990, 1993a].

For the $\alpha\beta$-interface, $\eta^{\alpha\beta}$ will be used to represent the specific entropy per unit mass. Entropy can be exchanged between the interface and its surroundings. The outward advective movement of entropy is represented by the divergence of the product of $\eta^{\alpha\beta}$ and the mean interfacial velocity. The non-advective movement of entropy out of $\mathcal{A}_{\alpha\beta}$ is represented as $\mathbf{j}_{\psi}^{\alpha\beta} = \phi^{\alpha\beta}$ where $\phi^{\alpha\beta}$ is the entropy flux for the interface, $\mathcal{S}^{\alpha\beta} = b^{\alpha\beta}$ where $b^{\alpha\beta}$ is the external supply of entropy, and $\mathcal{P}^{\alpha\beta} = \Lambda^{\alpha\beta}$ where $\Lambda^{\alpha\beta}$ is specific production of entropy.

$$\overbrace{\frac{\partial(\langle a\rangle^{\alpha\beta}\ \langle\rho\rangle^{\alpha\beta}\ \overline{\eta}^{\alpha\beta})}{\partial t}}^{\text{Accumulation of entropy}} = -\overbrace{\nabla\cdot(\langle a\rangle^{\alpha\beta}\ \langle\rho\rangle^{\alpha\beta}\ \overline{\mathbf{v}}^{\alpha\beta}\ \overline{\eta}^{\alpha\beta})}^{\text{Advection out of interface}} - \overbrace{\nabla\cdot\left(\langle a\rangle^{\alpha\beta}\ \phi^{\alpha\beta}\right)}^{\text{Non-advective transfer out of interface}} + \overbrace{\langle a\rangle^{\alpha\beta}\ \langle\rho\rangle^{\alpha\beta}\ \overline{b^{\alpha\beta}}}^{\text{Supply of entropy}}$$
$$+\underbrace{\langle a\rangle^{\alpha\beta}\ \langle\rho\rangle^{\alpha\beta}\ \overline{\Lambda^{\alpha\beta}}}_{\text{Production of entropy}} + \underbrace{\sum_{i=\alpha,\beta}\left[\hat{\mathrm{e}}^{i}_{\alpha\beta}(\overline{\eta}^{i} - \tilde{\eta}^{i}) + \hat{\mathrm{n}}^{i}_{\alpha\beta}\right]}_{\text{Advective and non-advective transfer from volumes}} - \underbrace{\sum_{\gamma\neq\alpha,\beta}\left[\hat{\mathrm{e}}^{\alpha\beta}_{\alpha\beta\gamma}(\overline{\eta}^{\alpha\beta} - \tilde{\eta}^{\alpha\beta}) + \hat{\mathrm{n}}^{\alpha\beta}_{\alpha\beta\gamma}\right]}_{\text{Advective and non-advective transfer into interfaces}} \tag{4.133}$$

where

$$\phi^{\alpha\beta} = \langle\phi\rangle^{\alpha\beta} - \langle\rho\rangle^{\alpha\beta}\ \overline{\tilde{\mathbf{v}}^{\alpha\beta}\tilde{\eta}^{\alpha\beta}}^{\alpha\beta} \tag{4.134}$$

$$\hat{\mathrm{n}}^{\alpha\beta}_{\alpha\beta\gamma} = \frac{1}{V}\int_{C_{\alpha\beta\gamma}} \mathbf{n}^{\alpha\beta}\cdot\phi^{\alpha\beta}\,dC \tag{4.135}$$

Multiplication of Eq. (4.109) by $\eta^{\alpha\beta}$ and subtraction from Eq. (4.133) yields:

$$\langle a\rangle^{\alpha\beta}\ \langle\rho\rangle^{\alpha\beta}\ \frac{D(\overline{\eta}^{\alpha\beta})}{Dt} = -\nabla\cdot\left(\langle a\rangle^{\alpha\beta}\ \phi^{\alpha\beta}\right) + \langle a\rangle^{\alpha\beta}\ \langle\rho\rangle^{\alpha\beta}\ \overline{b^{\alpha\beta}}$$
$$+\langle a\rangle^{\alpha\beta}\ \langle\rho\rangle^{\alpha\beta}\ \overline{\Lambda^{\alpha\beta}} + \sum_{i=\alpha,\beta}\left[\hat{\mathrm{e}}^{i}_{\alpha\beta}(\overline{\eta}^{i,\alpha\beta} - \tilde{\eta}^{i,\alpha\beta}) + \hat{\mathrm{n}}^{i}_{\alpha\beta}\right] - \sum_{\gamma\neq\alpha,\beta}\left(\hat{\mathrm{n}}^{\alpha\beta}_{\alpha\beta\gamma}\right) \tag{4.136}$$

where

$$\eta^{i,\alpha\beta} = \eta^{i} - \eta^{\alpha\beta} \tag{4.137}$$

The entropy of the interface is of importance in swelling colloidal systems [*Achanta et al.*, 1994] and for describing thermodynamically constrained constitutive relations.

4.6.5 Summary of Interface Equations

In summary, a systematic description of averaged quantities for interfaces including the description of contact lines has been derived from the microscale. Physical information from the microscale is filtered and utilized at the macroscale. Processes occurring at contact lines are represented as precisely defined averaged quantities. Admittedly, a large number of equations are presented in an effort to clearly describe the integral macroscopic conservation equation, Eq. (4.106), and its application to mass, momentum, energy, and entropy balances. Table 4.3 summarizes the quantities that are substituted into Eq. (4.106) to obtain independent conservation equations for mass [Eq. (4.110)], momentum [Eq. (4.115)], energy [Eq. (4.132)], and entropy [Eq. (4.136)].

Table 4.3: Quantities for interface equations

Quantity	ψ	$\mathbf{j}_\psi$	$\mathcal{S}$	$\mathcal{P}$
Mass	1	0	0	0
Momentum	$\mathbf{v}^{\alpha\beta}$	$\mathbf{T}^{\alpha\beta}$	$\mathbf{g}$	0
Energy	$E^{\alpha\beta} + \frac{1}{2}(v^{\alpha\beta})^2$	$\mathbf{T}^{\alpha\beta} \cdot \mathbf{v}^{\alpha\beta} + \mathbf{q}^{\alpha\beta}$	$\mathbf{g} \cdot \mathbf{v}^{\alpha\beta} + h^{\alpha\beta}$	0
Entropy	$\eta^{\alpha\beta}$	$\phi^{\alpha\beta}$	$b^{\alpha\beta}$	$\Lambda^{\alpha\beta}$

4.7 Contact Lines

Contact lines are formed at the intersection of three-phases. Figure 4.8 depicts a three-phase system and shows the $C_{\alpha\beta\gamma}$-contact line at the intersection of the three phases. Figure 4.18 again highlights a contact line with pertinent notation. The contact line may be bounded by the surface interfaces and both internal and boundary end points. The contact line is ignored by conventional approaches as negligible, however, the integral approach provides balance equations to account for the potential contributions of the contact lines. Upon application to a specific system, it will be determined whether contact lines may be treated as jump conditions or discounted altogether.

The general microscale conservation equation for a given scalar or vector property, ψ, for the $\alpha\beta\gamma$-contact line adheres to the previously derived conservation equations

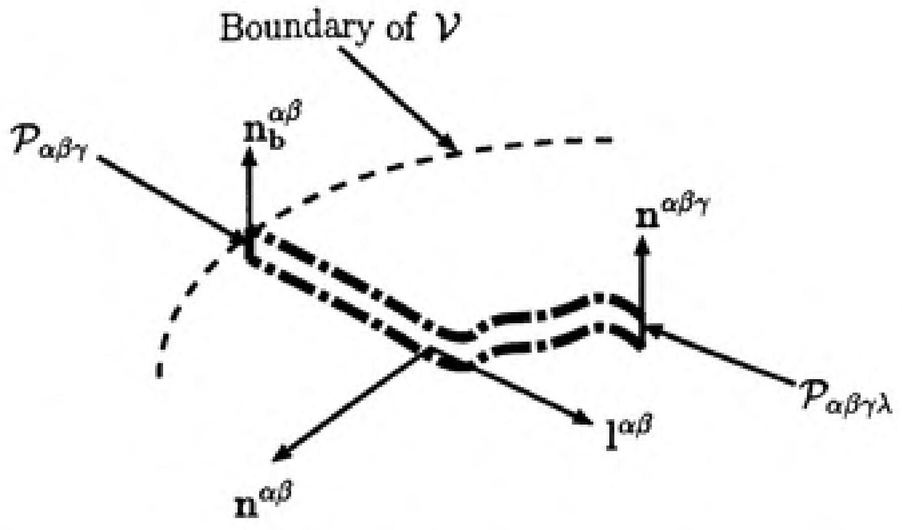


Figure 4.18: A Contact Line Showing Internal and External Endpoints

and is stated as [*Gray*, 1994]:

$$\overbrace{\frac{d}{dt}\int\limits_{C_{\alpha\beta\gamma}} \rho^{\alpha\beta\gamma}\psi\,dC}^{\substack{\text{Accumulation}\\ \text{in contact line}}} = -\overbrace{\sum_{P}\mathbf{n}^{\alpha\beta\gamma}\cdot\left(\rho^{\alpha\beta\gamma}\mathbf{v}^{\alpha\beta\gamma}\,\psi + \mathbf{j}_{\psi}^{\alpha\beta\gamma}\right)}^{\substack{\text{Advective and}\\ \text{non-advective transfer}\\ \text{into endpoints}}}$$

$$+\underbrace{\sum_{ij=\alpha\beta,\beta\gamma}^{\alpha\gamma}\int\limits_{C_{\alpha\beta\gamma}} \mathbf{n}^{ij}\cdot\left(\rho^{ij}(\mathbf{v}^{\alpha\beta}-\mathbf{v}^{\alpha\beta\gamma})\psi + \mathbf{j}_{\psi}\right)dC}_{\substack{\text{Advective and}\\ \text{non-advective transfer}\\ \text{from interfaces}}} + \underbrace{\int\limits_{C_{\alpha\beta\gamma}} \rho^{\alpha\beta\gamma}(\mathcal{S}+\mathcal{P})\,dC}_{\substack{\text{Supply and}\\ \text{production}}} \qquad (4.138)$$

where

$$\sum_{P}\mathbf{n}^{\alpha\beta\gamma}\cdot\left(\rho^{\alpha\beta\gamma}\mathbf{v}^{\alpha\beta\gamma}\,\psi + \mathbf{j}_{\psi}^{\alpha\beta\gamma}\right) = \sum_{\mathcal{P}_{\alpha\beta\gamma}}\mathbf{n}_{\mathbf{b}}^{\alpha\beta\gamma}\cdot\left(\rho^{\alpha\beta\gamma}(\mathbf{v}^{\alpha\beta\gamma}-\mathbf{v}_{\mathbf{b}}^{\alpha\beta\gamma})\psi + \mathbf{j}_{\psi}^{\alpha\beta\gamma}\right)$$

$$+\sum_{\mathcal{P}_{\alpha\beta\gamma\lambda}}\mathbf{n}^{\alpha\beta\gamma}\cdot\left(\rho^{\alpha\beta\gamma}\mathbf{v}^{\alpha\beta\gamma}\psi + \mathbf{j}_{\psi}\right) \qquad (4.139)$$

and $\rho^{\alpha\beta\gamma}$ is the mass density of the contact line; $\mathbf{v}^{\alpha\beta\gamma}$ is the velocity of the contact line; $\mathbf{j}_{\psi}^{\alpha\beta\gamma}$ is a non-advective flux; $\mathbf{n}_{\mathbf{b}}^{\alpha\beta\gamma}$ is the unit vector tangent to $\mathcal{C}_{\alpha\beta\gamma}$ oriented outward from the line at a common point $P_{\alpha\beta\gamma}$ that is an endpoint of the contact line; $\mathcal{S}$ is an external source of ψ; and $\mathcal{P}$ is a measure of the net production of ψ within the $\alpha\beta\gamma$-contact line.

The transport theorem for a fixed contact line, Eq. (4.31), is used to express the total time derivative in the accumulation term on the LHS of Eq. (4.138) as a partial time derivative. The divergence theorem, Eq. (4.27), is used to transform the sum of fluxes through boundary edge endpoints into a divergence of an integral over the contact line. Combined, this allows the macroscale balance equation, still containing microscale quantities inside the integrals, to be stated as:

$$\frac{\partial}{\partial t}\int\limits_{C_{\alpha\beta\gamma}} \rho^{\alpha\beta\gamma}\psi \, dC = -\nabla\cdot\int\limits_{C_{\alpha\beta\gamma}} (\rho^{\alpha\beta\gamma}\mathbf{v}^{\alpha\beta\gamma}\psi + \mathbf{j}_{\psi}^{\alpha\beta\gamma})\, dC - \sum_{\mathcal{P}_{\alpha\beta\gamma\lambda}} \mathbf{n}^{\alpha\beta\gamma}\cdot\left(\rho^{\alpha\beta\gamma}\mathbf{v}^{\alpha\beta\gamma}\psi + \mathbf{j}_{\psi}\right)$$
$$+ \sum_{ij=\alpha\beta,\beta\gamma}^{\alpha\gamma}\int\limits_{C_{\alpha\beta\gamma}} \mathbf{n}^{ij}\cdot\left[\rho^{ij}(\mathbf{v}^{\alpha\beta} - \mathbf{v}^{\alpha\beta\gamma})\psi + \mathbf{j}_{\psi}\right] dC + \int\limits_{C_{\alpha\beta\gamma}} \rho^{\alpha\beta\gamma}(\mathcal{S}+\mathcal{P})\, dC \quad (4.140)$$

Noting that the specific length, $\langle l\rangle^{\alpha\beta\gamma}$, from Eq. (4.35) can be stated as:

$$\frac{1}{V} = \frac{\langle l\rangle^{\alpha\beta\gamma}}{C_{\alpha\beta\gamma}} \quad (4.141)$$

Therefore dividing Eq. (4.140) by the macroscopic volume, V, yields:

$$\left(\frac{\langle l\rangle^{\alpha\beta\gamma}}{C_{\alpha\beta\gamma}}\right)\frac{\partial}{\partial t}\int\limits_{C_{\alpha\beta\gamma}} \rho^{\alpha\beta\gamma}\psi\, dC = -\left(\frac{\langle l\rangle^{\alpha\beta\gamma}}{C_{\alpha\beta\gamma}}\right)\nabla\cdot\int\limits_{C_{\alpha\beta\gamma}} (\rho^{\alpha\beta\gamma}\mathbf{v}^{\alpha\beta\gamma}\psi + \mathbf{j}_{\psi}^{\alpha\beta\gamma})\, dC$$
$$-\left(\frac{\langle l\rangle^{\alpha\beta\gamma}}{C_{\alpha\beta\gamma}}\right)\sum_{\mathcal{P}_{\alpha\beta\gamma\lambda}} \mathbf{n}^{\alpha\beta\gamma}\cdot\left[\rho^{\alpha\beta\gamma}\mathbf{v}^{\alpha\beta\gamma}\psi + \mathbf{j}_{\psi}\right] + \left(\frac{\langle l\rangle^{\alpha\beta\gamma}}{C_{\alpha\beta\gamma}}\right)\int\limits_{C_{\alpha\beta\gamma}} \rho^{\alpha\beta\gamma}(\mathcal{S}+\mathcal{P})\, dC$$
$$+\left(\frac{\langle l\rangle^{\alpha\beta\gamma}}{C_{\alpha\beta\gamma}}\right)\sum_{ij=\alpha\beta,\beta\gamma}^{\alpha\gamma}\int\limits_{C_{\alpha\beta\gamma}} \mathbf{n}^{ij}\cdot\left[\rho^{ij}(\mathbf{v}^{\alpha\beta} - \mathbf{v}^{\alpha\beta\gamma})\psi + \mathbf{j}_{\psi}\right] dC \quad (4.142)$$

Using the previously defined line average, Eq. (4.36), and the mass average for line, Eq. (4.39), and defining fluctuation terms as described in Eq. (4.42) allows us to write Eq. (4.142) in terms of macroscopic quantities as [*Gray*, 1994]:

$$\frac{\partial(\langle l\rangle^{\alpha\beta\gamma}\ \langle\rho\psi\rangle^{\alpha\beta\gamma})}{\partial t} = -\nabla\cdot(\langle l\rangle^{\alpha\beta\gamma}\ \langle\rho\mathbf{v}^{\alpha\beta\gamma}\psi\rangle^{\alpha\beta\gamma}) - \nabla\cdot(\langle l\rangle^{\alpha\beta\gamma}\ \langle\mathbf{j}_{\psi}\rangle^{\alpha\beta\gamma})$$
$$-\left(\frac{\langle l\rangle^{\alpha\beta\gamma}}{C_{\alpha\beta\gamma}}\right)\sum_{\mathcal{P}_{\alpha\beta\gamma\lambda}} \mathbf{n}^{\alpha\beta\gamma}\cdot\left(\rho^{\alpha\beta\gamma}\mathbf{v}^{\alpha\beta\gamma}\psi + \mathbf{j}_{\psi}\right) + \langle l\rangle^{\alpha\beta\gamma}\ \langle\rho(\mathcal{S}+\mathcal{P})\rangle^{\alpha\beta\gamma}$$
$$+\left(\frac{\langle l\rangle^{\alpha\beta\gamma}}{C_{\alpha\beta\gamma}}\right)\sum_{ij=\alpha\beta,\beta\gamma}^{\alpha\gamma}\int\limits_{C_{\alpha\beta\gamma}} \mathbf{n}^{ij}\cdot\left[\rho^{ij}(\mathbf{v}^{\alpha\beta} - \mathbf{v}^{\alpha\beta\gamma})\psi + \mathbf{j}_{\psi}\right] dC \quad (4.143)$$

Simplifying Eq. (4.143) with identities (4.43) through (4.46) yields:

$$\begin{aligned}\frac{\partial(\langle l\rangle^{\alpha\beta\gamma}\,\langle\rho\rangle^{\alpha\beta\gamma}\,\overline{\psi}^{\alpha\beta\gamma})}{\partial t} &= -\nabla\cdot(\langle l\rangle^{\alpha\beta\gamma}\,\langle\rho\rangle^{\alpha\beta\gamma}\,\overline{\mathbf{v}^{\alpha\beta\gamma}}\,\overline{\psi}^{\alpha\beta\gamma}) \\ &\quad -\nabla\cdot\left[\langle l\rangle^{\alpha\beta\gamma}\,(\langle\mathbf{j}_\psi\rangle^{\alpha\beta\gamma}+\langle\rho\rangle^{\alpha\beta\gamma}\,\overline{\tilde{\mathbf{v}}^{\alpha\beta\gamma}\tilde{\psi}^{\alpha\beta\gamma}}^{\alpha\beta\gamma})\right] \\ &\quad -\sum_{P_{\alpha\beta\gamma\lambda}}\left[\hat{e}^{\alpha\beta\gamma}_{\alpha\beta\gamma\lambda}(\overline{\psi}^{\alpha\beta\gamma}+\tilde{\psi}^{\alpha\beta\gamma})+\hat{i}^{\alpha\beta\gamma}_{\alpha\beta\gamma\lambda}\right] \\ +\sum_{ij=\alpha\beta,\beta\gamma}^{\alpha\gamma}\left[\hat{e}^{ij}_{\alpha\beta\gamma}(\overline{\psi}^{ij}+\tilde{\psi}^{ij})+\hat{i}^{ij}_{\alpha\beta\gamma}\right] &+\langle l\rangle^{\alpha\beta\gamma}\,\langle\rho\rangle^{\alpha\beta\gamma}\,(\overline{\mathcal{S}}^{\alpha\beta\gamma}+\overline{\mathcal{P}}^{\alpha\beta\gamma}) \end{aligned} \tag{4.144}$$

where

$$\hat{e}^{\alpha\beta\gamma}_{\alpha\beta\gamma\lambda}=\frac{1}{V}\sum_{P_{\alpha\beta\gamma\lambda}}\mathbf{n}^{\alpha\beta\gamma}\cdot\left[\rho^{\alpha\beta\gamma}(\mathbf{v}^{\alpha\beta\gamma}-\mathbf{v}^{\alpha\beta\gamma\lambda})\right] \tag{4.145}$$

and

$$\hat{i}^{\alpha\beta\gamma}_{\alpha\beta\gamma\lambda}=\frac{1}{V}\sum_{P_{\alpha\beta\gamma\lambda}}\mathbf{n}^{\alpha\beta\gamma}\cdot\mathbf{j}^{\alpha\beta\gamma}_{\psi} \tag{4.146}$$

$\hat{e}^{\alpha\beta\gamma}_{\alpha\beta\gamma\lambda}$ accounts for mass transferred from the contact line to the end-points of the contact line and $\hat{i}^{\alpha\beta\gamma}_{\alpha\beta\gamma\lambda}$ is an expression for the non-advective flux out of the contact line into the end-point.

4.7.1 Conservation of Mass

For the conservation of mass for the $\alpha\beta\gamma$-contact line, $\psi = 1$, $\mathbf{j}^{\alpha\beta\gamma}_{\psi} = 0$ stating that the net diffusive flux is zero, $\mathcal{S} = 0$ assuming that there are no sources, and $\mathcal{P} = 0$ assuming that there are no mass producing processes. Substitution into Eq. (4.144) yields:

$$\begin{aligned}\frac{\partial(\langle l\rangle^{\alpha\beta\gamma}\,\langle\rho\rangle^{\alpha\beta\gamma})}{\partial t} &= -\nabla\cdot(\langle l\rangle^{\alpha\beta\gamma}\,\langle\rho\rangle^{\alpha\beta\gamma}\,\overline{\mathbf{v}}^{\alpha\beta\gamma}) \\ &\quad +\hat{e}^{\alpha\beta}_{\alpha\beta\gamma}+\hat{e}^{\beta\gamma}_{\alpha\beta\gamma}+\hat{e}^{\alpha\gamma}_{\alpha\beta\gamma}-\sum_{P_{\alpha\beta\gamma\lambda}}\hat{e}^{\alpha\beta\gamma}_{\alpha\beta\gamma\lambda}\end{aligned} \tag{4.147}$$

where the term on the LHS represents any accumulation of mass within the contact line due to changes in length or density. The first term on the RHS accounts for advection of mass out of the contact line. The second, third, and fourth terms on the RHS represent a transfer of mass from the respective interfaces into the contact line.

The final term on the RHS accounts for mass transferred out of the contact line into the endpoint.

In the case that the contact line is massless, $\rho^{\alpha\beta\gamma} \to 0$. Eq. (4.147) reduces to the following:

$$\frac{\partial \langle l \rangle^{\alpha\beta\gamma}}{\partial t} + \nabla \cdot \left(\langle l \rangle^{\alpha\beta\gamma} \, \overline{\mathbf{v}^{\alpha\beta\gamma}} \right) = -\hat{e}^{*}_{\alpha\beta\gamma} + \sum_{P_{\alpha\beta\gamma\lambda}} \hat{e}^{*\alpha\beta\gamma}_{\alpha\beta\gamma\lambda} \tag{4.148}$$

where

$$\hat{e}^{*}_{\alpha\beta\gamma} = \lim_{\rho^{\alpha\beta\gamma} \to 0} \left(\frac{\hat{e}^{\alpha\beta}_{\alpha\beta\gamma} + \hat{e}^{\beta\gamma}_{\alpha\beta\gamma} + \hat{e}^{\alpha\gamma}_{\alpha\beta\gamma}}{\rho^{\alpha\beta\gamma}} \right) \tag{4.149}$$

and

$$\hat{e}^{*\alpha\beta\gamma}_{\alpha\beta\gamma\lambda} = \lim_{\rho^{\alpha\beta\gamma} \to 0} \left(\frac{\hat{e}^{\alpha\beta\gamma}_{\alpha\beta\gamma\lambda}}{\rho^{\alpha\beta\gamma}} \right) = \frac{1}{V} \sum_{P_{\alpha\beta\gamma\lambda}} \mathbf{n}^{\alpha\beta\gamma} \cdot \left[\left(\mathbf{v}^{\alpha\beta\gamma} - \mathbf{v}^{\alpha\beta\gamma\lambda} \right) \right] \tag{4.150}$$

Additionally, as $\rho^{\alpha\beta\gamma} \to 0$ the net mass transferred from all interfaces to the contact line will be zero and the mass transferred from the contact line to a point at the end of the line will also be zero, stated as:

$$\hat{e}^{\alpha\beta}_{\alpha\beta\gamma} + \hat{e}^{\beta\gamma}_{\alpha\beta\gamma} + \hat{e}^{\alpha\gamma}_{\alpha\beta\gamma} = 0 \tag{4.151}$$

and

$$\hat{e}^{\alpha\beta\gamma}_{\alpha\beta\gamma\lambda} = 0 \tag{4.152}$$

Eq. (4.151) and Eq. (4.152), when assumed, are useful in closing the system of equations in multiphase applications.

4.7.2 Conservation of Momentum

A contact line must conserve momentum in the same manner as the volume and the interface [*Hassanizadeh and Gray*, 1993a]. For the conservation of momentum of the $\alpha\beta\gamma$-contact line, $\boldsymbol{\psi} = \mathbf{v}^{\alpha\beta\gamma}$ such that the accumulation term is the product of mass per length and velocity representing the momentum per length.

The terms on the RHS of the equation now represent the sum of forces acting on the $\alpha\beta\gamma$-contact line per unit length. The forces that act on an contact line are surface forces and body forces [*Slattery*, 1972]. To account for surface forces, we define

$\mathbf{j}_{\psi}^{\alpha\beta\gamma} = \mathbf{T}^{\alpha\beta\gamma}$ where the stress tensor is assumed to be a continuous function with the three following properties:

1. A stress vector, $\mathbf{t}^{\alpha\beta\gamma}$, may be written in terms of the divergence of the stress tensor, $\mathbf{T}^{\alpha\beta\gamma}$, as [*Slattery*, 1990]:

$$\mathbf{t}^{\alpha\beta\gamma} = \nabla \cdot \mathbf{T}^{\alpha\beta\gamma} \tag{4.153}$$

2. The interfacial stress tensor is symmetric [*Hassanizadeh and Gray*, 1993a] as all portions of the medium are assumed non-polar [*Slattery*, 1990];

3. The stress vectors acting upon opposite sides of the same edge of the interface at a given point are equal in magnitude and opposite in direction (e.g., $\mathbf{t}_{\mathbf{n}}^{\alpha\beta\gamma} = -\mathbf{t}_{-\mathbf{n}}^{\alpha\beta\gamma}$ where n indicates that the stress is acting in the normal outward direction) [*Whitaker*, 1981];

$\mathcal{S} = \mathbf{g}$ where gravity is the only body force per unit mass considered. Additionally, $\mathcal{P} = 0$ as there are no velocity producing processes occurring on the contact line. Substitution into Eq. (4.144) yields:

$$\begin{aligned} \frac{\partial(\langle l\rangle^{\alpha\beta\gamma}\ \langle\rho\rangle^{\alpha\beta\gamma}\ \overline{\mathbf{v}^{\alpha\beta\gamma}})}{\partial t} &= -\nabla\cdot(\langle l\rangle^{\alpha\beta\gamma}\ \langle\rho\rangle^{\alpha\beta\gamma}\ \overline{\mathbf{v}^{\alpha\beta\gamma}\mathbf{v}^{\alpha\beta\gamma}}) \\ &\quad -\nabla\cdot\left[\langle l\rangle^{\alpha\beta\gamma}\ \mathbf{T}^{\alpha\beta\gamma}\right] + \langle l\rangle^{\alpha\beta\gamma}\ \langle\rho\rangle^{\alpha\beta\gamma}\ \mathbf{g} \\ + \sum_{ij=\alpha\beta,\beta\gamma}^{\alpha\gamma} \left[\hat{e}_{\alpha\beta\gamma}^{ij}(\overline{\mathbf{v}}^{\,ij} + \tilde{\mathbf{v}}^{ij}) + \hat{\mathbf{t}}_{\alpha\beta\gamma}^{ij}\right] &- \sum_{P_{\alpha\beta\gamma\lambda}} \left[\hat{e}_{\alpha\beta\gamma\lambda}^{\alpha\beta\gamma}(\overline{\mathbf{v}^{\alpha\beta\gamma}} + \tilde{\mathbf{v}}^{\alpha\beta\gamma}) + \hat{\mathbf{t}}_{\alpha\beta\gamma\lambda}^{\alpha\beta\gamma}\ \right] \end{aligned} \tag{4.154}$$

where the cross-fluctuations of $\mathbf{v}^{\alpha\beta\gamma}$ with itself have been reinserted as these are not expected to be zero and where

$$\mathbf{T}^{\alpha\beta\gamma} = \langle\mathbf{T}\rangle^{\alpha\beta\gamma}\ + \langle\rho\rangle^{\alpha\beta\gamma}\ \overline{\tilde{\mathbf{v}}^{\alpha\beta\gamma}\tilde{\mathbf{v}}^{\alpha\beta\gamma}}^{\alpha\beta\gamma} \tag{4.155}$$

$$\hat{\mathbf{t}}_{\alpha\beta\gamma\lambda}^{\alpha\beta\gamma} = \frac{1}{V}\sum_{P_{\alpha\beta\gamma\lambda}} \mathbf{n}^{\alpha\beta\gamma}\cdot\mathbf{T}^{\alpha\beta\gamma} \tag{4.156}$$

Similar to phase and interface derivations, Eq. (4.147) is multiplied by $\mathbf{v}^{\alpha\beta\gamma}$ and subtracted from Eq. (4.154) to yield the macroscale momentum balance for a contact line as:

$$\langle l\rangle^{\alpha\beta\gamma}\,\langle\rho\rangle^{\alpha\beta\gamma}\,\frac{D\mathbf{v}^{\alpha\beta\gamma}}{Dt} = -\nabla\cdot\left(\langle l\rangle^{\alpha\beta\gamma}\,\mathbf{T}^{\alpha\beta\gamma}\right) - \langle l\rangle^{\alpha\beta\gamma}\,\langle\rho\rangle^{\alpha\beta\gamma}\,\mathbf{g} + \sum_{ij=\alpha\beta,\beta\gamma}^{\alpha\gamma}\left[\hat{e}^{ij}_{\alpha\beta\gamma}(\mathbf{v}^{\,ij,\alpha\beta\gamma} + \tilde{\mathbf{v}}^{ij,\alpha\beta\gamma}) + \hat{\mathbf{t}}^{ij}_{\alpha\beta\gamma}\right] - \sum_{P_{\alpha\beta\gamma\lambda}}\hat{\mathbf{t}}^{\alpha\beta\gamma}_{\alpha\beta\gamma\lambda} \tag{4.157}$$

where

$$\mathbf{v}^{ij,\alpha\beta\gamma} = \mathbf{v}^{ij} - \mathbf{v}^{\alpha\beta\gamma} \tag{4.158}$$

When the contact line is assumed massless, the contact line may still sustain a stress [*Gray*, 1994]. In light of this, the limit as $\rho^{\alpha\beta\gamma} \to 0$ for Eq. (4.157) is taken to yield:

$$-\nabla\cdot\left(\langle l\rangle^{\alpha\beta\gamma}\,\langle\mathbf{T}^{\alpha\beta\gamma}\rangle\right) + \sum_{ij=\alpha\beta,\beta\gamma}^{\alpha\gamma}\left[\hat{e}^{ij}_{\alpha\beta\gamma}(\mathbf{v}^{\,ij,\alpha\beta\gamma} + \tilde{\mathbf{v}}^{ij,\alpha\beta\gamma}) + \hat{\mathbf{t}}^{ij}_{\alpha\beta\gamma}\right] - \sum_{P_{\alpha\beta\gamma\lambda}}\hat{\mathbf{t}}^{\alpha\beta\gamma}_{\alpha\beta\gamma\lambda} = 0 \tag{4.159}$$

Additionally, if the contact line is assumed to not possess any thermodynamic properties, the net momentum transferred from all interfaces to the contact line will be zero and the momentum transferred from the contact line to a point at the end of the line will also be zero, reducing Eq. (4.157) to:

$$\sum_{ij=\alpha\beta,\beta\gamma}^{\alpha\gamma}\left[\hat{e}^{ij}_{\alpha\beta\gamma}(\mathbf{v}^{\,ij,\alpha\beta\gamma} + \tilde{\mathbf{v}}^{ij,\alpha\beta\gamma}) + \hat{\mathbf{t}}^{ij}_{\alpha\beta\gamma}\right] = 0 \tag{4.160}$$

and

$$\sum_{P_{\alpha\beta\gamma\lambda}}\hat{\mathbf{t}}^{\alpha\beta\gamma}_{\alpha\beta\gamma\lambda} = 0 \tag{4.161}$$

4.7.3 Conservation of Energy

For conservation of energy of the $\alpha\beta\gamma$-contact line, $\psi = E + (v^{\alpha\beta\gamma})^2/2 = E^{\alpha\beta\gamma}_{\psi}$ where E is the internal energy density function and $v^{\alpha\beta\gamma}$ is the magnitude of the contact line velocity, $\mathbf{j}^{\alpha\beta\gamma}_{\psi} = \mathbf{T}^{\alpha\beta\gamma}\cdot\mathbf{v}^{\alpha\beta\gamma} + \mathbf{q}$ where $\mathbf{T}^{\alpha\beta\gamma}$ is the stress tensor and $\mathbf{q}$ is the heat flux vector, $\mathcal{S}^{\alpha\beta\gamma} = \mathbf{g}\cdot\mathbf{v}^{\alpha\beta\gamma} + h$, and $\mathcal{P}^{\alpha\beta\gamma} = 0$ assuming that there are no energy producing processes. Simple substitution into Eq. (4.144) yields:

$$\begin{aligned}\frac{\partial(\langle l\rangle^{\alpha\beta\gamma}\ \langle\rho\rangle^{\alpha\beta\gamma}\ \overline{E}_{\psi}^{\alpha\beta\gamma})}{\partial t} &= -\nabla\cdot(\langle l\rangle^{\alpha\beta\gamma}\ \langle\rho\rangle^{\alpha\beta\gamma}\ \overline{\mathbf{v}^{\alpha\beta\gamma}E}_{\psi}^{\alpha\beta\gamma}) \\ &+\nabla\cdot\left[\langle l\rangle^{\alpha\beta\gamma}\ \left(\langle\mathbf{T}^{\alpha\beta\gamma}\cdot\mathbf{v}^{\alpha\beta\gamma}+\mathbf{q}\rangle^{\alpha\beta\gamma}\ -\langle\rho\rangle^{\alpha\beta\gamma}\ \overline{\tilde{\mathbf{v}}^{\alpha\beta\gamma}\tilde{E}_{\psi}}^{\alpha\beta\gamma}\right)\right] \\ +\langle l\rangle^{\alpha\beta\gamma}\ \langle\rho\rangle^{\alpha\beta\gamma}\ \overline{\mathbf{g}\cdot\mathbf{v}^{\alpha\beta\gamma}+h}^{\alpha\beta\gamma} &- \sum_{ij=\alpha\beta,\beta\gamma}^{\alpha\gamma}\left[\hat{e}_{\alpha\beta\gamma}^{ij}(\overline{E}_{\psi}^{ij}+\tilde{E}_{\psi}^{ij})+\hat{q}_{\alpha\beta\gamma}^{ij}\right] \\ &+\sum_{P_{\alpha\beta\gamma\lambda}}\left[\hat{e}_{\alpha\beta\gamma\lambda}^{\alpha\beta\gamma}(\overline{E}_{\psi}^{\alpha\beta\gamma}+\tilde{E}_{\psi}^{\alpha\beta\gamma})+\hat{q}_{\alpha\beta\gamma\lambda}^{\alpha\beta\gamma}\right] \qquad (4.162)\end{aligned}$$

where

$$\begin{aligned}\hat{q}^{*\,\alpha\beta\gamma}_{\ \alpha\beta\gamma\lambda} &= \frac{1}{V}\sum_{P_{\alpha\beta\gamma\lambda}}\mathbf{n}^{\alpha\beta\gamma}\cdot\left[\mathbf{T}\cdot(\overline{\mathbf{v}}+\tilde{\mathbf{v}})+\mathbf{q}+\rho^{\alpha\beta\gamma}\tilde{\mathbf{v}}^{\alpha\beta\gamma}\tilde{E}_{\psi}^{\alpha\beta\gamma}\right] \\ &= \hat{\mathbf{t}}_{\alpha\beta\gamma\lambda}^{\alpha\beta\gamma}\cdot\overline{\mathbf{v}}^{\alpha\beta\gamma}+\hat{q}_{\alpha\beta\gamma\lambda}^{\alpha\beta\gamma} \qquad (4.163)\end{aligned}$$

such that

$$\hat{q}_{\alpha\beta\gamma\lambda}^{\alpha\beta\gamma}=\frac{1}{V}\sum_{P_{\alpha\beta\gamma\lambda}}\mathbf{n}^{\alpha\beta\gamma}\cdot\left[\mathbf{T}\cdot\tilde{\mathbf{v}}+\mathbf{q}+\rho^{\alpha\beta\gamma}\tilde{\mathbf{v}}^{\alpha\beta\gamma}\tilde{E}_{\psi}^{\alpha\beta\gamma}\right]dC \qquad (4.164)$$

Similar to phase and interface derivations, Eq. (4.147) is multiplied by $E_{\psi}^{\alpha\beta\gamma}$ and subtracted from Eq. (4.162) to yield the macroscale energy balance for a contact line as:

$$\begin{aligned}\langle l\rangle^{\alpha\beta\gamma}\ \langle\rho\rangle^{\alpha\beta\gamma}\ \frac{D\overline{E}_{\psi}^{\alpha\beta\gamma}}{Dt} &= \nabla\cdot\left[\langle l\rangle^{\alpha\beta\gamma}\ \left(\langle\mathbf{T}^{\alpha\beta\gamma}\cdot\mathbf{v}^{\alpha\beta\gamma}+\mathbf{q}\rangle^{\alpha\beta\gamma}\ -\langle\rho\rangle^{\alpha\beta\gamma}\ \overline{\tilde{\mathbf{v}}^{\alpha\beta\gamma}\tilde{E}_{\psi}}^{\alpha\beta\gamma}\right)\right] \\ &+\langle l\rangle^{\alpha\beta\gamma}\ \langle\rho\rangle^{\alpha\beta\gamma}\ \overline{\mathbf{g}\cdot\mathbf{v}}^{\alpha\beta\gamma}-\sum_{ij=\alpha\beta,\beta\gamma}^{\alpha\gamma}\left[\hat{e}_{\alpha\beta\gamma}^{ij}(\overline{E}_{\psi}^{ij,\alpha\beta\gamma}+\tilde{E}_{\psi}^{ij,\alpha\beta\gamma})+\hat{q}_{\alpha\beta\gamma}^{ij}\right] \\ &+\sum_{P_{\alpha\beta\gamma\lambda}}\hat{q}_{\alpha\beta\gamma\lambda}^{\alpha\beta\gamma} \qquad (4.165)\end{aligned}$$

where

$$E_{\psi}^{ij,\alpha\beta\gamma}=E_{\psi}^{ij}-E_{\psi}^{\alpha\beta\gamma} \qquad (4.166)$$

When the contact line is massless, the contact line may still be a source of internal energy. Considering the limit as $\rho^{\alpha\beta\gamma}\rightarrow 0$ for Eq. (4.165) is taken to yield:

$$\begin{aligned}&\nabla\cdot\left(\langle l\rangle^{\alpha\beta\gamma}\ \langle\mathbf{t}^{\alpha\beta\gamma}\cdot\mathbf{v}^{\alpha\beta\gamma}+\mathbf{q}\rangle^{\alpha\beta\gamma}\ \right) \\ &\quad-\sum_{ij=\alpha\beta,\beta\gamma}^{\alpha\gamma}\left[\hat{e}_{\alpha\beta\gamma}^{ij}(\overline{E}_{\psi}^{ij,\alpha\beta\gamma}+\tilde{E}_{\psi}^{ij,\alpha\beta\gamma})+\hat{q}_{\alpha\beta\gamma}^{ij}\right]+\sum_{P_{\alpha\beta\gamma\lambda}}\hat{q}_{\alpha\beta\gamma\lambda}^{\alpha\beta\gamma}=0 \qquad (4.167)\end{aligned}$$

Additionally, if the contact line is assumed to not possess any thermodynamic properties, the net energy transferred from all interfaces to the contact line will be zero and the energy transferred from the contact line to a point at the end of the line will also be zero, reducing Eq. (4.165) to:

$$\sum_{ij=\alpha\beta,\beta\gamma}^{\alpha\gamma} \left[\hat{\mathrm{e}}_{\alpha\beta\gamma}^{ij}(\overline{E}_{\psi}^{\,ij,\alpha\beta\gamma} + \tilde{E}_{\psi}^{ij,\alpha\beta\gamma}) + \hat{\mathrm{q}}_{\alpha\beta\gamma}^{ij}\right] = 0 \tag{4.168}$$

and

$$\sum_{P_{\alpha\beta\gamma\lambda}} \hat{\mathrm{q}}_{\alpha\beta\gamma\lambda}^{\alpha\beta\gamma} = 0 \tag{4.169}$$

4.7.4 Balance of Entropy

For the entropy inequality at the $\alpha\beta\gamma$-contact line $\psi = \eta^{\alpha\beta\gamma}$ with inherent deviations, $\mathbf{j}_{\psi}^{\alpha\beta\gamma} = \boldsymbol{\phi}^{\alpha\beta\gamma}$ where $\boldsymbol{\phi}^{\alpha\beta\gamma}$ is the flux of entropy, $\mathcal{S}^{\alpha\beta\gamma} = b^{\alpha\beta\gamma}$ where $b^{\alpha\beta\gamma}$ is external supply of entropy and $\mathcal{P}^{\alpha\beta\gamma} = \Lambda^{\alpha\beta\gamma}$ where $\Lambda^{\alpha\beta\gamma}$ is the specific production of entropy.

Substitution into Eq. (4.144) yields:

$$\begin{aligned}
\frac{\partial(\langle l\rangle^{\alpha\beta\gamma}\ \langle\rho\rangle^{\alpha\beta\gamma}\ \overline{\eta}^{\ \alpha\beta\gamma})}{\partial t} &= -\nabla\cdot(\langle l\rangle^{\alpha\beta\gamma}\ \langle\rho\rangle^{\alpha\beta\gamma}\ \overline{\mathbf{v}^{\alpha\beta\gamma}\overline{\eta}}^{\ \alpha\beta\gamma}) \\
-\nabla\cdot\left[\langle l\rangle^{\alpha\beta\gamma}\ \left(\langle\boldsymbol{\phi}\rangle^{\alpha\beta\gamma}\ + \langle\rho\rangle^{\alpha\beta\gamma}\ \overline{\tilde{\mathbf{v}}^{\alpha\beta\gamma}\tilde{\eta}}^{\alpha\beta\gamma}\right)\right] &+ \langle l\rangle^{\alpha\beta\gamma}\ \langle\rho\rangle^{\alpha\beta\gamma}\ \overline{b}^{\alpha\beta\gamma} \\
+\langle l\rangle^{\alpha\beta\gamma}\ \langle\rho\rangle^{\alpha\beta\gamma}\ \overline{\Lambda}^{\alpha\beta\gamma} + \sum_{ij=\alpha\beta,\beta\gamma}^{\alpha\gamma} &\left[\hat{\mathrm{e}}_{\alpha\beta\gamma}^{ij}(\overline{\eta}^{\ ij} + \tilde{\eta}^{ij}) + \hat{\mathrm{n}}_{\alpha\beta\gamma}^{ij}\right] \\
-\sum_{P_{\alpha\beta\gamma\lambda}} &\left[\hat{\mathrm{e}}_{\alpha\beta\gamma\lambda}^{\alpha\beta\gamma}(\overline{\eta}^{\ \alpha\beta\gamma} + \tilde{\eta}^{\alpha\beta\gamma}) + \hat{\mathrm{n}}_{\alpha\beta\gamma\lambda}^{\alpha\beta\gamma}\right]
\end{aligned} \tag{4.170}$$

where

$$\hat{\mathrm{n}}_{\alpha\beta\gamma\lambda}^{\alpha\beta\gamma} = \frac{1}{V}\sum_{P_{\alpha\beta\gamma\lambda}} \mathbf{n}^{\alpha\beta\gamma}\cdot\boldsymbol{\phi}^{\alpha\beta\gamma} \tag{4.171}$$

Similar to phase and interface derivations, Eq. (4.147) is multiplied by $\eta^{\alpha\beta\gamma}$ and subtracted from Eq. (4.170) to yield the macroscale entropy balance for a contact line as:

$$\langle l\rangle^{\alpha\beta\gamma}\ \langle\rho\rangle^{\alpha\beta\gamma}\ \frac{(D\overline{\eta}^{\ \alpha\beta\gamma})}{Dt} = -\nabla\cdot\left[\langle l\rangle^{\alpha\beta\gamma}\ \left(\langle\boldsymbol{\phi}\rangle^{\alpha\beta\gamma}\ + \langle\rho\rangle^{\alpha\beta\gamma}\ \overline{\tilde{\mathbf{v}}^{\alpha\beta\gamma}\tilde{\eta}}^{\alpha\beta\gamma}\right)\right]$$

$$+\langle l\rangle^{\alpha\beta\gamma}\ \langle\rho\rangle^{\alpha\beta\gamma}\ \overline{b}^{\alpha\beta\gamma}+\langle l\rangle^{\alpha\beta\gamma}\ \langle\rho\rangle^{\alpha\beta\gamma}\ \overline{\Lambda}^{\alpha\beta\gamma}$$

$$+\sum_{ij=\alpha\beta,\beta\gamma}^{\alpha\gamma}\left[\hat{\mathrm{e}}^{ij}_{\alpha\beta\gamma}(\overline{\eta}^{\ ij,\alpha\beta\gamma}+\tilde{\eta}^{ij,\alpha\beta\gamma})+\hat{\mathrm{n}}^{ij}_{\alpha\beta\gamma}\right]-\sum_{P_{\alpha\beta\gamma\lambda}}\hat{\mathrm{n}}^{\alpha\beta\gamma}_{\alpha\beta\gamma\lambda} \quad (4.172)$$

where

$$\eta^{ij,\alpha\beta\gamma}=\eta^{ij}-\eta^{\alpha\beta\gamma} \quad (4.173)$$

When the contact line is massless, the contact line may still be a source of entropy. Considering the limit as $\rho^{\alpha\beta\gamma}\rightarrow 0$ for Eq. (4.172) is taken to yield:

$$-\nabla\cdot\left(\langle l\rangle^{\alpha\beta\gamma}\ \langle\phi\rangle^{\alpha\beta\gamma}\right)+\sum_{ij=\alpha\beta,\beta\gamma}^{\alpha\gamma}\left[\hat{\mathrm{e}}^{ij}_{\alpha\beta\gamma}(\overline{\eta}^{\ ij,\alpha\beta\gamma}+\tilde{\eta}^{ij,\alpha\beta\gamma})+\hat{\mathrm{n}}^{ij}_{\alpha\beta\gamma}\right]$$

$$\sum_{P_{\alpha\beta\gamma\lambda}}\hat{\mathrm{n}}^{\alpha\beta\gamma}_{\alpha\beta\gamma\lambda}=0 \quad (4.174)$$

Additionally, if the contact line is assumed to not possess any thermodynamic properties, the net entropy transferred from all interfaces to the contact line will be zero and the entropy transferred from the contact line to a point at the end of the line will also be zero, reducing Eq. (4.165) to:

$$\sum_{ij=\alpha\beta,\beta\gamma}^{\alpha\gamma}\left[\hat{\mathrm{e}}^{ij}_{\alpha\beta\gamma}(\overline{\eta}^{\ ij,\alpha\beta\gamma}+\tilde{\eta}^{ij,\alpha\beta\gamma})+\hat{\mathrm{n}}^{ij}_{\alpha\beta\gamma}\right]=0 \quad (4.175)$$

and

$$\sum_{P_{\alpha\beta\gamma\lambda}}\hat{\mathrm{n}}^{\alpha\beta\gamma}_{\alpha\beta\gamma\lambda}=0 \quad (4.176)$$

4.7.5 Summary of Contact Line Equations

To summarize, macroscopic contact line conservation equations have been derived with accumulation, flux, source, and production terms that have been derived from microscale terms. Table 4.4 presents the quantities that are substituted into Eq. (4.144) to obtain conservation equations for mass, momentum, energy, and entropy.

4.8 Application of Integral Equations

The equations summarized in Tables 4.2, 4.3, and 4.4 provide a means for solution of field-scale multiphase flow and transport problems. However, two obstacles

Table 4.4: Quantities for contact line equations

Quantity	ψ	$\mathbf{j}_{\psi}^{\alpha\beta\gamma}$	$\mathcal{S}^{\alpha\beta\gamma}$	$\mathcal{P}^{\alpha\beta\gamma}$
Mass	1	0	0	0
Momentum	$\mathbf{v}^{\alpha\beta\gamma}$	$\mathbf{T}^{\alpha\beta\gamma}$	$\mathbf{g}$	0
Energy	$E^{\alpha\beta\gamma} + \frac{1}{2}(v^{\alpha\beta\gamma})^2$	$\mathbf{T}^{\alpha\beta\gamma} \cdot \mathbf{v}^{\alpha\beta\gamma} + \mathbf{q}^{\alpha\beta\gamma}$	$\mathbf{g} \cdot \mathbf{v}^{\alpha\beta\gamma} + h^{\alpha\beta\gamma}$	0
Entropy	$\eta^{\alpha\beta\gamma}$	$\phi^{\alpha\beta\gamma}$	$b^{\alpha\beta\gamma}$	$\Lambda^{\alpha\beta\gamma}$

remain. First, thermodynamically based constitutive relationships must be developed for multiphase systems. Second, accurate solution is beyond our current computational capabilities, since the overall system of integral conservation equations requiring solution becomes too large. As computational capabilities increase, the ICA provide a rigorous solution to MPFT problem.

With current computational limitations, insight into the effects of interfacial and contact line effects can be gained through application of the ICA to simplified systems. The following chapter will examine a two-phase system to gain such insights.

Chapter 5

Application of Integral Equations to Two-Phase Flow Through Porous Media

"It is a mathematical fact that the casting of this pebble from my hand alters the center of gravity of the universe." Thomas Carlyle

5.1 Applications of the Integral Approach

The focus of this chapter will be the systematic application of the integral continuum balance equations, bounded by thermodynamic constraints. The integral balance equations for mass, momentum, energy, and entropy are summarized in Tables 4.2, 4.3, and 4.4 for volumes, interfaces, and contact lines respectively. While the macroscale integral approach is theoretically appealing and promises to resolve the inconsistencies contained in current differential continuum compositional models, much work remains to be done. Due to the large number of variables, both the logical application and judicial choice of independent variables is necessary. Also, formal averaging approaches lead to large systems of equations, that must be simplified substantially in order to be tractable with currently available computational resources. Finally, constitutive relationships for the many additional dependent variables are necessary before predictions can be made.

Macroscale integral equations have been applied to two-phase fluid systems. Table 5.1 reviews applications of the integral continuum approach to various simplified systems and shows:

1. more independent variables exist (as well as many more unlisted secondary variables) than governing equations;
2. much work remains to be done in order to develop the necessary constitutive theory for closure of even simple systems;
3. a large number of equations will need to be solved simultaneously;
4. few researchers have applied macroscale integral equations to porous media systems; and
5. applications of integral equations have not been extended to more than two flowing fluids.

5.2 The Integral Approach Applied to Two-Phase Flow

In this report, integral continuum balance equations will be applied to two-phase flow with full consideration given to the interfacial balances. Thermodynamic constraints will be applied following the methodology of *Coleman and Noll* [1963]. Two-phase flow formulations with consideration of interfaces, utilizing a formal averaging procedure, currently exist in the literature [*Hassanizadeh and Gray*, 1990; *Gray and Hassanizadeh*, 1991b; *Achanta et al.*, 1994; *Gray et al.*, 1995] as shown in Table 5.1. While this current work is not novel, it remains very educational.

Consider a porous media system composed of a solid phase, an aqueous phase that preferentially wets the solid phase, and a NAPL phase. The phases will be referred to

Table 5.1: Integral continuum approaches

Researcher(s)	Phases	Inter-faces	No. of Equations Ma	Mo	Ener	Ent	Independent Variables
Hassanizadeh and Gray [1980a]	a, s	–	2	6	1	1	s^α, ρ^α, $\mathbf{v}^{\alpha,s}$, $\mathbf{f}^s$, T, Λ
Gray [1983]	a, g, s	summed effects	4	12	4	1	$\varepsilon\, s^\alpha \rho^\alpha$, $\mathbf{v}^\alpha$, T^α, $\hat{e}^s_{\alpha\beta}$, $\hat{\mathbf{t}}^s_{\alpha\beta}$, $\hat{q}^s_{\alpha\beta}$, Λ
Hassanizadeh and Gray [1990]	a, n, s	an, as, ns	6	18	6	2	$\varepsilon\, s^\alpha \rho^\alpha$, $a^{\alpha\beta}\rho^{\alpha\beta}$, $\mathbf{v}^{\alpha,s}$, $\mathbf{v}^{\alpha\beta,s}$, $\mathbf{E}^s$, T^α, ∇T^α, $T^{\alpha\beta}$, $\nabla T^{\alpha\beta}$, $\nabla(\varepsilon\, s^\alpha \rho^\alpha)$, $\nabla(a^{\alpha\beta}\rho^{\alpha\beta})$, Λ^α, $\Lambda^{\alpha\beta}$
Gray and Hassanizadeh [1991b]	a, g, s	ag, as, gs	6	18	6	2	ρ^α, $\rho^{\alpha\beta}$, $\mathbf{v}^{\alpha,s}$, $\mathbf{v}^{\alpha\beta,s}$, $\mathbf{E}^s$, T^α, ∇T^α, ε, $\nabla\varepsilon$, s^α, ∇s^α, $a^{\alpha\beta}$, $\nabla a^{\alpha\beta}$, Λ^α, $\Lambda^{\alpha\beta}$
Hassanizadeh and Gray [1993b]	a, n, s	summed effects	2	6	2	2	s^α, s^n, ρ^α, ρ^n, $\mathbf{v}^{\alpha,s}$, $\mathbf{v}^{n,s}$, p^α, p^n, p^c, a^{wn}, Λ^α, $\Lambda^{\alpha\beta}$
Achanta et al. [1994]	a, g, s	ag, as, gs	6	18	6	2	ρ^α, $\nabla\rho^\alpha$, ε^α, $\nabla\varepsilon^\alpha$, $a^{\alpha\beta}$, $\nabla a^{\alpha\beta}$ $\rho^{\alpha\beta}$, $\nabla\rho^{\alpha\beta}$, $\mathbf{v}^{\alpha,s}$, $\mathbf{v}^{\alpha\beta,s}$, $\mathbf{E}^s$, T^α, ∇T^α, Λ^α, $\Lambda^{\alpha\beta}$
Murad et al. [1995]	a, s	–	2	6	2	1	s^α, ∇s^α $\mathbf{E}^s$, $\mathbf{v}^{\alpha,s}$,T, Λ
Gray et al. [1995]	a, n, s	an, as, ns	6	18	6	2	ρ^α, $\rho^{\alpha\beta}$, $\mathbf{v}^{\alpha,s}$, $\mathbf{v}^{\alpha\beta,s}$, $\mathbf{E}^s$, T^α, ∇T^α, $T^{\alpha\beta}$, $\nabla T^{\alpha\beta}$, ε, $\nabla\varepsilon$, s^α, ∇s^α, $a^{\alpha\beta}$, $\nabla a^{\alpha\beta}$, Λ^α, $\Lambda^{\alpha\beta}$

respectively as s, a, and n. The three phases are separated by interfaces that possess thermodynamic properties. The interfaces will be referred to as an, as, and ns for the aqueous-NAPL, the aqueous-solid, and the NAPL-solid interfaces respectively. The three phases may also come together to form a contact line, ans. In this development, the contact line will be assumed to possess no thermodynamic properties. All variables are formally averaged from the microscale to the macroscale with averaged quantities not indicated with the cumbersome notation of the previous chapter.

5.2.1 Notation

Fluid particles are described with spatial coordinates (x, y, z) at a specific time. The motion in multiphase flow systems can be described relative to a fixed spatial coordinate system (Eulerian approach) or relative to the material of interest (Lagrangian approach) [*Bear*, 1972; *Whitaker*, 1981]. Equations written for a fixed control volume relate the conditions in a control volume to the flow of mass, momentum, energy or entropy through that region. Alternatively, equations can be written that follow the motion of the particles.

At an arbitrary initial time, defined as $t = 0$, the position of a fluid particle can be referred to as:

$$x = X, \qquad y = Y, \qquad z = Z, \qquad t = 0 \tag{5.1}$$

If we define a spatial position vector as [*Whitaker*, 1981]:

$$\mathbf{r} = \mathbf{i}x + \mathbf{j}y + \mathbf{k}z \tag{5.2}$$

and a material position vector as [*Whitaker*, 1981]:

$$\mathbf{R} = \mathbf{i}X + \mathbf{j}Y + \mathbf{k}Z \tag{5.3}$$

Then, as time progresses, a particle's position can be described as [*Whitaker*, 1981]:

$$\mathbf{r} = \mathbf{R} + \int_0^t \left(\frac{d\mathbf{r}}{dt}\right) dt \tag{5.4}$$

stating that the spatial position will be the initial position plus the change in the particle's position over time.

In the solution of multiphase flow systems, the motion of fluids relative to the solid matrix is of primary interest. Therefore, in this report, motion will be described relative to motion of the solid matrix. Solid phase motion is defined by the transformation vector, $\mathbf{f}^s$. Using $\mathbf{R}$ as the initial position at time $t = 0$, the Eulerian position of the solid is stated as [*Hassanizadeh and Gray*, 1979b]:

$$\mathbf{r} = \mathbf{f}^s(\mathbf{R}, t) \tag{5.5}$$

Deformation of the solid phase will then be described by the Lagrangian strain tensor $\mathbf{E}^s$, that by definition is stated as [*Hassanizadeh and Gray*, 1979b]:

$$\mathbf{E}^s = \frac{1}{2}\left((\nabla^* \mathbf{f}^s)(\nabla^* \mathbf{f}^s)^T - \mathbf{I}\right) \tag{5.6}$$

where ∇^* indicates that differentiation takes place with respect to the material reference coordinates, the superscript T indicates the transpose of a tensorial quantity, and $\mathbf{I}$ indicates the unit tensor.

The material derivative of the deformation strain tensor is defined as [*Eringen*, 1980]:

$$\frac{D^s \mathbf{E}^s}{Dt} = (\nabla^* \mathbf{f}^s)\,\mathbf{D}^s\,(\nabla^* \mathbf{f}^s)^T \tag{5.7}$$

where $\mathbf{D}^s$ is the deformation rate tensor for the solid phase and can be defined for any phase as [*Hassanizadeh and Gray*, 1990]:

$$\mathbf{D}^\alpha = \frac{1}{2}\left[\nabla \mathbf{v}^\alpha + (\nabla \mathbf{v}^\alpha)^T\right] \tag{5.8}$$

and for the interface as [*Hassanizadeh and Gray*, 1990]:

$$\mathbf{D}^{\alpha\beta} = \frac{1}{2}\left[\nabla \mathbf{v}^{\alpha\beta} + (\nabla \mathbf{v}^{\alpha\beta})^T\right] \tag{5.9}$$

The velocity of the solid phase can be stated as [*Hassanizadeh and Gray*, 1990]:

$$\mathbf{v}^s = \mathbf{v}^s(\mathbf{r}, t) \tag{5.10}$$

Relative velocities for phases and interfaces with respect to the solid phase are then defined as [*Hassanizadeh and Gray*, 1990]:

$$\mathbf{v}^{\alpha,s} = \mathbf{v}^{\alpha} - \mathbf{v}^{s} \tag{5.11}$$

$$\mathbf{v}^{\alpha\beta,s} = \mathbf{v}^{\alpha\beta} - \mathbf{v}^{s} \tag{5.12}$$

This leads to the additional relative velocities of the form:

$$\mathbf{v}^{\alpha,\beta} = \mathbf{v}^{\alpha,s} - \mathbf{v}^{\beta,s} \tag{5.13}$$

$$\mathbf{v}^{\alpha\beta,\gamma} = \mathbf{v}^{\alpha\beta,s} - \mathbf{v}^{\gamma,s} \tag{5.14}$$

Relative forms of the material derivative, that was first defined in Eq. (4.48), may also be defined for the volume and the interface as:

$$\frac{D^{\beta}\psi}{Dt} = \frac{D^{\alpha}\psi}{Dt} + \left(\mathbf{v}^{\beta,s} - \mathbf{v}^{\alpha,s}\right) \cdot \nabla\psi \tag{5.15}$$

$$\frac{D^{\alpha\beta}\psi}{Dt} = \frac{D^{\alpha}\psi}{Dt} + \left(\mathbf{v}^{\alpha\beta,s} - \mathbf{v}^{\alpha,s}\right) \cdot \nabla\psi \tag{5.16}$$

The following sections describe the assumptions and manipulations to formulate a closed problem.

5.2.2 Balance Equations about Volumes

Mass, momentum (3 equations), and energy conservation equations are written about a representative elementary volume for each phase. Thus, formulation renders 15 equations for a three phase system. Table 5.2 highlights the 17 primary unknowns that are chosen as independent variables for the system in concurrence with *Hassanizadeh and Gray* [1990] and *Gray et al.* [1995]. Independent variables are chosen from a knowledge of the system's expected behavior [*Hassanizadeh and Gray*, 1990, p. 176]. Independent variables must also be independent of the frame of reference.

5.2.3 Secondary Variables for Volumes

Many additional variables are used in the 15 governing volume balance equations. Therefore, the volume balance laws must be supplemented by identities, equations of

Table 5.2: Primary variables for integral equations about volumes

Variable	Nomenclature	Number of Unknowns
Saturation	s^a, s^n	1, 1
Density	ρ^a, ρ^n, ρ^s	1, 1, 1
Phase velocity	$\mathbf{v}^a$, $\mathbf{v}^n$	3, 3
Displacement vector	$\mathbf{f}^s$	3
Temperature	T^a, T^n, T^s	1, 1, 1
	Total	17

state, and constitutive relations for the eventual closure of the equations describing the multiphase system. Constitutive relations can be expressed in terms of the primary unknowns and their derivatives.

First, by definition, all volume fractions will add to one; therefore:

$$\varepsilon^a + \varepsilon^n + \varepsilon^s = 1 \tag{5.17}$$

The total void space will be $1 - \varepsilon^s = \varepsilon$; allowing saturations to be defined as:

$$\varepsilon^a = \varepsilon s^a \tag{5.18}$$

Saturations are defined for a phase as the ratio of the volume fraction to the total void space. Therefore, the following identity will hold:

$$\sum_{\alpha, \alpha \neq s} s^\alpha = \sum_{\alpha, \alpha \neq s} \frac{\varepsilon^\alpha}{\varepsilon} = 1 \tag{5.19}$$

Next, all source terms are assumed known. Body force terms such as gravity, $\mathbf{g}$, that act as momentum sources are assumed known. Likewise, all energy source terms, h, are assumed known. Entropy fluxes are assumed to depend solely upon the heat input and external entropy source terms are assumed to be due solely from external energy sources [*Eringen*, 1980]. The entropy flux vector and supply are then stated for volumes as [*Hassanizadeh and Gray*, 1980a]:

$$\phi^\alpha = \frac{\mathbf{q}^\alpha}{T^\alpha}, \quad b^\alpha = \frac{h^\alpha}{T^\alpha} \tag{5.20}$$

Third, note that the stress tensors, $\mathbf{T}^\alpha$, have previously been assumed symmetric [*Hassanizadeh and Gray*, 1979b]. This reduces the number of unknowns from nine to six for these tensorial variables.

The 63 remaining variables, for which constitutive relations are required, are listed in Table 5.3. (Note that Helmholtz free energy is defined as $A^\alpha = E^\alpha - T^\alpha \eta^\alpha$ [*Sonntag and Van Wylen*, 1982; *Greiner et al.*, 1994])

Table 5.3: Secondary variables for integral equations about volumes

Variable	Nomenclature	Number of Unknowns
Helmholtz free energy	A^a, A^n, A^s	1, 1, 1
Stress tensor (symmetric)	$\mathbf{T}^a$, $\mathbf{T}^n$, $\mathbf{T}^s$	6, 6, 6
Mass transfer to interfaces		
from aqueous	$\hat{e}^a_{an}, \hat{e}^a_{as}$	1, 1
from NAPL	$\hat{e}^n_{an}, \hat{e}^n_{ns}$	1, 1
from solid	$\hat{e}^s_{as}, \hat{e}^s_{ns}$	1, 1
Momentum transfer to interfaces		
from aqueous	$\hat{\mathbf{t}}^a_{an}, \hat{\mathbf{t}}^a_{as}$	3, 3
from NAPL	$\hat{\mathbf{t}}^n_{an}, \hat{\mathbf{t}}^n_{ns}$	3, 3
from solid	$\hat{\mathbf{t}}^s_{as}, \hat{\mathbf{t}}^s_{ns}$	3, 3
Energy transfer to interfaces		
from aqueous	$\hat{q}^a_{an}, \hat{q}^a_{as}$	1, 1
from NAPL	$\hat{q}^n_{an}, \hat{q}^n_{ns}$	1, 1
from solid	$\hat{q}^s_{as}, \hat{q}^s_{ns}$	1, 1
Heat flux vector	$\mathbf{q}^a$, $\mathbf{q}^n$, $\mathbf{q}^s$	3, 3, 3
Specific entropy per unit mass	η^a, η^n, η^s	1, 1, 1
	Total	63

5.2.4 Balance Equations about Interfacial Areas

Mass, momentum (3 equations), and energy conservation equations are written about each interface in the same manner as the volumes. A three phase system will contain three interfaces and therefore an additional 15 balance equations are added. 18 primary unknowns, that are highlighted in Table 5.4, are chosen as independent variables for the system in concurrence with *Hassanizadeh and Gray* [1990] and *Gray et al.* [1995].

Table 5.4: Primary variables for integral equations about interfaces

Variable	Nomenclature	Number of Unknowns
Specific surface area	a^{an}, a^{as}, a^{ns}	1, 1, 1
Interface density	ρ^{an}, ρ^{as}, ρ^{ns}	1, 1, 1
Interface velocity	$\mathbf{v}^{an}$, $\mathbf{v}^{as}$, $\mathbf{v}^{ns}$	3, 3, 3
Temperature	T^{an}, T^{as}, T^{ns}	1, 1, 1
	Total	18

5.2.5 Secondary Variables for Interfacial Areas

The area balance laws must be supplemented by constitutive relations in pursuit of a closed system of equations. The same methodology applied to volumes will be applied to the interfaces.

All source terms are assumed known. External entropy source terms are assumed to be due solely from external energy sources and are stated for interfaces as [*Hassanizadeh and Gray*, 1990]:

$$\phi^{\alpha\beta} = \frac{\mathbf{q}^{\alpha\beta}}{T^{\alpha\beta}}, \quad b^{\alpha\beta} = \frac{h^{\alpha\beta}}{T^{\alpha\beta}} \tag{5.21}$$

Next, note that the stress tensors, $\mathbf{T}^{\alpha\beta}$, have previously been assumed symmetric [*Hassanizadeh and Gray*, 1990]. This reduces the number of unknowns from nine to six for each tensorial variable. The 48 remaining variables for which constitutive relations are required are listed in Table 5.5. (Note that the Helmholtz free energy for an interface is defined as $A^{\alpha\beta} = E_{\psi}^{\alpha\beta} - T^{\alpha\beta}\eta^{\alpha\beta}$ [*Slattery*, 1972])

Table 5.5: Secondary variables for integral equations about interfaces

Variable	Nomenclature	Number of Unknowns
Helmholtz free energy	A^{an}, A^{as}, A^{ns}	1, 1, 1
Stress tensor (symmetric)	$\mathbf{T}^{an}$, $\mathbf{T}^{as}$, $\mathbf{T}^{ns}$	6, 6, 6
Mass transfer		
to the contact line	$\hat{e}^{an}_{ans}$, $\hat{e}^{as}_{ans}$, $\hat{e}^{ns}_{ans}$	1, 1, 1
Momentum transfer		
to the contact line	$\hat{\mathbf{t}}^{an}_{ans}$, $\hat{\mathbf{t}}^{as}_{ans}$, $\hat{\mathbf{t}}^{ns}_{ans}$	3, 3, 3
Energy transfer		
to the contact line	$\hat{q}^{an}_{ans}$, $\hat{q}^{as}_{ans}$, $\hat{q}^{ns}_{ans}$	1, 1, 1
Heat flux vector	$\mathbf{q}^{an}$, $\mathbf{q}^{as}$, $\mathbf{q}^{ns}$	3, 3, 3
Specific entropy per unit mass	η^{an}, η^{as}, η^{ns}	1, 1, 1
	Total	48

5.2.6 Balance Equations about Contact Lines

The *ans*-contact line for this two-phase system is restricted such that it is not permitted to possess thermodynamic properties. Furthermore, the effects of the contact points at the ends of contact lines are assumed negligible. Constraint equations have been derived for mass, momentum, energy, and entropy within a contact line [*Gray and Hassanizadeh*, 1991b; *Gray et al.*, 1995]. For the conservation of mass, Eq. (4.151) can be restated as:

$$\sum_{\alpha\beta} \hat{e}^{\alpha\beta}_{ans} = 0 \tag{5.22}$$

Assuming that deviations from mean interfacial velocity are negligible and the contact line is fixed in space, Eq. (4.160) is restated as:

$$\sum_{\alpha\beta=an,as}^{ns} \left(\hat{e}^{\alpha\beta}_{ans} \mathbf{v}^{\alpha\beta} + \hat{\mathbf{t}}^{\alpha\beta}_{ans} \right) = 0 \tag{5.23}$$

The material derivative with respect to density for the solid is developed following similar steps as for the fluid phases. We begin by stating the integral mass balance equation for the solid phase within a volume, Eq. (4.76), as:

$$\begin{aligned} \frac{D^s(\varepsilon^s\rho^s)}{Dt} &= \\ \varepsilon^s\frac{D^s\rho^s}{Dt} + \rho^s\frac{D^s\varepsilon^s}{Dt} &= -\varepsilon^s\rho^s\nabla\cdot\mathbf{v}^s - \sum_{\beta\neq\alpha}\hat{e}^s_{\alpha\beta} \end{aligned} \tag{5.56}$$

Expressing $D^s\varepsilon^s/Dt$ in Eq. (5.56) as $\dot{\varepsilon^s}$ and rearranging yields the material derivative of density as:

$$\frac{D\rho^s}{Dt} = -\rho^s\nabla\cdot\mathbf{v}^s - \frac{\rho^s}{\varepsilon^s}\dot{\varepsilon} - \frac{1}{\varepsilon^s}\sum_{\beta\neq\alpha}\hat{e}^s_{\alpha\beta} \tag{5.57}$$

Eq. (5.53) can be used to express the material derivative of the aqueous phase saturation. Eq. (5.7) expresses the material derivative of the deformation strain tensor. Incorporating Eqs. (5.53), (5.7) and (5.57) into Eq. (5.55) and expanding yields:

$$\begin{aligned} \frac{DA^s}{Dt} = \frac{\partial A^s}{\partial\rho^s}\left(-\rho^s\nabla\cdot\mathbf{v}^s - \frac{\rho^s}{\varepsilon}\dot{\varepsilon} - \frac{1}{\varepsilon^s}\sum_{\beta\neq\alpha}\hat{e}^s_{\alpha\beta}\right) + \frac{\partial A^\alpha}{\partial s^a}\dot{s^a} \\ + \frac{\partial A^s}{\partial\mathbf{E}^s}\left[(\nabla^*\mathbf{f}^s)\cdot\mathbf{D}^s\cdot(\nabla^*\mathbf{f}^s)^T\right] + \frac{\partial A^s}{\partial T^s}\frac{DT^s}{Dt} \end{aligned} \tag{5.58}$$

Similarly, the expansion of the Helmholtz free energy for interfaces in terms of independent variables yields:

$$\begin{aligned} \frac{D^{\alpha\beta}A^{\alpha\beta}}{Dt} = \frac{\partial A^{\alpha\beta}}{\partial a^{\alpha\beta}}\frac{D^{\alpha\beta}a^{\alpha\beta}}{Dt} + \frac{\partial A^{\alpha\beta}}{\partial\rho^{\alpha\beta}}\frac{D^{\alpha\beta}\rho^{\alpha\beta}}{Dt} + \frac{\partial A^{\alpha\beta}}{\partial s^a}\frac{D^{\alpha\beta}s^a}{Dt} \\ + \frac{\partial A^{\alpha\beta}}{\partial T^{\alpha\beta}}\frac{D^{\alpha\beta}T^{\alpha\beta}}{Dt} \end{aligned} \tag{5.59}$$

The following relations for interfacial quantities will prove helpful to further expand the equation. By definition:

$$\frac{D^{\alpha\beta}a^{\alpha\beta}}{Dt} = \frac{\partial a^{\alpha\beta}}{\partial t} + \mathbf{v}^{\alpha\beta}\cdot\nabla a^{\alpha\beta} \tag{5.60}$$

$$\frac{D^{\alpha\beta}a^{\alpha\beta}}{Dt} = \frac{D^s a^{\alpha\beta}}{Dt} + \mathbf{v}^{\alpha\beta}\cdot\nabla a^{\alpha\beta} = \dot{a^{\alpha\beta}} + \mathbf{v}^{\alpha\beta}\cdot\nabla a^{\alpha\beta} \tag{5.61}$$

and

$$\frac{D^{\alpha\beta}\psi}{Dt} = \frac{D^{\alpha}\psi}{Dt} + (\mathbf{v}^{\alpha\beta} - \mathbf{v}^{\alpha}) \cdot \nabla\psi \tag{5.62}$$

Eq. (5.60) and Eq. (5.61) can be compared to conclude that:

$$\frac{D^{s}a^{\alpha\beta}}{Dt} = \frac{\partial a^{\alpha\beta}}{\partial t} \tag{5.63}$$

stating that the material derivative of the interfacial area relative to the solid phase will be equal to the partial derivative of the interfacial area, which agrees with the previous assumption that the solid phase is fixed.

To describe the terms on the RHS of Eq. (5.59), we begin with the interfacial area mass balance, Eq (4.110), stated as:

$$\begin{aligned} \frac{D^{\alpha\beta}(a^{\alpha\beta}\rho^{\alpha\beta})}{Dt} &= \\ a^{\alpha\beta}\frac{D^{\alpha\beta}\rho^{\alpha\beta}}{Dt} + \rho^{\alpha\beta}\frac{D^{\alpha\beta}a^{\alpha\beta}}{Dt} &= -a^{\alpha\beta}\rho^{\alpha\beta}\nabla \cdot \mathbf{v}^{\alpha\beta} + \hat{e}^{\alpha}_{\alpha\beta} + \hat{e}^{\beta}_{\alpha\beta} \end{aligned} \tag{5.64}$$

noting that the mass exchange term with the contact line has been assumed to be zero. Rearrangement of Eq. (5.64) in terms of the material derivative for the interfacial density gives:

$$\frac{D^{\alpha\beta}\rho^{\alpha\beta}}{Dt} = -\rho^{\alpha\beta}\nabla \cdot \mathbf{v}^{\alpha\beta} - \frac{\rho^{\alpha\beta}}{a^{\alpha\beta}}\frac{D^{\alpha\beta}a^{\alpha\beta}}{Dt} + \frac{1}{a^{\alpha\beta}}\hat{e}^{\alpha}_{\alpha\beta} + \frac{1}{a^{\alpha\beta}}\hat{e}^{\beta}_{\alpha\beta} \tag{5.65}$$

Incorporating Eq. (5.61) into Eq. (5.65) yields:

$$\frac{D^{\alpha\beta}\rho^{\alpha\beta}}{Dt} = -\rho^{\alpha\beta}\nabla \cdot \mathbf{v}^{\alpha\beta} - \frac{\rho^{\alpha\beta}}{a^{\alpha\beta}}\left(\dot{a^{\alpha\beta}} + \mathbf{v}^{\alpha\beta} \cdot \nabla a^{\alpha\beta}\right) + \frac{1}{a^{\alpha\beta}}\hat{e}^{\alpha}_{\alpha\beta} + \frac{1}{a^{\alpha\beta}}\hat{e}^{\beta}_{\alpha\beta} \tag{5.66}$$

where $\dot{a^{\alpha\beta}}$ is used to indicate $D^{\alpha\beta}(a^{\alpha\beta})/Dt$.

Next in our expansion of the RHS of Eq. (5.59), using Eq. (5.62) allows the material derivative of s^{a} to be stated as:

$$\begin{aligned} \frac{D^{\alpha\beta}s^{a}}{Dt} &= \frac{D^{\alpha}s^{a}}{Dt} + (\mathbf{v}^{\alpha\beta} - \mathbf{v}^{\alpha}) \cdot \nabla s^{a} \\ &= \dot{s^{a}} + \mathbf{v}^{\alpha\beta,s} \cdot \nabla s^{a} \end{aligned} \tag{5.67}$$

Incorporating Eq. (5.61), Eq. (5.66), and Eq. (5.67) into Eq. (5.59) yields:

$$\frac{D^{\alpha\beta}A^{\alpha\beta}}{Dt} = \frac{\partial A^{\alpha\beta}}{\partial a^{\alpha\beta}}\left(\dot{a^{\alpha\beta}} + \mathbf{v}^{\alpha\beta} \cdot \nabla a^{\alpha\beta}\right)$$

$$
\begin{aligned}
&+\frac{\partial A^{\alpha\beta}}{\partial \rho^{\alpha\beta}}\left[-\rho^{\alpha\beta}\nabla\cdot\mathbf{v}^{\alpha\beta}-\frac{\rho^{\alpha\beta}}{a^{\alpha\beta}}\left(\dot{a}^{\alpha\beta}+\mathbf{v}^{\alpha\beta}\cdot\nabla a^{\alpha\beta}\right)+\frac{1}{a^{\alpha\beta}}\dot{\hat{e}}^{\alpha}_{\alpha\beta}+\frac{1}{a^{\alpha\beta}}\dot{\hat{e}}^{\beta}_{\alpha\beta}\right]\\
&\qquad+\frac{\partial A^{\alpha\beta}}{\partial s^{a}}\left(\dot{s}^{a}+\mathbf{v}^{\alpha\beta,s}\cdot\nabla s^{a}\right)+\frac{\partial A^{\alpha\beta}}{\partial T^{\alpha\beta}}\frac{D^{\alpha\beta}T^{\alpha\beta}}{Dt}
\end{aligned}
\tag{5.68}
$$

And now we will plug the expansions of Helmholtz free energies [Eq.(5.54), Eq.(5.58), and Eq.(5.68)] into Eq. (5.45) for the following:

$$
\begin{aligned}
&\sum_{\alpha}\varepsilon\, s^{\alpha}\,\rho^{\alpha}\Lambda^{\alpha}+\sum_{\alpha\beta}a^{\alpha\beta}\rho^{\alpha\beta}\Lambda^{\alpha\beta}=\\
&\qquad-\frac{\varepsilon s^{a}\rho^{a}}{T^{a}}\frac{\partial A^{a}}{\partial \rho^{a}}\left[-\rho^{a}\nabla\cdot\mathbf{v}^{a}-\frac{\rho^{a}}{\varepsilon s^{a}}\left[\varepsilon\,\dot{s}^{a}+s^{a}\,\dot{\varepsilon}+\mathbf{v}^{a,s}\cdot\nabla\varepsilon s^{a}\right]\right]\\
&\qquad-\frac{\rho^{a}}{T^{a}}\frac{\partial A^{a}}{\partial \rho^{a}}\sum_{\beta\neq\alpha}\dot{\hat{e}}^{a}_{\alpha\beta}-\frac{\varepsilon s^{a}}{T^{a}}\mathbf{T}^{a}:\mathbf{D}^{a}-\varepsilon s^{a}\mathbf{q}^{a}\cdot\nabla\frac{1}{T^{a}}\\
&\qquad-\frac{\varepsilon s^{a}\rho^{a}}{T^{a}}\left[\frac{\partial A^{a}}{\partial s^{a}}\left(\dot{s}^{a}+\mathbf{v}^{a,s}\cdot\nabla s^{a}\right)+\frac{\partial A^{a}}{\partial T^{a}}\frac{DT^{a}}{Dt}+\eta^{a}\frac{D\,T^{a}}{Dt}\right]\\
&\qquad-\frac{\varepsilon s^{n}\rho^{n}}{T^{n}}\frac{\partial A^{n}}{\partial \rho^{n}}\left[-\rho^{n}\nabla\cdot\mathbf{v}^{n}-\frac{\rho^{n}}{\varepsilon s^{n}}\left[\varepsilon\,\dot{s}^{n}+s^{n}\,\dot{\varepsilon}+\mathbf{v}^{n,s}\cdot\nabla\varepsilon s^{n}\right]\right]\\
&\qquad-\frac{\rho^{a}}{T^{a}}\frac{\partial A^{a}}{\partial \rho^{a}}\sum_{\beta\neq\alpha}\dot{\hat{e}}^{n}_{\alpha\beta}-\frac{\varepsilon s^{n}}{T^{n}}\mathbf{T}^{n}:\mathbf{D}^{n}-\varepsilon s^{n}\mathbf{q}^{n}\cdot\nabla\frac{1}{T^{n}}\\
&\qquad-\frac{\varepsilon s^{n}\rho^{n}}{T^{n}}\left[\frac{\partial A^{n}}{\partial s^{n}}\left(\dot{s}^{n}+\mathbf{v}^{n,s}\cdot\nabla s^{n}\right)+\frac{\partial A^{n}}{\partial T^{n}}\frac{DT^{n}}{Dt}+\eta^{n}\frac{D\,T^{n}}{Dt}\right]\\
&\qquad-\frac{(1-\varepsilon)\rho^{s}}{T^{s}}\frac{\partial A^{s}}{\partial \rho^{s}}\left(-\rho^{s}\nabla\cdot\mathbf{v}^{s}-\frac{\rho^{s}}{\varepsilon^{s}}\dot{\varepsilon}-\frac{1}{\varepsilon^{s}}\sum_{\beta\neq\alpha}\dot{\hat{e}}^{s}_{\alpha\beta}\right)-\frac{(1-\varepsilon)\rho^{s}}{T^{s}}\frac{\partial A^{s}}{\partial s^{a}}\dot{s}^{a}\\
&\qquad-\frac{(1-\varepsilon)\rho^{s}}{T^{s}}\frac{\partial A^{s}}{\partial \mathbf{E}^{s}}\left((\nabla^{s}\mathbf{f}^{s})\cdot\mathbf{D}^{s}\cdot(\nabla^{s}\mathbf{f}^{s})^{T}\right)\\
&\qquad-\frac{(1-\varepsilon)\rho^{s}}{T^{s}}\left(\frac{\partial A^{s}}{\partial T^{s}}\frac{DT^{s}}{Dt}+\eta^{s}\frac{D\,T^{s}}{Dt}\right)-\frac{\varepsilon^{s}}{T^{s}}\mathbf{T}^{s}:\mathbf{D}^{s}-(1-\varepsilon)\mathbf{q}^{s}\cdot\nabla\frac{1}{T^{s}}\\
&\qquad-\sum_{\alpha\beta}\frac{a^{\alpha\beta}\rho^{\alpha\beta}}{T^{\alpha\beta}}\frac{\partial A^{\alpha\beta}}{\partial a^{\alpha\beta}}\left(\dot{a}^{\alpha\beta}+\mathbf{v}^{\alpha\beta}\cdot\nabla a^{\alpha\beta}\right)\\
&\qquad-\sum_{\alpha\beta}\frac{a^{\alpha\beta}\rho^{\alpha\beta}}{T^{\alpha\beta}}\frac{\partial A^{\alpha\beta}}{\partial \rho^{\alpha\beta}}\left[-\rho^{\alpha\beta}\nabla\cdot\mathbf{v}^{\alpha\beta}-\frac{\rho^{\alpha\beta}}{a^{\alpha\beta}}\left(\dot{a}^{\alpha\beta}+\mathbf{v}^{\alpha\beta}\cdot\nabla a^{\alpha\beta}\right)\right]\\
&\qquad-\sum_{\alpha\beta}\frac{a^{\alpha\beta}\rho^{\alpha\beta}}{T^{\alpha\beta}}\left[\frac{\partial A^{\alpha\beta}}{\partial \rho^{\alpha\beta}}\left(\frac{1}{a^{\alpha\beta}}\dot{\hat{e}}^{\alpha}_{\alpha\beta}+\frac{1}{a^{\alpha\beta}}\dot{\hat{e}}^{\beta}_{\alpha\beta}\right)+\frac{\partial A^{\alpha\beta}}{\partial s^{a}}\left(\dot{s}^{a}+\mathbf{v}^{\alpha\beta,s}\cdot\nabla s^{a}\right)\right]\\
&\qquad-\sum_{\alpha\beta}\frac{a^{\alpha\beta}\rho^{\alpha\beta}}{T^{\alpha\beta}}\left(\frac{\partial A^{\alpha\beta}}{\partial T^{\alpha\beta}}\frac{D^{\alpha\beta}T^{\alpha\beta}}{Dt}+\eta^{\alpha\beta}\frac{D\,T^{\alpha\beta}}{Dt}\right)
\end{aligned}
$$

$$
\begin{aligned}
&+\sum_{\alpha\beta} a^{\alpha\beta}\mathbf{q}^{\alpha\beta}\cdot\nabla\frac{1}{T^{\alpha\beta}}-\sum_{\alpha\beta}\frac{a^{\alpha\beta}}{T^{\alpha\beta}}\mathbf{T}^{\alpha\beta}:\mathbf{D}^{\alpha\beta}\\
&+\sum_{\alpha}\sum_{\beta\neq\alpha}\frac{1}{T^{\alpha\beta}}\left[\frac{\hat{q}^{\alpha}_{\alpha\beta}T^{\alpha,\alpha\beta}}{T^{\alpha}}+\hat{e}^{\alpha}_{\alpha\beta}\left(A^{\alpha,\alpha\beta}+T^{\alpha,\alpha\beta}\eta^{\alpha}\right)+\hat{\mathbf{t}}^{\alpha}_{\alpha\beta}\cdot\mathbf{v}^{\alpha,\alpha\beta}\right]\\
&+\sum_{\alpha\beta}\sum_{\gamma\neq\alpha,\beta}\left[\frac{-1}{T^{\alpha\beta}}\left(\hat{\mathbf{t}}^{\alpha\beta}_{\alpha\beta\gamma}\cdot\mathbf{v}^{\alpha\beta,s}+\hat{q}^{\alpha\beta}_{\alpha\beta\gamma}\right)+\hat{e}^{\alpha\beta}_{wns}\left(A^{\alpha,\alpha\beta}+T^{\alpha,\alpha\beta}\eta^{\alpha}\right)\right]\ \geq 0 \qquad (5.69)
\end{aligned}
$$

Combining like terms and simplification yields:

$$
\begin{aligned}
&\sum_{\alpha}\varepsilon\, s^{\alpha}\,\rho^{\alpha}\Lambda^{\alpha}+\sum_{\alpha\beta}a^{\alpha\beta}\rho^{\alpha\beta}\Lambda^{\alpha\beta}=\\
&\frac{(\rho^{w})^{2w}}{T}\frac{\partial A^{w}}{\partial\rho^{w}}\left(s^{w}\dot{\varepsilon}+\varepsilon\dot{s^{w}}+\mathbf{v}^{w,s}\cdot\nabla\varepsilon s^{w}+\varepsilon s^{w}\nabla\cdot\mathbf{v}^{w}-\frac{1}{\rho^{w}}\hat{e}^{w}_{\alpha\beta}\right)\\
&-\frac{\varepsilon s^{w}\rho^{w}}{T^{w}}\left[\frac{\partial A^{w}}{\partial s^{w}}\left(\dot{s^{w}}+\mathbf{v}^{w,s}\cdot\nabla s^{w}\right)+\frac{DT^{w}}{Dt}\left(\frac{\partial A^{w}}{\partial T^{w}}+\eta^{w}\right)\right]\\
&-\frac{\varepsilon s^{w}}{T^{w}}\mathbf{T}^{w}:\mathbf{D}^{w}-\varepsilon s^{w}\mathbf{q}^{w}\cdot\nabla\frac{1}{T^{w}}\\
&+\frac{(\rho^{n})^{2}}{T^{n}}\frac{\partial A^{n}}{\partial\rho^{n}}\left(s^{n}\dot{\varepsilon}+\varepsilon\dot{s^{n}}+\mathbf{v}^{n,s}\cdot\nabla\varepsilon s^{n}+\varepsilon s^{n}\nabla\cdot\mathbf{v}^{n}-\frac{1}{\rho^{n}}\hat{e}^{n}_{\alpha\beta}\right)\\
&-\frac{\varepsilon s^{n}\rho^{n}}{T^{n}}\left[\frac{\partial A^{n}}{\partial s^{n}}\left(\dot{s^{n}}+\mathbf{v}^{n,s}\cdot\nabla s^{n}\right)+\frac{DT^{n}}{Dt}\left(\frac{\partial A^{n}}{\partial T^{n}}+\eta^{n}\right)\right]\\
&-\frac{\varepsilon s^{n}}{T^{n}}\mathbf{T}^{n}:\mathbf{D}^{n}-\varepsilon s^{n}\mathbf{q}^{n}\cdot\nabla\frac{1}{T^{n}}\\
&+\frac{(\rho^{s})^{2}}{T^{s}}\frac{\partial A^{s}}{\partial\rho^{s}}\left(\dot{\varepsilon}+(1-\varepsilon)\nabla\cdot\mathbf{v}^{s}+\frac{1}{\rho^{s}}\sum_{\beta\neq\alpha}\hat{e}^{s}_{\alpha\beta}\right)-\frac{(1-\varepsilon)\rho^{s}}{T^{s}}\frac{\partial A^{s}}{\partial s^{w}}\dot{s^{w}}\\
&-\frac{(1-\varepsilon)\rho^{s}}{T^{s}}\frac{\partial A^{s}}{\partial\mathbf{E}^{s}}\left[(\nabla^{s}\mathbf{f}^{s})\cdot\mathbf{D}^{s}\cdot(\nabla^{s}\mathbf{f}^{s})^{T}\right]\\
&-\frac{(1-\varepsilon)\rho^{s}}{T^{s}}\left[\frac{DT^{s}}{Dt}\left(\frac{\partial A^{s}}{\partial T^{s}}+\eta^{s}\right)\right]-\frac{\varepsilon^{s}}{T^{s}}\mathbf{T}^{s}:\mathbf{D}^{s}-(1-\varepsilon)\mathbf{q}^{s}\cdot\nabla\frac{1}{T^{s}}\\
&-\sum_{\alpha\beta}\frac{a^{\alpha\beta}\rho^{\alpha\beta}}{T^{\alpha\beta}}\left[\frac{D\,T^{\alpha\beta}}{Dt}\left(\frac{\partial A^{\alpha\beta}}{\partial T^{\alpha\beta}}+\eta^{\alpha\beta}\right)\right]-\sum_{\alpha\beta}\frac{a^{\alpha\beta}\rho^{\alpha\beta}}{T^{\alpha\beta}}\frac{\partial A^{\alpha\beta}}{\partial a^{\alpha\beta}}\left(\dot{a^{\alpha\beta}}+\mathbf{v}^{\alpha\beta}\cdot\nabla a^{\alpha\beta}\right)\\
&-\sum_{\alpha\beta}\frac{(\rho^{\alpha\beta})^{2}}{T^{\alpha\beta}}\frac{\partial A^{\alpha\beta}}{\partial\rho^{\alpha\beta}}\left[-a^{\alpha\beta}\nabla\cdot\mathbf{v}^{\alpha\beta}-\dot{a^{\alpha\beta}}-\mathbf{v}^{\alpha\beta}\cdot\nabla a^{\alpha\beta}+\frac{1}{\rho^{\alpha\beta}}\left(\hat{e}^{\alpha}_{\alpha\beta}+\hat{e}^{\beta}_{\alpha\beta}\right)\right]\\
&-\sum_{\alpha\beta}\left[\frac{a^{\alpha\beta}\rho^{\alpha\beta}}{T^{\alpha\beta}}\frac{\partial A^{\alpha\beta}}{\partial s^{w}}\left(\dot{s^{w}}+\mathbf{v}^{\alpha\beta,s}\cdot\nabla s^{w}\right)\right]-a^{\alpha\beta}\mathbf{q}^{\alpha\beta}\cdot\nabla\frac{1}{T^{\alpha\beta}}+\frac{a^{\alpha\beta}}{T^{\alpha\beta}}\mathbf{T}^{\alpha\beta}:\mathbf{D}^{\alpha\beta}\\
&+\sum_{\alpha}\sum_{\beta\neq\alpha}\frac{1}{T^{\alpha\beta}}\left[\frac{\hat{q}^{\alpha}_{\alpha\beta}T^{\alpha,\alpha\beta}}{T^{\alpha}}+\hat{e}^{\alpha}_{\alpha\beta}\left(A^{\alpha,\alpha\beta}+T^{\alpha,\alpha\beta}\eta^{\alpha}\right)+\hat{\mathbf{t}}^{\alpha}_{\alpha\beta}\cdot\mathbf{v}^{\alpha,\alpha\beta}\right]
\end{aligned}
$$

$$+\sum_{\alpha\beta}\sum_{\gamma\neq\alpha,\beta}\left[\frac{-1}{T^{\alpha\beta}}\left(\hat{\mathbf{t}}_{\alpha\beta\gamma}^{\alpha\beta}\cdot\mathbf{v}^{\alpha\beta,s}+\hat{q}_{\alpha\beta\gamma}^{\alpha\beta}\right)+\hat{e}_{ans}^{\alpha\beta}\left(A^{\alpha,\alpha\beta}+T^{\alpha,\alpha\beta}\eta^{\alpha}\right)\right]\ \geq 0 \tag{5.70}$$

Eq. (5.70) can be further simplified. Let us consider the first law of thermodynamics. The conservation of energy follows from the first law of thermodynamics stating that the accumulation of energy (the sum of internal and kinetic) in a volume is equal to the rate of surface work done by the volume plus the rate that heat, magnetic, electrical, and chemical energies are transferred out of the volume plus the rate at which work is done on the body by body forces such as gravity [*Whitaker*, 1981; *Chung*, 1996]. The energy balance for a system can be written as [*Sonntag and Van Wylen*, 1982, p. 89]:

$$dE = \delta q - \delta w \tag{5.71}$$

where q is heat transferred to the system, E is the internal energy in the system, and w is work. Now, let us define work as any form of energy that applies a force acting through a displacement. This can be described as [*Greiner et al.*, 1994, p. 15]:

$$\delta w = p^{\alpha}dV - p^{\alpha\beta}dA - \phi\, d\breve{q} - \mu^{\alpha}dN^{\alpha} + ... \tag{5.72}$$

where p^{α} is pressure, V is volume, $p^{\alpha\beta}$ is the surface tension, A is the area, ϕ is electric potential, $\breve{q}$ is the charge, μ^{α} is the chemical potential, N^{α} is the particle number. Additional forms of work can take the form of magnetic work, electrical work, tensile work, etc. The minus sign is necessary for some terms of Eq. (5.72). For example, work is done by the system when δA is negative (surface area is reduced); therefore the term has a negative sign. Furthermore, let us now define the heat transferred to a system equivalently as [*Sonntag and Van Wylen*, 1982, p. 211]:

$$\delta q = T\eta \tag{5.73}$$

Incorporation of Eq. (5.73) and Eq. (5.72) into Eq. (5.71), ignoring electrical work and the additional undefined terms of work as negligible in the porous media system of concern, yields the energy of the system as:

$$E^{\alpha} = T^{\alpha}\eta^{\alpha} - p^{\alpha}V + p^{\alpha\beta}A + \mu^{\alpha}N^{\alpha} \tag{5.74}$$

Rearrangement of terms produces:

$$E^\alpha - T^\alpha \eta^\alpha = -p^\alpha V + p^{\alpha\beta} A + \mu^\alpha N^\alpha \tag{5.75}$$

Considering only the α-phase and ignoring the interfacial work, Eq. (5.75) can be written in terms of the Helmholtz free energy that has been listed as a secondary variable for our porous media system. Eq. (5.75) takes the form:

$$A^\alpha = E^\alpha - T^\alpha \eta^\alpha = -p^\alpha V + \mu^\alpha N^\alpha \tag{5.76}$$

Let us normalize by mass, M, where $\rho^\alpha = M/V$ such that:

$$\frac{A^\alpha}{M} = \frac{E^\alpha}{M} - \frac{T^\alpha \eta^\alpha}{M} = -\frac{p^\alpha}{\rho^\alpha} + \frac{\mu^\alpha N^\alpha}{M} \tag{5.77}$$

If we state the total differential of energy for the α-phase from Eq. (5.74), normalized by mass we obtain:

$$\frac{dE^\alpha}{M} = \frac{T^\alpha d\eta^\alpha}{M} - \frac{p^\alpha}{d\rho^\alpha} + \frac{\mu^\alpha dN^\alpha}{M} \tag{5.78}$$

Correspondingly, the total differential of Eq. (5.77) is:

$$\frac{dA^\alpha}{M} = \frac{dE^\alpha}{M} - \frac{\eta^\alpha dT^\alpha}{M} - \frac{T^\alpha d\eta^\alpha}{M} \tag{5.79}$$

Using the Legendre transformation and substituting Eq. (5.78) into Eq. (5.79) yields the Helmholtz free energy for a phase as [*Greiner et al.*, 1994, p. 91]:

$$\frac{dA^\alpha}{M} = -\frac{\eta^\alpha dT^\alpha}{M} - \frac{p^\alpha}{d\rho^\alpha} + \frac{\mu^\alpha dN^\alpha}{M^\alpha} \tag{5.80}$$

Therefore, we can express the partial derivative of A^α with respect to ρ^α, ignoring compositional effects and assuming that T^α is independent of ρ^α, as:

$$\frac{\partial A^\alpha}{\partial \rho^\alpha} = \frac{p^\alpha}{(\rho^\alpha)^2} \tag{5.81}$$

Allowing the pressure of a phase, p^α, to be stated as [*Hassanizadeh and Gray*, 1990]:

$$p^\alpha = (\rho^\alpha)^2 \frac{\partial A^\alpha}{\partial \rho^\alpha} \tag{5.82}$$

Additionally, the Gibbs potential, G^{α}, for the α-phase can be defined in terms of Helmholtz free energy as [*Sonntag and Van Wylen*, 1982, p. 211]:

$$G^{\alpha} = A^{\alpha} + \frac{p^{\alpha}}{\rho^{\alpha}} \tag{5.83}$$

Similarly, considering now the interface, we will express the surface tension, $p^{\alpha\beta}$, through a Legendre transformation of the Helmholtz free energy. The energy of the interface, assuming surface tension and chemical potential as the only driving forces for work, can be described as:

$$E^{\alpha\beta} = T^{\alpha\beta}\eta^{\alpha\beta} + p^{\alpha\beta}A + \mu^{\alpha\beta}N^{\alpha\beta} \tag{5.84}$$

where $\mu^{\alpha\beta}$ is the surface chemical potential and $N^{\alpha\beta}$ is the surface particle number. Rearrangement of terms produces:

$$E^{\alpha\beta} - T^{\alpha\beta}\eta^{\alpha\beta} = p^{\alpha\beta}A + \mu^{\alpha\beta}N^{\alpha\beta} \tag{5.85}$$

Eq. (5.85) can be written in terms of the interfacial Helmholtz free as:

$$A^{\alpha\beta} = E^{\alpha\beta} - T^{\alpha\beta}\eta^{\alpha\beta} = p^{\alpha\beta}A + \mu^{\alpha\beta}N^{\alpha\beta} \tag{5.86}$$

Let us normalize by the mass of the interface, $M^{\alpha\beta}$, where $\rho^{\alpha\beta} = M^{\alpha\beta}/A$ such that:

$$\frac{A^{\alpha\beta}}{M^{\alpha\beta}} = \frac{E^{\alpha\beta}}{M^{\alpha\beta}} - \frac{T^{\alpha\beta}\eta^{\alpha\beta}}{M^{\alpha\beta}} = \frac{p^{\alpha\beta}}{\rho^{\alpha\beta}} + \frac{\mu^{\alpha\beta}N^{\alpha\beta}}{M^{\alpha\beta}} \tag{5.87}$$

If we state the total differential of energy for the $\alpha\beta$-interface from Eq. (5.84), normalized by mass we obtain:

$$\frac{dE^{\alpha\beta}}{M^{\alpha\beta}} = \frac{T^{\alpha\beta}d\eta^{\alpha\beta}}{M^{\alpha\beta}} + \frac{p^{\alpha\beta}}{d\rho^{\alpha\beta}} + \frac{\mu^{\alpha\beta}dN^{\alpha\beta}}{M^{\alpha\beta}} \tag{5.88}$$

Correspondingly, the total differential of Eq. (5.87) is:

$$\frac{dA^{\alpha\beta}}{M^{\alpha\beta}} = \frac{dE^{\alpha\beta}}{M^{\alpha\beta}} - \frac{\eta^{\alpha\beta}dT^{\alpha\beta}}{M^{\alpha\beta}} - \frac{T^{\alpha\beta}d\eta^{\alpha\beta}}{M^{\alpha\beta}} \tag{5.89}$$

Using the Legendre transformation and substituting Eq. (5.88) into Eq. (5.89) yields the Helmholtz free energy for an interface as:

$$\frac{dA^{\alpha\beta}}{M^{\alpha\beta}} = -\frac{\eta^{\alpha\beta}dT^{\alpha\beta}}{M^{\alpha\beta}} + \frac{p^{\alpha\beta}}{d\rho^{\alpha\beta}} + \frac{\mu^{\alpha\beta}dN^{\alpha\beta}}{M^{\alpha\beta}} \tag{5.90}$$

Therefore, the partial derivative of $A^{\alpha\beta}$ with respect to $\rho^{\alpha\beta}$, ignoring compositional effects and assuming that $T^{\alpha\beta}$ is independent of $\rho^{\alpha\beta}$, is stated as:

$$\frac{\partial A^{\alpha\beta}}{\partial \rho^{\alpha\beta}} = -\frac{p^{\alpha\beta}}{(\rho^{\alpha\beta})^2} \tag{5.91}$$

Allowing the pressure of an interface $p^{\alpha\beta}$ to be stated as [*Hassanizadeh and Gray*, 1990]:

$$p^{\alpha\beta} = -(\rho^{\alpha\beta})^2 \frac{\partial A^{\alpha\beta}}{\partial \rho^{\alpha\beta}} \tag{5.92}$$

Alternatively, the partial derivative of $A^{\alpha\beta}$ in Eq. (5.90) with respect to $a^{\alpha\beta}$ allows [*Hassanizadeh and Gray*, 1990]:

$$\frac{\partial A^{\alpha\beta}}{\partial a^{\alpha\beta}} = -\frac{p^{\alpha\beta}}{a^{\alpha\beta}\rho^{\alpha\beta}} \tag{5.93}$$

Which when rearranged yields an alternative expression of surface tension as:

$$p^{\alpha\beta} = -a^{\alpha\beta}\rho^{\alpha\beta} \frac{\partial A^{\alpha\beta}}{\partial a^{\alpha\beta}} \tag{5.94}$$

Additionally, the Gibbs free potential for the $\alpha\beta$-interface, ignoring chemical surface potential, is defined in terms of Helmholtz free energy as [*Slattery*, 1990, p. 764]:

$$G^{\alpha\beta} = A^{\alpha\beta} - \frac{p^{\alpha\beta}}{\rho^{\alpha\beta}} \tag{5.95}$$

The Legendre transformation was used to make a change of variables such that Eqs. (5.82), (5.83), (5.92), (5.94), and (5.95) are expressed in quantities that can be more readily measured. Rewriting Eq. (5.70) in terms of these quantities yields:

$$\begin{aligned}
\sum_{\alpha} \varepsilon\, s^{a}\, \rho^{a} \Lambda^{a} + \sum_{\alpha\beta} a^{\alpha\beta}\rho^{\alpha\beta}\Lambda^{\alpha\beta} = \\
-\frac{\varepsilon s^{a}\rho^{a}}{T^{a}}\left[\frac{DT^{a}}{Dt}\left(\frac{\partial A^{a}}{\partial T^{a}} + \eta^{a}\right) + \frac{\partial A^{a}}{\partial s^{a}}\left(\dot{s^{a}} + \mathbf{v}^{a,s}\cdot\nabla s^{a}\right)\right] \\
+\frac{p^{a}}{T^{a}}\left(s^{a}\dot{\varepsilon} + \varepsilon\dot{s^{a}} + \mathbf{v}^{a,s}\cdot\nabla\varepsilon s^{a} + \varepsilon s^{a}\nabla\cdot\mathbf{v}^{a}\right) - \frac{\varepsilon s^{a}}{T^{a}}\mathbf{T}^{a} : \mathbf{D}^{a} - \varepsilon s^{a}\mathbf{q}^{a}\cdot\nabla\frac{1}{T^{a}} \\
-\frac{\varepsilon s^{n}\rho^{n}}{T^{n}}\left[\frac{DT^{n}}{Dt}\left(\frac{\partial A^{n}}{\partial T^{n}} + \eta^{n}\right) + \frac{\partial A^{n}}{\partial s^{n}}\left(\dot{s^{n}} + \mathbf{v}^{n,s}\cdot\nabla s^{n}\right)\right] \\
+\frac{p^{n}}{T^{n}}\left(s^{n}\dot{\varepsilon} + \varepsilon\dot{s^{n}} + \mathbf{v}^{n,s}\cdot\nabla\varepsilon s^{n} + \varepsilon s^{n}\nabla\cdot\mathbf{v}^{n}\right) - \frac{\varepsilon s^{n}}{T^{n}}\mathbf{T}^{n} : \mathbf{D}^{n} - \varepsilon s^{n}\mathbf{q}^{n}\cdot\nabla\frac{1}{T^{n}}
\end{aligned}$$

$$
\begin{aligned}
&+\frac{p^s}{T^s}\left[\dot{\varepsilon}+(1-\varepsilon)\nabla\cdot\mathbf{v}^s\right]-\frac{(1-\varepsilon)\rho^s}{T^s}\frac{\partial A^s}{\partial s^a}\dot{s^a}\\
&-\frac{(1-\varepsilon)\rho^s}{T^s}\frac{\partial A^s}{\partial \mathbf{E}^s}\left[(\nabla^* \mathbf{f}^s)\cdot\mathbf{D}^s\cdot(\nabla^* \mathbf{f}^s)^T\right]\\
&-\frac{(1-\varepsilon)\rho^s}{T^s}\left[\frac{DT^s}{Dt}\left(\frac{\partial A^s}{\partial T^s}+\eta^s\right)\right]-\frac{\varepsilon^s}{T^s}\mathbf{T}^s:\mathbf{D}^s-(1-\varepsilon)\mathbf{q}^s\cdot\nabla\frac{1}{T^s}\\
&-\sum_{\alpha\beta}\frac{a^{\alpha\beta}\rho^{\alpha\beta}}{T^{\alpha\beta}}\left[\frac{DT^{\alpha\beta}}{Dt}\left(\frac{\partial A^{\alpha\beta}}{\partial T^{\alpha\beta}}+\eta^{\alpha\beta}\right)\right]-\sum_{\alpha\beta}\frac{p^{\alpha\beta}}{T^{\alpha\beta}}\left(-a^{\alpha\beta}\nabla\cdot\mathbf{v}^{\alpha\beta}\right)\\
&-\sum_{\alpha\beta}\left[\frac{a^{\alpha\beta}\rho^{\alpha\beta}}{T^{\alpha\beta}}\frac{\partial A^{\alpha\beta}}{\partial s^a}\left(\dot{s^a}+\mathbf{v}^{\alpha\beta,s}\cdot\nabla s^a\right)\right]-a^{\alpha\beta}\mathbf{q}^{\alpha\beta}\cdot\nabla\frac{1}{T^{\alpha\beta}}+\frac{a^{\alpha\beta}}{T^{\alpha\beta}}\mathbf{T}^{\alpha\beta}:\mathbf{D}^{\alpha\beta}\\
&+\sum_{\alpha}\sum_{\beta\neq\alpha}\frac{1}{T^{\alpha\beta}}\left(\frac{\hat{q}^{\alpha}_{\alpha\beta}T^{\alpha,\alpha\beta}}{T^{\alpha}}+\hat{\mathbf{t}}^{\alpha}_{\alpha\beta}\cdot\mathbf{v}^{\alpha,\alpha\beta}\right)+\sum_{\alpha\beta}\sum_{\gamma\neq\alpha,\beta}\frac{1}{T^{\alpha\beta}}\left(\frac{\hat{q}^{\alpha\beta}_{\alpha\beta\gamma}T^{\alpha\beta,\alpha}}{T^{\alpha}}+\hat{\mathbf{t}}^{\alpha\beta}_{\alpha\beta\gamma}\cdot\mathbf{v}^{\alpha\beta}\right)\\
&-\sum_{\alpha\beta}\frac{\hat{e}^{\alpha\beta}_{\alpha\beta\gamma}}{T^s}\left(G^{\alpha\beta,s}+\eta^{\alpha\beta}T^{\alpha\beta,s}-\frac{p^{\alpha\beta}T^{\alpha\beta,s}}{\rho^{\alpha\beta}T^{\alpha\beta}}\right)\\
&+\sum_{\alpha}\sum_{\beta\neq\alpha}\frac{\hat{e}^{\alpha}_{\alpha\beta}}{T^{\alpha\beta}}\left(G^{\alpha\beta,\alpha}+\eta^{\alpha\beta}T^{\alpha\beta,\alpha}-\frac{p^{\alpha}T^{\alpha\beta,\alpha}}{\rho^{\alpha}T^{\alpha}}\right)\ \geq 0 \qquad (5.96)
\end{aligned}
$$

We will now simplify Eq. (5.96) through physical constraints. Note that some quantities will be braced with the subscript *ne* for future reference. First, in a two-phase, if we assume that the solid phase is non-deforming such that porosity is constant, then $\dot{s^n}=-\dot{s^a}$ from the fact that $s^a+s^n=1$ so that an increase in s^n requires an equivalent decrease in s^a. Second, noting that pressure will act equally in all directions, the pressure term can be multiplied by the identity tensor, $\mathbf{I}$, and applied as described below to further simplify the displacement terms in Eq. (5.96):

$$
\frac{\varepsilon\, s^{\alpha}}{T^{\alpha}}\mathbf{T}^{\alpha}:\mathbf{D}^{\alpha}+p^{\alpha}\frac{\varepsilon\, s^{\alpha}}{T^{\alpha}}\nabla\cdot\mathbf{v}^{\alpha}=\frac{\mathbf{D}^{\alpha}}{T^{\alpha}}:\left[\varepsilon\, s^{\alpha}\left(p^{\alpha}\mathbf{I}+\mathbf{T}^{\alpha}\right)\right]_{ne} \qquad (5.97)
$$

and

$$
\frac{a^{\alpha\beta}}{T^{\alpha\beta}}\mathbf{T}^{\alpha\beta}:\mathbf{D}^{\alpha\beta}+p^{\alpha\beta}\frac{a^{\alpha\beta}}{T^{\alpha\beta}}\nabla\cdot\mathbf{v}^{\alpha\beta}=\frac{\mathbf{D}^{\alpha\beta}}{T^{\alpha\beta}}:\left[a^{\alpha\beta}\left(p^{\alpha\beta}\mathbf{I}+\mathbf{T}^{\alpha\beta}\right)\right]_{ne} \qquad (5.98)
$$

Additionally, through rearrangement we note:

$$
\begin{aligned}
&\frac{(1-\varepsilon)\rho^s}{T^s}\frac{\partial A^s}{\partial \mathbf{E}^s}\left[(\nabla^* \mathbf{f}^s)\cdot\mathbf{D}^s\cdot(\nabla^* \mathbf{f}^s)^T\right]\\
&\qquad=\frac{(1-\varepsilon)}{T^s}\mathbf{D}^s:\left[-\rho^s(\nabla^* \mathbf{f}^s)^T\cdot\frac{\partial A^s}{\partial \mathbf{E}^s}\cdot(\nabla^* \mathbf{f}^s)\right]_{ne} \qquad (5.99)
\end{aligned}
$$

Yielding the reduced form of the total entropy inequality for non-equilibrium and equilibrium conditions as [*Hassanizadeh and Gray*, 1990, p. 184]:

$$
\begin{aligned}
&\sum_{\alpha} \varepsilon\, s^{\alpha}\, \rho^{\alpha} \Lambda^{\alpha} + \sum_{\alpha\beta} a^{\alpha\beta} \rho^{\alpha\beta} \Lambda^{\alpha\beta} = \\
&\qquad -\frac{\varepsilon s^{a} \rho^{a}}{T^{a}} \left[\frac{DT^{a}}{Dt} \left(\frac{\partial A^{a}}{\partial T^{a}} + \eta^{a} \right)_{nc} \right] - \frac{\varepsilon s^{a} \rho^{a}}{T^{a}} \frac{\partial A^{a}}{\partial s^{a}} \left(\dot{s^{a}} + \mathbf{v}^{a,s} \cdot \nabla s^{a} \right) \\
&\qquad + \frac{p^{a}}{T^{a}} \left(s^{a} \dot{\varepsilon} + \varepsilon \dot{s^{a}} + \mathbf{v}^{a,s} \cdot \nabla \varepsilon s^{a} \right) - \frac{\mathbf{D}^{a}}{T^{a}} : \left[\varepsilon s^{a} \left(p^{a} \mathbf{I} + \mathbf{T}^{a} \right) \right]_{nc} - \varepsilon s^{a} \mathbf{q}^{a} \cdot \nabla \frac{1}{T^{a}} \\
&\qquad -\frac{\varepsilon s^{n} \rho^{n}}{T^{n}} \left[\frac{DT^{n}}{Dt} \left(\frac{\partial A^{n}}{\partial T^{n}} + \eta^{n} \right)_{nc} \right] - \frac{\varepsilon s^{n} \rho^{n}}{T^{n}} \frac{\partial A^{n}}{\partial s^{n}} \left(-\dot{s^{a}} + \mathbf{v}^{n,s} \cdot \nabla s^{n} \right) \\
&\qquad + \frac{p^{n}}{T^{n}} \left(s^{n} \dot{\varepsilon} - \varepsilon \dot{s^{a}} + \mathbf{v}^{n,s} \cdot \nabla \varepsilon s^{n} \right) - \frac{\mathbf{D}^{n}}{T^{n}} : \left[\varepsilon s^{n} \left(p^{n} \mathbf{I} + \mathbf{T}^{n} \right) \right]_{nc} - \varepsilon s^{n} \mathbf{q}^{n} \cdot \nabla \frac{1}{T^{n}} \\
&\qquad + \frac{p^{s}}{T^{s}} \dot{\varepsilon} + \frac{(1-\varepsilon)\rho^{s}}{T^{s}} \frac{\partial A^{s}}{\partial s^{a}} \dot{s^{a}} \\
&\qquad - \frac{(1-\varepsilon)}{T^{s}} \mathbf{D}^{s} : \left[-\rho^{s} (\nabla^{s} \mathbf{f}^{s})^{T} \cdot \frac{\partial A^{s}}{\partial \mathbf{E}^{s}} \cdot (\nabla^{s} \mathbf{f}^{s}) + p^{s} \mathbf{I} + \mathbf{T}^{s} \right]_{nc} \\
&\qquad - \frac{(1-\varepsilon)\rho^{s}}{T^{s}} \left[\frac{DT^{s}}{Dt} \left(\frac{\partial A^{s}}{\partial T^{s}} + \eta^{s} \right)_{nc} \right] - (1-\varepsilon) \mathbf{q}^{s} \cdot \nabla \frac{1}{T^{s}} \\
&\qquad - \sum_{\alpha\beta} \frac{a^{\alpha\beta} \rho^{\alpha\beta}}{T^{\alpha\beta}} \left[\frac{D\,T^{\alpha\beta}}{Dt} \left(\frac{\partial A^{\alpha\beta}}{\partial T^{\alpha\beta}} + \eta^{\alpha\beta} \right)_{nc} \right] + \frac{\mathbf{D}^{\alpha\beta}}{T^{\alpha\beta}} : \left[a^{\alpha\beta} \left(-p^{\alpha\beta} \mathbf{I} + \mathbf{T}^{\alpha\beta} \right) \right]_{nc} \\
&\qquad - \sum_{\alpha\beta} \frac{a^{\alpha\beta} \rho^{\alpha\beta}}{T^{\alpha\beta}} \left[\frac{\partial A^{\alpha\beta}}{\partial s^{a}} \left(\dot{s^{a}} + \mathbf{v}^{\alpha\beta,s} \cdot \nabla s^{a} \right) \right] - a^{\alpha\beta} \mathbf{q}^{\alpha\beta} \cdot \nabla \frac{1}{T^{\alpha\beta}} \\
&\qquad + \sum_{\alpha} \sum_{\beta \neq \alpha} \frac{1}{T^{\alpha\beta}} \left(\frac{\hat{q}^{\alpha}_{\alpha\beta} T^{\alpha,\alpha\beta}}{T^{\alpha}} + \hat{\mathbf{t}}^{\alpha}_{\alpha\beta} \cdot \mathbf{v}^{\alpha,\alpha\beta} \right) + \sum_{\alpha\beta} \sum_{\gamma \neq \alpha,\beta} \frac{1}{T^{\alpha\beta}} \left(\frac{\hat{q}^{\alpha\beta}_{\alpha\beta\gamma} T^{\alpha\beta,\alpha}}{T^{\alpha}} + \hat{\mathbf{t}}^{\alpha\beta}_{\alpha\beta\gamma} \cdot \mathbf{v}^{\alpha\beta} \right) \\
&\qquad - \sum_{\alpha\beta} \frac{\hat{e}^{\alpha\beta}_{\alpha\beta\gamma}}{T^{s}} \left(G^{\alpha\beta,s} + \eta^{\alpha\beta} T^{\alpha\beta,s} - \frac{p^{\alpha\beta} T^{\alpha\beta,s}}{\rho^{\alpha\beta} T^{\alpha\beta}} \right) \\
&\qquad + \sum_{\alpha} \sum_{\beta \neq \alpha} \frac{\hat{e}^{\alpha}_{\alpha\beta}}{T^{\alpha\beta}} \left(G^{\alpha\beta,\alpha} + \eta^{\alpha\beta} T^{\alpha\beta,\alpha} - \frac{p^{\alpha} T^{\alpha\beta,\alpha}}{\rho^{\alpha} T^{\alpha}} \right) \ \geq 0 \qquad (5.100)
\end{aligned}
$$

Note that the terms multiplied by the variables $D^{\alpha}T^{\alpha}/Dt$, $D^{\alpha\beta}T^{\alpha\beta}/Dt$, $\mathbf{D}^{\alpha}$, and $\mathbf{D}^{\alpha\beta}$ are bracketed for reference in the following section.

From the entropy inequality expressed in Eq. (5.100), we can derive three sets of constraints for constitutive relationships [*Bennethum*, 1994]. The first set of results will hold during equilibrium and non-equilibrium conditions. The second set of results will hold only at equilibrium. The third set of results will hold near equilibrium for situations in which variables are linearized about the equation. The definition of near equilibrium conditions is subject to interpretation [*Achanta et al.*, 1994].

5.4.2 Non-equilibrium Simplifications of Constitutive Relationships

Now, the quintessential point of the *Coleman and Noll* [1963] method can be seen in the following. Eq. (5.100) requires that the production of entropy be non-negative. In formulating Eq. (5.100), we hypothesized that each secondary variable could be a function of each of the independent variables listed in Tables 5.2 and Tables 5.4. However, upon expansion of the entropy inequality, the variables $D^{\alpha}T^{\alpha}/Dt$, $D^{\alpha\beta}T^{\alpha\beta}/Dt$, $\mathbf{D}^{\alpha}$, and $\mathbf{D}^{\alpha\beta}$ were introduced. The constitutive functions were not assumed to depend upon these variables that appear linearly in Eq. (5.100). Therefore, if the inequality is to remain valid for all thermodynamic states, the terms that are multiplied by these variables (bracketed in Eq. (5.100)) must be zero so that the total entropy may not be allowed to decrease. This produces the following constitutive relationships:

$$\eta^{\alpha} = -\frac{\partial A^{\alpha}}{\partial T^{\alpha}} \qquad \alpha = a, n, s \tag{5.101}$$

$$\eta^{\alpha\beta} = -\frac{\partial A^{\alpha\beta}}{\partial T^{\alpha\beta}} \qquad \alpha\beta = an, as, ns \tag{5.102}$$

$$\mathbf{T}^{\alpha} = -p^{\alpha}\mathbf{I} \qquad \alpha = a, n \tag{5.103}$$

$$\mathbf{T}^{s} + p^{s}\mathbf{I} = \rho^{s}(\nabla^{*}\mathbf{f}^{s})^{T} \cdot \frac{\partial A^{s}}{\partial \mathbf{E}^{s}} \cdot (\nabla^{*}\mathbf{f}^{s}) \tag{5.104}$$

$$\mathbf{T}^{\alpha\beta} = p^{\alpha\beta}\mathbf{I} \qquad \alpha\beta = an, as, ns \tag{5.105}$$

Additionally, by defining the effective stress tensor for the solid phase as $\mathbf{T}^{s}_{e} = \mathbf{T}^{s} + p^{s}\mathbf{I}$ allows:

$$\mathbf{T}^{s}_{e} = \rho^{s}(\nabla^{*}\mathbf{f}^{s})^{T} \cdot \frac{\partial A^{s}}{\partial \mathbf{E}^{s}} \cdot (\nabla^{*}\mathbf{f}^{s}) \tag{5.106}$$

Although obtained by different means, Eq. (5.101) and Eq. (5.102) agree with the classical results from *Eringen* [1980] for a single-phase fluid and *Slattery* [1990] for an interface. Eqs. (5.103) through (5.106) relate the stress tensor for liquids, interfaces, and the solid matrix to the respective pressures.

The incorporation of Eq. (5.101) through Eq. (5.106) into Eq. (5.100) yields:

$$\begin{aligned}
&\sum_{\alpha} \varepsilon\, s^{\alpha}\, \rho^{\alpha} \Lambda^{\alpha} + \sum_{\alpha\beta} a^{\alpha\beta} \rho^{\alpha\beta} \Lambda^{\alpha\beta} = \\
&-\frac{\varepsilon s^{a} \rho^{a}}{T^{a}} \frac{\partial A^{a}}{\partial s^{a}} \left(\dot{s^{a}} + \mathbf{v}^{a,s} \cdot \nabla s^{a} \right) + \frac{p^{a}}{T^{a}} \left(s^{a} \dot{\varepsilon} + \varepsilon \dot{s^{a}} + \mathbf{v}^{a,s} \cdot \nabla \varepsilon s^{a} \right) - \varepsilon s^{a} \mathbf{q}^{a} \cdot \nabla \frac{1}{T^{a}} \\
&-\frac{\varepsilon s^{n} \rho^{n}}{T^{n}} \frac{\partial A^{n}}{\partial s^{n}} \left(-\dot{s^{a}} + \mathbf{v}^{n,s} \cdot \nabla s^{n} \right) + \frac{p^{n}}{T^{n}} \left(s^{n} \dot{\varepsilon} - \varepsilon \dot{s^{a}} + \mathbf{v}^{n,s} \cdot \nabla \varepsilon s^{n} \right) - \varepsilon s^{n} \mathbf{q}^{n} \cdot \nabla \frac{1}{T^{n}} \\
&+\frac{p^{s}}{T^{s}} \dot{\varepsilon} + \frac{(1-\varepsilon)\rho^{s}}{T^{s}} \frac{\partial A^{s}}{\partial s^{a}} \dot{s^{a}} - (1-\varepsilon) \mathbf{q}^{s} \cdot \nabla \frac{1}{T^{s}} \\
&-\sum_{\alpha\beta} \frac{a^{\alpha\beta} \rho^{\alpha\beta}}{T^{\alpha\beta}} \left[\frac{\partial A^{\alpha\beta}}{\partial s^{a}} \left(\dot{s^{a}} + \mathbf{v}^{\alpha\beta,s} \cdot \nabla s^{a} \right) \right] - a^{\alpha\beta} \mathbf{q}^{\alpha\beta} \cdot \nabla \frac{1}{T^{\alpha\beta}} \\
&+\sum_{\alpha} \sum_{\beta \neq \alpha} \frac{1}{T^{\alpha\beta}} \left(\frac{\hat{q}^{\alpha}_{\alpha\beta} T^{\alpha,\alpha\beta}}{T^{\alpha}} + \hat{\mathbf{t}}^{\alpha}_{\alpha\beta} \cdot \mathbf{v}^{\alpha,\alpha\beta} \right) + \sum_{\alpha\beta} \sum_{\gamma \neq \alpha,\beta} \frac{1}{T^{\alpha\beta}} \left(\frac{\hat{q}^{\alpha\beta}_{\alpha\beta\gamma} T^{\alpha\beta,\alpha}}{T^{\alpha}} + \hat{\mathbf{t}}^{\alpha\beta}_{\alpha\beta\gamma} \cdot \mathbf{v}^{\alpha\beta} \right) \\
&-\sum_{\alpha\beta} \frac{\hat{e}^{\alpha\beta}_{\alpha\beta\gamma}}{T^{s}} \left(G^{\alpha\beta,s} + \eta^{\alpha\beta} T^{\alpha\beta,s} - \frac{p^{\alpha\beta} T^{\alpha\beta,s}}{\rho^{\alpha\beta} T^{\alpha\beta}} \right) \\
&+\sum_{\alpha} \sum_{\beta \neq \alpha} \frac{\hat{e}^{\alpha}_{\alpha\beta}}{T^{\alpha\beta}} \left(G^{\alpha\beta,\alpha} + \eta^{\alpha\beta} T^{\alpha\beta,\alpha} - \frac{p^{\alpha} T^{\alpha\beta,\alpha}}{\rho^{\alpha} T^{\alpha}} \right) \geq 0 \qquad (5.107)
\end{aligned}$$

5.4.3 Equilibrium Simplifications of Constitutive Relationships

To further simplify the entropy inequality as stated in Eq. (5.107), the macroscopic capillary pressure, p^c, can be defined as [*Hassanizadeh and Gray*, 1993b, p. 1859] and [*Hassanizadeh and Gray*, 1993a, p. 3400]:

$$p^{c} = -s^{n} \rho^{n} \frac{\partial A^{n}}{\partial s^{n}} - s^{a} \rho^{a} \frac{\partial A^{a}}{\partial s^{a}} - (1-\varepsilon)\rho^{s} \frac{\partial A^{s}}{\partial s^{a}} - \sum_{\alpha\beta} \rho^{\alpha\beta} \frac{\partial A^{\alpha\beta}}{\partial s^{a}} \qquad (5.108)$$

(Note: capillary pressure is incorrectly defined in [*Hassanizadeh and Gray*, 1990, p. 178] with a positive sign preceding the NAPL term). According to Eq. (5.108), the macroscopic capillary pressure is related to the change in the free energy of both phases and interfaces as a result of a change in saturations [*Hassanizadeh and Gray*, 1993a]. Eq. (5.108) includes the effects of interfacial areas and surface densities which have long been believed to affect the capillary pressure. At equilibrium, Eq. (5.108) will reduce to the standard definition of capillary pressure as the difference in pressure between the non-wetting and wetting fluids.

Incorporation of Eq. (5.108) into Eq. (5.107), rearranging the equation so that the capillary pressure relationship is the first term, yields [*Hassanizadeh and Gray*, 1990, p. 178]:

$$
\begin{aligned}
&\sum_{\alpha} \varepsilon s^{\alpha} \rho^{\alpha} \Lambda^{\alpha} + \sum_{\alpha\beta} a^{\alpha\beta} \rho^{\alpha\beta} \Lambda^{\alpha\beta} = \\
&\dot{s}^{a} \left(\frac{\varepsilon p^{c}}{T^{an}} + \frac{\varepsilon p^{a}}{T^{a}} - \frac{\varepsilon p^{n}}{T^{n}} \right) - \frac{\varepsilon s^{a} \rho^{a}}{T^{a}} \frac{\partial A^{a}}{\partial s^{a}} (\mathbf{v}^{a,s} \cdot \nabla s^{a}) + \frac{p^{a}}{T^{a}} (s^{a} \dot{\varepsilon} + \mathbf{v}^{a,s} \cdot \nabla \varepsilon s^{a}) - \varepsilon s^{a} \mathbf{q}^{a} \cdot \nabla \frac{1}{T^{a}} \\
&\qquad - \frac{\varepsilon s^{n} \rho^{n}}{T^{n}} \frac{\partial A^{n}}{\partial s^{n}} (\mathbf{v}^{n,s} \cdot \nabla s^{n}) + \frac{p^{n}}{T^{n}} (s^{n} \dot{\varepsilon} + \mathbf{v}^{n,s} \cdot \nabla \varepsilon s^{n}) - \varepsilon s^{n} \mathbf{q}^{n} \cdot \nabla \frac{1}{T^{n}} \\
&\qquad - \frac{p^{s}}{T^{s}} \dot{\varepsilon} - (1 - \varepsilon) \mathbf{q}^{s} \cdot \nabla \frac{1}{T^{s}} \\
&\qquad - \sum_{\alpha\beta} \left[\frac{a^{\alpha\beta} \rho^{\alpha\beta}}{T^{\alpha\beta}} \frac{\partial A^{\alpha\beta}}{\partial s^{a}} \left(\mathbf{v}^{\alpha\beta,s} \cdot \nabla s^{a} \right) - a^{\alpha\beta} \mathbf{q}^{\alpha\beta} \cdot \nabla \frac{1}{T^{\alpha\beta}} \right] \\
&+ \sum_{\alpha} \sum_{\beta \neq \alpha} \frac{1}{T^{\alpha\beta}} \left(\frac{\hat{q}^{\alpha}_{\alpha\beta} T^{\alpha,\alpha\beta}}{T^{\alpha}} + \hat{\mathbf{t}}^{\alpha}_{\alpha\beta} \cdot \mathbf{v}^{\alpha,\alpha\beta} \right) + \sum_{\alpha\beta} \sum_{\gamma \neq \alpha,\beta} \frac{1}{T^{\alpha\beta}} \left(\frac{\hat{q}^{\alpha\beta}_{\alpha\beta\gamma} T^{\alpha\beta,\alpha}}{T^{\alpha}} + \hat{\mathbf{t}}^{\alpha\beta}_{\alpha\beta\gamma} \cdot \mathbf{v}^{\alpha\beta} \right) \\
&\qquad - \sum_{\alpha\beta} \frac{\hat{e}^{\alpha\beta}_{\alpha\beta\gamma}}{T^{s}} \left(G^{\alpha\beta,s} + \eta^{\alpha\beta} T^{\alpha\beta,s} - \frac{p^{\alpha\beta} T^{\alpha\beta,s}}{\rho^{\alpha\beta} T^{\alpha\beta}} \right) \\
&\qquad + \sum_{\alpha} \sum_{\beta \neq \alpha} \frac{\hat{e}^{\alpha}_{\alpha\beta}}{T^{\alpha\beta}} \left(G^{\alpha\beta,\alpha} + \eta^{\alpha\beta} T^{\alpha\beta,\alpha} - \frac{p^{\alpha} T^{\alpha\beta,\alpha}}{\rho^{\alpha} T^{\alpha}} \right) \geq 0 \qquad (5.109)
\end{aligned}
$$

Additional constraints can be added to a system that is at equilibrium. At equilibrium, total entropy reaches a maximum and the production of entropy reaches a minimum [*Greiner et al.*, 1994]. We will assume that the temperature of the solid and the fluid become identical almost at once and that the temperature differences between phases throughout each REV is negligible [*de Marsily*, 1986, p. 277]. *Houpert et. al. [1965]* have shown that in porous media with grain sizes less than one millimeter thermal equilibrium will be reached in less than a minute. The assumption of local thermal equilibrium implies that all phases and interfaces will have the same temperature, therefore $T^{\alpha,s} = T^{\alpha\beta,\alpha} = \nabla T^{\alpha,s} = \nabla T^{\alpha\beta,\alpha} = 0$. The temperature may still vary in space and time, but within each REV, the temperature is constant across all phases, interfaces, and contact lines.

Additionally, at a state of thermodynamic equilibrium, there will be no relative movement of phases and interfaces and the rate of change of porosity and saturation will be zero.

Rearrangement of Eq. (5.109) in terms of the variables noted above as equal to zero will facilitate a discussion of equilibrium restrictions. This manipulated form of Eq. (5.109) is stated as:

$$\begin{aligned}
&\sum_{\alpha} \varepsilon\, s^{\alpha}\, \rho^{\alpha} \Lambda^{\alpha} + \sum_{\alpha\beta} a^{\alpha\beta} \rho^{\alpha\beta} \Lambda^{\alpha\beta} = \\
&\qquad \dot{\varepsilon} \left(\frac{s^{a} p^{a}}{T^{a}} + \frac{s^{n} p^{n}}{T^{n}} - \frac{p^{s}}{T^{s}} \right)_{eq} + \dot{s^{a}} \left(\frac{\varepsilon p^{c}}{T^{an}} + \frac{\varepsilon p^{a}}{T^{a}} - \frac{\varepsilon p^{n}}{T^{n}} \right)_{eq} \\
&- \sum_{\alpha \neq s} \frac{\mathbf{v}^{\alpha,s}}{T^{\alpha}} \cdot \left[\varepsilon\, s^{\alpha}\, \rho^{\alpha} \frac{\partial A^{\alpha}}{\partial s^{a}} \nabla s^{a} - p^{\alpha} \nabla \varepsilon\, s^{\alpha} - \sum_{\beta \neq \alpha} \hat{\mathbf{t}}^{\alpha}_{\alpha\beta} + \left(\sum_{\beta \neq \alpha} \hat{\mathbf{t}}^{\alpha}_{\alpha\beta} \frac{T^{\alpha\beta,\alpha}}{T^{\alpha}} \right)_{eq} \right]_{eq} \\
&- \sum_{\alpha\beta} \frac{\mathbf{v}^{\alpha\beta,s}}{T^{\alpha\beta}} \cdot \left[a^{\alpha\beta} \rho^{\alpha\beta} \frac{\partial A^{\alpha\beta}}{\partial s^{a}} \nabla s^{a} + \hat{\mathbf{t}}^{\alpha}_{\alpha\beta} + \hat{\mathbf{t}}^{\beta}_{\alpha\beta} - \hat{\mathbf{t}}^{\alpha\beta}_{\alpha\beta\gamma} - \left(\hat{\mathbf{t}}^{\alpha\beta}_{\alpha\beta\gamma} \frac{T^{\alpha\beta,s}}{T^{s}} \right)_{eq} \right]_{eq} \\
&- \sum_{\alpha} \left[\varepsilon^{\alpha} \mathbf{q}^{\alpha} \right]_{eq} \cdot \nabla \frac{1}{T^{\alpha}} - \sum_{\alpha\beta} \left(a^{\alpha\beta} \mathbf{q}^{\alpha\beta} \right)_{eq} \cdot \nabla \frac{1}{T^{\alpha\beta}} + \frac{1}{T^{s}} \sum_{\alpha\beta} \left(\frac{\hat{q}^{\alpha\beta}_{\alpha\beta\gamma} T^{\alpha\beta,s}}{T^{\alpha\beta}} \right)_{eq} \\
&+ \sum_{\alpha} \sum_{\beta \neq \alpha} \left(\frac{\hat{q}^{\alpha}_{\alpha\beta} T^{\alpha\beta,\alpha}}{T^{\alpha\beta} T^{\alpha}} \right)_{eq} - \sum_{\alpha\beta} \frac{\hat{e}^{\alpha\beta}_{\alpha\beta\gamma}}{T^{s}} \left[G^{\alpha\beta,s} + \left(\eta^{\alpha\beta} T^{\alpha\beta,s} \right)_{eq} - \left(\frac{p^{\alpha\beta} T^{\alpha\beta,s}}{\rho^{\alpha\beta} T^{\alpha\beta}} \right)_{eq} \right] \\
&\qquad + \sum_{\alpha} \sum_{\beta \neq \alpha} \frac{\hat{e}^{\alpha}_{\alpha\beta}}{T^{\alpha\beta}} \left[G^{\alpha\beta,\alpha} + \left(\eta^{\alpha\beta} T^{\alpha\beta,\alpha} \right)_{eq} - \left(\frac{p^{\alpha} T^{\alpha\beta,\alpha}}{\rho^{\alpha} T^{\alpha}} \right)_{eq} \right] \geq 0 \qquad (5.110)
\end{aligned}$$

At equilibrium, the production of entropy, Λ, reaches a minimum. Therefore, by the definition of a minimum for Λ:

$$\begin{aligned}
\frac{\partial \Lambda}{\partial X_e} &= 0 \qquad\qquad \forall X_e \\
\frac{\partial^2 \Lambda}{\partial X_e\, \partial Y_e} &> 0 \qquad\qquad \forall X_e, Y_e \qquad (5.111)
\end{aligned}$$

where X_e and Y_e represent the set of independent and dependent variables which will be zero at equilibrium ($T^{\alpha,s}$, $T^{\alpha\beta,\alpha}$, $\nabla T^{\alpha,s}$, $\nabla T^{\alpha\beta,\alpha}$, $\mathbf{v}^{\alpha,s}$, $\mathbf{v}^{\alpha\beta,s}$, $\dot{\varepsilon}$, $\dot{s^{a}}$)

Application of Eq. (5.111) to Eq. (5.110) requires that the bracketed terms go to zero at equilibrium. After rearrangement, the following restrictions can be developed

[*Hassanizadeh and Gray*, 1990]:

$$\left(\frac{s^a p^a}{T^a} + \frac{s^n p^n}{T^n} - \frac{p^s}{T^s}\right)_{eq} = 0 \tag{5.112}$$

$$(p^c + p^a - p^n)_{eq} = 0 \tag{5.113}$$

$$\left(\varepsilon\, s^\alpha\, \rho^\alpha \frac{\partial A^\alpha}{\partial s^a} \nabla s^a - p^\alpha \nabla \varepsilon\, s^\alpha\, - \sum_{\beta \neq \alpha} \hat{\mathbf{t}}^{\alpha}_{\alpha\beta}\right)_{eq} = 0 \tag{5.114}$$

$$\left(a^{\alpha\beta} \rho^{\alpha\beta} \frac{\partial A^{\alpha\beta}}{\partial s^a} \nabla s^a + \hat{\mathbf{t}}^{\alpha}_{\alpha\beta} + \hat{\mathbf{t}}^{\beta}_{\alpha\beta} - \hat{\mathbf{t}}^{\alpha\beta}_{\alpha\beta\gamma}\right)_{eq} = 0 \tag{5.115}$$

$$(\mathbf{q}^\alpha)_{eq} = 0 \tag{5.116}$$

$$\left(\mathbf{q}^{\alpha\beta}\right)_{eq} = 0 \tag{5.117}$$

$$\left(\hat{q}^{\alpha}_{\alpha\beta}\right)_{eq} = 0 \tag{5.118}$$

$$\left(\hat{q}^{\alpha\beta}_{\alpha\beta\gamma}\right)_{eq} = 0 \tag{5.119}$$

$$\left(G^{\alpha\beta,s}\right)_{eq} = 0 \tag{5.120}$$

$$\left(G^{\alpha\beta,a}\right)_{eq} = 0 \tag{5.121}$$

where $(\ )_{eq}$ indicates a quantity at equilibrium.

If the wettability potential, Ω^α, is defined as [*Hassanizadeh and Gray*, 1990]:

$$\Omega^\alpha = s^\alpha \rho^\alpha \frac{\partial A^\alpha}{\partial s^\alpha} \tag{5.122}$$

then Eq. (5.114) can be stated as:

$$\varepsilon\, \Omega^\alpha\, \nabla s^a - p^\alpha \nabla \varepsilon\, s^\alpha\, = \left(\sum_{\beta \neq \alpha} \hat{\mathbf{t}}^{\alpha}_{\alpha\beta}\right)_e \tag{5.123}$$

Several conclusions can now be drawn from equilibrium conditions. First, the capillary pressure in Eq. (5.113) will be equal to the difference in pressure between the non-wetting and wetting phases at equilibrium. If only equilibrium conditions are considered, as is often the case in standard approaches, the capillary pressure could erroneously be based on only s^a. However, Eq. (5.108) includes interfacial areas and surface densities in the functional dependence of the capillary pressure. A complete description of the capillary pressure, therefore, needs to be developed that considers not only s^α but also $a^{\alpha\beta}$ and $\rho^{\alpha\beta}$ [*Gray and Hassanizadeh*, 1991b]. Second, both the momentum exchange terms for a phase and for an interface have terms that are not present at equilibrium which suggest that the terms have both equilibrium and non-equilibrium portions. Several conclusions can be drawn from the above equations that are consistent with thermodynamics expectations based upon the definition of thermodynamic equilibrium. Equations (5.116) and (5.117) suggest that no heat transfer within a phase or interface will occur at equilibrium. Along similar reason, Equations (5.118) and (5.119) suggest that no exchange of heat will occur between phases and interfaces within a given REV at equilibrium. Equations (5.120) and (5.121) indicate that at equilibrium the Gibbs free energy per unit mass will be equal for each phase and interface. This is consistent with the microscopic condition of equilibrium for Gibbs free energy [*Gray and Hassanizadeh*, 1991b].

5.4.4 Linear Theory and Simplifications of Constitutive Relationships

In this section, we will consider linear applications of the entropy inequality, Eq. (5.110), applied to equations of motion. At near equilibrium conditions, the non-equilibrium restrictions can be expanded in a Taylor series about equilibrium and a linear approximation that neglects quadratic and higher order terms can be used to gain useful insights into the multiphase flow equations [*Murad et al.*, 1995]. Near equilibrium assumptions have been used to derive generalized Darcy's laws and Fick's laws [*Gray*, 1983; *Hassanizadeh and Gray*, 1990, 1993b; *Achanta et al.*, 1994].

As suggested in the previous section, we may describe the momentum exchange terms with an equilibrium and non-equilibrium portion for phases as: [*Hassanizadeh and Gray*, 1990; *Achanta et al.*, 1994]

$$\hat{\mathbf{t}}^{\alpha}_{\alpha\beta} = \sum_{\alpha,\beta} \hat{\mathbf{t}}^{\alpha}_{\alpha\beta} = \boldsymbol{\tau}^{\alpha} + \left(\sum_{\alpha,\beta} \hat{\mathbf{t}}^{\alpha}_{\alpha\beta} \right)_{e} \tag{5.124}$$

and for interfaces as [*Hassanizadeh and Gray*, 1990; *Achanta et al.*, 1994]:

$$\hat{\mathbf{t}}^{\alpha\beta}_{\alpha\beta\gamma} - \hat{\mathbf{t}}^{\alpha}_{\alpha\beta} - \hat{\mathbf{t}}^{\beta}_{\alpha\beta} = \boldsymbol{\tau}^{\alpha\beta} + \left(\hat{\mathbf{t}}^{\alpha\beta}_{\alpha\beta\gamma} - \hat{\mathbf{t}}^{\alpha}_{\alpha\beta} - \hat{\mathbf{t}}^{\beta}_{\alpha\beta}\right)_{e} \tag{5.125}$$

where $\boldsymbol{\tau}^{\alpha}$ and $\boldsymbol{\tau}^{\alpha\beta}$ are the non-equilibrium portions of the momentum equation which can be compared to the $\hat{\boldsymbol{\tau}}^{\alpha}$ term used in the differential continuum development [Eq. (3.17)]. Physically, $\boldsymbol{\tau}^{\alpha}$ and $\boldsymbol{\tau}^{\alpha\beta}$ can be described respectively as the dissipative drag exerted by adjacent phases on the α-phase and the drag forces exerted by adjacent interfaces on the $\alpha\beta$-phase.

For the flowing phases, substitution of equations Eq. (5.103), Eq. (5.112), and Eq. (5.124) into the previously developed integral momentum balance equation for a phase, Eq. (4.82), yields:

$$0 = -\nabla p^{\alpha} - \rho^{\alpha}\mathbf{g} - \frac{\Omega^{\alpha}}{s^{\alpha}}\nabla s^{\alpha} + \frac{\boldsymbol{\tau}^{\alpha}}{\varepsilon s^{\alpha}} \tag{5.126}$$

Likewise for the interfaces, substitution of equations Eq. (5.104), Eq. (5.105), Eq. (5.113), and Eq. (5.125) into the previously developed integral momentum balance equation for an interface, Eq. (4.115), making use of the mathematical identity Eq. (4.53) yields:

$$0 = -\nabla\cdot\left(a^{\alpha\beta}p^{\alpha\beta}\right) - a^{\alpha\beta}\rho^{\alpha\beta}\mathbf{g} + a^{\alpha\beta}\rho^{\alpha\beta}\frac{\partial A^{\alpha\beta}}{\partial s^{\alpha}}\nabla s^{\alpha} - \boldsymbol{\tau}^{\alpha\beta} \tag{5.127}$$

In Eq. (5.126) and Eq. (5.127) gravity is assumed to be the only body force acting on the system and hence the only supply of momentum to the system.

$\boldsymbol{\tau}^{\alpha}$ and $\boldsymbol{\tau}^{\alpha\beta}$ are general functions of the independent variables [*Hassanizadeh and Gray*, 1990]. This relationship for a phase takes the form [*Hassanizadeh and Gray*, 1993b; *Achanta et al.*, 1994]:

$$\boldsymbol{\tau}^{\alpha} \approx -\mathbf{R}^{\alpha}_{\mathbf{a}}\cdot\mathbf{v}^{\mathbf{a},s} - \mathbf{R}^{\alpha}_{\mathbf{n}}\cdot\mathbf{v}^{\mathbf{n},s} - \sum_{\beta\gamma}\mathbf{R}^{\alpha}_{\beta\gamma}\cdot\mathbf{v}^{\beta\gamma,s} \tag{5.128}$$

where $\mathbf{R}$ is a tensor of viscous drag forces with $\mathbf{R}^{\alpha}_{\mathbf{a}}$ representing the forces between the α-phase and the aqueous phase and $\mathbf{R}^{\alpha}_{\beta\gamma}$ representing the forces between the α-phase and the $\beta\gamma$-interface. Substitution of Eq. (5.128) into Eq. (5.126) then yields:

$$\nabla p^{\alpha} + \rho^{\alpha}\mathbf{g} = -\frac{\Omega^{\alpha}}{s^{\alpha}}\nabla s^{\alpha} + \frac{1}{\varepsilon s^{\alpha}}\left(-\mathbf{R}^{\alpha}_{\mathbf{a}}\cdot\mathbf{v}^{\mathbf{a},s} - \mathbf{R}^{\alpha}_{\mathbf{n}}\cdot\mathbf{v}^{\mathbf{n},s} - \sum_{\beta\gamma}\mathbf{R}^{\alpha}_{\beta\gamma}\cdot\mathbf{v}^{\beta\gamma,s}\right) \tag{5.129}$$

Similarly for the interfaces, we can describe the dissipative drag force on the interface as [*Hassanizadeh and Gray*, 1993b; *Achanta et al.*, 1994]:

$$\tau^{\alpha\beta} \approx -\mathbf{R}_{\mathbf{a}}^{\alpha\beta} \cdot \mathbf{v}^{\mathbf{a},s} - \mathbf{R}_{\mathbf{n}}^{\alpha\beta} \cdot \mathbf{v}^{\mathbf{n},s} - \sum_{\gamma\epsilon} \mathbf{R}_{\gamma\epsilon}^{\alpha\beta} \cdot \mathbf{v}^{\gamma\epsilon,s} \tag{5.130}$$

where $\mathbf{R}_{\gamma\epsilon}^{\alpha\beta}$ represents the forces between the $\alpha\beta$-interface and the $\gamma\epsilon$-interface. Substitution of Eq. (5.130) into Eq. (5.127) then yields:

$$\begin{aligned}\nabla \cdot \left(a^{\alpha\beta} p^{\alpha\beta}\right) + a^{\alpha\beta} \rho^{\alpha\beta} \mathbf{g} = a^{\alpha\beta} \rho^{\alpha\beta} \frac{\partial A^{\alpha\beta}}{\partial s^{a}} \nabla s^{a} \\ + \mathbf{R}_{\mathbf{a}}^{\alpha\beta} \cdot \mathbf{v}^{\mathbf{a},s} + \mathbf{R}_{\mathbf{n}}^{\alpha\beta} \cdot \mathbf{v}^{\mathbf{n},s} + \sum_{\gamma\epsilon} \mathbf{R}_{\gamma\epsilon}^{\alpha\beta} \cdot \mathbf{v}^{\gamma\epsilon,s}\end{aligned} \tag{5.131}$$

Alternatively, the differential momentum balance yielded Eq(3.21), restated as:

$$\left(\nabla p^{\alpha} + \rho^{\alpha} g \nabla z\right) = -\frac{1}{\varepsilon s^{\alpha}} \left(\mathbf{R}^{\alpha\alpha} \cdot \mathbf{v}^{\alpha,s}\right) \tag{5.132}$$

The integral continuum approach has rigorously defined the momentum balance with consideration given to the wettability potential and to interfacial drag forces. Unless the drag associated with the relative interfacial velocity and the dependence of free energy on saturation are negligible, the differential momentum balance will not correctly describe the multiphase flow system.

Eq. (5.129) is a complete momentum conservation equation for a phase. We note that when the effects of the motion of interfaces on the motion of phases is small, the third term in the braces involving the relative interfacial velocity will be negligible. However, the term involving Ω^{α} seems to have some potential significance [*Hassanizadeh and Gray*, 1990; *Gray and Hassanizadeh*, 1991a]. The wettability potential term must be much less than the drag forces if the term is to be neglected. This is stated as:

$$\varepsilon \left|\Omega^{\alpha} \nabla s^{\alpha}\right| \ll \left|\mathbf{R}_{\alpha}^{\alpha} \cdot \mathbf{v}^{\alpha,s}\right| \tag{5.133}$$

Hassanizadeh and Gray [1990] suggest that this restriction may not be true under equilibrium conditions or in low permeable media where $\mathbf{v}^{\alpha,s}$ is either zero or very small.

If we include the wettability potential and assume that the coupling between velocities is not considered, Eq. (5.129) reduces to:

$$\nabla p^{\alpha} - \rho^{\alpha} \mathbf{g} = -\frac{\Omega^{\alpha}}{s^{\alpha}} \nabla s^{\alpha} + \frac{1}{\varepsilon s^{\alpha}} \left(-\mathbf{R}_{\alpha}^{\alpha} \cdot \mathbf{v}^{\alpha,s}\right) \tag{5.134}$$

where the actual significance of the wettability potential is an important issue requiring experimental study. Note that Eq. (5.134) reduces to the classical Darcy's law for single-phase fluid flow if $\mathbf{R}^{\alpha\alpha} = \varepsilon\, s^{\alpha\,2} \mu^{\alpha} / (\mathbf{k} k_{r\alpha})$.

5.5 Continuing Issues of Integral Approach Application

In this chapter, we have applied the integral continuum approach to a two-phase system. Primary and secondary variables have been defined for both volumes and interfaces. Complete conservation equations describing the mass, momentum, and energy of the system allow for rigorous development of governing equations. Many constitutive relationships are necessary. These constitutive relations are derived in a thermodynamically consistent manner using the entropy inequality. The entropy inequality examined non-equilibrium, near equilibrium and equilibrium cases.

The integral continuum approach provides a means for thermodynamically based constitutive relationships. A more rigorous descriptions of capillary pressure, Eq. (5.108), which includes interfacial forces has been introduced. Also, a momentum balance, Eq. (5.134), that accounts for interfacial drag forces and incorporates the wettability potential provides more descriptive momentum balance than the traditional extension of Darcy's Law with relative permeability terms.

Many open issues remain in the application of integral continuum approaches [*Reeves and Celia*, 1996]. Thermodynamically consistent constitutive theories have been proposed that have not been defined with a relationship. In order to formulate a closed form of the integral approach, constitutive relations must be formulated. Due to the inherent difficulties in measuring interfacial area, alternative methods have been explored for the quantification of interfacial area effects [*Miller et al.*, 1990; *Mayer and Miller*, 1992a; *Imhoff et al.*, 1993]. Progressive methods, such as pore-scale modeling, will be necessary to develop the necessary constitutive theory for closure of the integral continuum conservation equations. Pore-scale models allow for a cost effective method for exploring dependencies in thermodynamically constrained constitutive relations.

As a prime example of defining relationship introduced by the integral continuum approach, *Reeves and Celia* [1996] have proposed a formal constitutive relationship between capillary pressure, saturation and interfacial area using a pore-scale network model. The results of this work support the importance of the wettability term in multiphase flow equations. Pore-scale models such as this will continue to serve as valuable computational tools to investigate a wide variety of multiphase porous media problems. Improvements in pore-scale modeling will improve our ability to further refine constitutive theories. It is important to continue the evolution of multiphase flow and transport conservation equations in order to describe the complex phenomena with which we are faced.

Much fundamental research is still necessary for the application of integral continuum approaches to the modeling of multiphase flow through porous media. However, the rigorously averaged equations for volumes, interfaces, and contact lines combined with thermodynamically constrained constitutive theory provides the basis to formulate fundamental balance equations.

Chapter 6

Conclusion

This report has presented approaches to the formulation of flow and transport equations in porous media systems. First, standard approaches to the development of a closed system of governing equation were reviewed. Second, the differential continuum approach, which is generally used in standard approaches, was formally presented. Third, integral continuum equations describing the conservation of mass, momentum, energy, and entropy were formulated for volumes, interfaces, and contact lines. Finally, the integral continuum equations were applied to a two fluid phase, porous media system and the entropy inequality was used to constrain constitutive relationships. Many insightful relationships were derived by use of the entropy inequality.

Standard approaches to the description of fluid flow in porous media exist despite severe limitations in predicting complex multiphase systems from *ad hoc* extensions of single phase theories [*Miller et al.*, 1996]. The inherent complexity of multiphase systems and the heterogeneity that is characteristic of most natural environments leads to a large and difficult set of problems associated with the accurate representation of fluid flow and contaminant transport. This report has pointed to several examples of the limitations of differential continuum descriptions of multiphase flow and transport which include the following:

1. length scales are mixed between governing equations and constitutive theory [*Gray et al.*, 1993; *Miller et al.*, 1996];

2. conservation equations are only written for mass;
3. Darcy's law cannot account for multiple flowing fluids [*Miller et al.*, 1996] and cannot account for the dissipation of of momentum [*Hassanizadeh and Gray*, 1993b];
4. single phase equations are empirically extended to multiphase systems [*Gray and Hassanizadeh*, 1991a];
5. interfaces are present yet neglected in the governing equations [*Abriola and Gray*, 1985]; and
6. the framework for extending governing equations to more complex systems is unclear and does not assure thermodynamic consistency [*Gray et al.*, 1993; *Hassanizadeh and Gray*, 1993b].

Paradoxes also exist in the traditional description of constitutive theory [*Gray and Hassanizadeh*, 1991a].

The limitations of traditional approaches motivate alternative formulations of multiphase flow and contaminant transport governing equations. The integral continuum approach has been explored by many researchers to rigorously describe MPFT in porous media systems [*Whitaker*, 1969; *Bear*, 1972; *Hassanizadeh and Gray*, 1979a, 1979b, 1980a; *Cushman*, 1983; *Gray*, 1983; *Quintard and Whitaker*, 1988; *Gray and Hassanizadeh*, 1991a, 1991b; *Hassanizadeh and Gray*, 1993a, 1993b; *Chen et al.*, 1994; *Quintard and Whitaker*, 1994]. The integral continuum approach provides a means for changing scale while retaining important physical processes from smaller scales. The integral approach also is based directly on first principles such that the equations are thermodynamically consistent. The integral continuum approach differs from traditional approaches in the following ways:

1. microscale events are systematically averaged to the macroscale and all resulting constitutive theory are developed with macroscale parameters;
2. mass, momentum, and energy conservation equations for multiphase systems

are developed for each of the multiple phases which can then be simplified to single phase equations if appropriate;

3. mass, momentum, and energy conservation equations are written for interfaces; and
4. the entropy inequality is used to ensure that constitutive relationships do not violate the second law of thermodynamics.

Balance equations have been presented in this report through a rigorous development of physical processes, averaged systematically from the microscale to the macroscale, to describe the conservation of mass, momentum, energy, and entropy in multiphase, porous media systems. In contrast to the differential continuum approach, the length scale of the governing equations and all constitutive relationships will be the averaged macroscale. Second, conservation of momentum, energy, and entropy are also included in the integral continuum formulation. Third, governing equations for multiphase systems are developed that can be shown to reduce down to single phase flow equations. Additionally, balance equations for interfaces are also averaged from the microscale to the macroscale and included in the governing equations. The integral continuum approach provides a fundamental basis on which to advance theories of multiphase flow in general [*Gray and Hassanizadeh*, 1991b].

In this work, the integral continuum balance equations are then used to formulate a general theory of two-phase flow that is based upon the fundamental principles of mass, momentum, and energy conservation and the second law of thermodynamics. Conservation equations were developed for both the two flowing phases, the solid phase, and for the three interfaces.

Next, the entropy inequality, developed through the integral continuum approach, was exploited through the use of the *Coleman and Noll* [1963] method to constrain the developed system of equations. From the entropy inequality, we derive three sets of constraining cases: results that can be proven at equilibrium and non-equilibrium conditions, results that can be shown only at equilibrium, and results that can be shown linearized about equilibrium for near equilibrium conditions.

For all conditions, we have demonstrated that the entropy of a phase and an interface will be proportional to the respective Helmholtz free energy divided by the temperature [Eq. (5.101) and Eq. (5.102)]. This result agrees with the classical results from *Eringen* [1980] for a single-phase fluid and *Slattery* [1990] for an interface. Although not being a verification of all results, this agreement with the thermodynamic literature by application of the *Coleman and Noll* [1963] method is promising for the development of other thermodynamically constrained constitutive relationships.

Of particular interest, for equilibrium conditions we have shown through Eq. (5.108) and Eq. (5.113) that capillary pressure depends upon the interfaces and surface densities as well as the pressures of the wetting and non-wetting fluids. The capillary pressure in Eq. (5.113) is shown to be equal to the difference in pressure between the non-wetting and wetting phases at equilibrium. Traditional constitutive relationships typically base capillary pressure on only s^{α}. However, if only equilibrium conditions are considered, as is often the case in standard approaches, the capillary pressure should include interfacial effects. The integral continuum approach provides a rigorous approach to these potential constitutive relationships. A complete description of the capillary pressure, therefore, needs to be developed that considers not only s^{α} but also $a^{\alpha\beta}$ and $\rho^{\alpha\beta}$ [*Gray and Hassanizadeh*, 1991b]. Also for equilibrium conditions, we note that both the momentum exchange terms for a phase and for an interface have terms that are not present at equilibrium which suggest that the terms have both equilibrium and non-equilibrium portions.

For near equilibrium conditions, we have shown that a complete description of the momentum balance will include drag forces and an interfacial dependence. This formulated momentum balance can be reduced to the traditional form of Darcy's law. The application of the entropy inequality to a rigorous description of the porous media system has shown that interfaces will effect multiphase flow and transport. The wettability term, Ω^{α} in Eq. (5.123), is a newly defined quantity which relates the dependence of free energy and saturation *Gray and Hassanizadeh* [1991b]. The inclusion of such parameters, with consideration given to the second law of thermodynamics, improves the current description of multiphase flow and transport as opposed to empirically based extensions of single phase equations which may only be applicable to a small subset of problems.

Much additional work is needed to resolve the issues facing the application of integral continuum approaches [*Reeves and Celia*, 1996]. First, the incorporation of reasonable assumptions and the formulation of constitutive relationships is necessary for the closure of the proposed set of equations. Additionally, the simultaneous solution of 30 equations will severely limit the size of any possible numerical solutions. Research directed towards a fundamental understanding of the processes governing multiphase flow and transport in porous media is well spent time and money. Conversely, the pursuit of additional empirical relationships, which define a small subset of multiphase flow and transport in porous media, may not increase our understanding. In conclusion, further research of integral continuum approaches is encouraged.

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