

# A constitutive model for non-reacting binary mixtures

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# Double diffusive convection



FIGURE 1. A field of salt fingers formed by setting up a stable temperature gradient and pouring a little salt solution on top. The downward-moving fingers were made visible by adding fluorescein to the salt and lighting through a slit from below.

Huppert & Turner (1981)

# Mixture theory – Truesdell

Idea of co-occupancy:

$v_s$	velocity
$v_w$	velocity
$\rho_s$	density
$\rho_w$	density
$\theta_s, e_s$	temperature/internal energy
$\theta_w, e_w$	temperature/internal energy

**Table:** Unknowns in problems for binary mixtures.

Eckart(1940), Truesdell (1957), Samohýl (1987), Rajagopal & Tao (1995)

# Governing equations

Governing equations for components - non-reacting binary mixture of non-polar constituents

$$\frac{d_s \rho_s}{dt} = -\rho_s \operatorname{div} \mathbf{v}_s,$$

$$\frac{d_w \rho_w}{dt} = -\rho_w \operatorname{div} \mathbf{v}_w,$$

$$\rho_s \frac{d_s \mathbf{v}_s}{dt} = \operatorname{div} \mathbb{T}_s + \rho_s \mathbf{b} + \boldsymbol{\pi},$$

$$\rho_w \frac{d_w \mathbf{v}_w}{dt} = \operatorname{div} \mathbb{T}_w + \rho_w \mathbf{b} - \boldsymbol{\pi}$$

$$\rho_s \frac{d_s}{dt} \left( e_s + \frac{1}{2} |\mathbf{v}_s|^2 \right) = \operatorname{div} (\mathbb{T}_s \mathbf{v}_s) - \operatorname{div} \mathbf{q}_s + q_s + e^i + \rho_s \mathbf{b}_s \bullet \mathbf{v}_s$$

$$\rho_w \frac{d_w}{dt} \left( e_w + \frac{1}{2} |\mathbf{v}_w|^2 \right) = \operatorname{div} (\mathbb{T}_w \mathbf{v}_w) - \operatorname{div} \mathbf{q}_w + q_w - e^i + \rho_w \mathbf{b}_w \bullet \mathbf{v}_w$$

# Governing equations

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$$\frac{d_w \rho_w}{dt} = -\rho_w \operatorname{div} \mathbf{v}_w,$$

$$\rho_s \frac{d_s \mathbf{v}_s}{dt} = \operatorname{div} \mathbb{T}_s + \rho_s \mathbf{b} + \boldsymbol{\pi},$$

$$\rho_w \frac{d_w \mathbf{v}_w}{dt} = \operatorname{div} \mathbb{T}_w + \rho_w \mathbf{b} - \boldsymbol{\pi}$$

$$\rho_s \frac{d_s e_s}{dt} = \mathbb{T}_s : \nabla \mathbf{v}_s - \operatorname{div} \mathbf{q}_s + q_s + e^i - \boldsymbol{\pi} \bullet \mathbf{v}_s + \rho_s \mathbf{b}_s \bullet \mathbf{v}_s$$

$$\rho_w \frac{d_w e_w}{dt} = \mathbb{T}_w : \nabla \mathbf{v}_w - \operatorname{div} \mathbf{q}_w + q_w - e^i + \boldsymbol{\pi} \bullet \mathbf{v}_w + \rho_w \mathbf{b}_w \bullet \mathbf{v}_w$$

# Single-component form

- We formulate balance laws for the mixture as a whole, rewrite them in a single-component form in terms of mixture properties and identify additional balances for complementary quantities .
- Mixture components properties  $\rho_s, \rho_w, \mathbf{v}_s, \mathbf{v}_w, e_s, e_w$
- Mixture properties

$$\rho := \rho_s + \rho_w$$

$$\rho \mathbf{v} := \rho_s \mathbf{v}_s + \rho_w \mathbf{v}_w$$

$$\rho e := \rho_s e_s + \rho_w e_w + \frac{1}{2} \rho_s \mathbf{u}_s \bullet \mathbf{u}_s + \frac{1}{2} \rho_w \mathbf{u}_w \bullet \mathbf{u}_w$$

where  $\mathbf{u}_s := \mathbf{v}_s - \mathbf{v}$ ,  $\mathbf{u}_w := \mathbf{v}_w - \mathbf{v}$ .

- Complementary properties (only  $c$  and  $\mathbf{J}_s$ , same temperature "  $e_s - e_w$  " not needed)

$$c := \frac{\rho_s}{\rho}$$

$$\mathbf{J}_s := \rho_s (\mathbf{v}_s - \mathbf{v})$$

# Governing equations in "new" variables

$$\begin{aligned} \frac{d\rho}{dt} &= -\rho \operatorname{div} \mathbf{v} \\ \rho \frac{dc}{dt} &= -\operatorname{div} \mathbf{J}_s \\ \rho \frac{d\mathbf{v}}{dt} &= \operatorname{div} \mathbb{T} + \rho \mathbf{b} \\ \frac{d\mathbf{J}_s}{dt} &= -\mathbf{J}_s \bullet (\nabla \mathbf{v} - (\operatorname{div} \mathbf{v}) \mathbb{I}) - \operatorname{div} \left( \frac{1}{\rho} \left( \frac{1}{c} - \frac{1}{1-c} \right) \mathbf{J}_s \otimes \mathbf{J}_s \right) \\ &\quad + \operatorname{div} ((1-c) \mathbb{T}_s - c \mathbb{T}_w) + \mathbb{T} \nabla c + \boldsymbol{\pi} \\ \rho \frac{de}{dt} &= -\operatorname{div} \mathbf{q} + \mathbb{T} : \mathbb{D}(\mathbf{v}) + q \end{aligned}$$

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with

$$\mathbb{T} := \mathbb{T}_s + \mathbb{T}_w - \rho_s \mathbf{u}_s \otimes \mathbf{u}_s - \rho_w \mathbf{u}_w \otimes \mathbf{u}_w$$



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with

$$\mathbb{T} := \mathbb{T}_s + \mathbb{T}_w - \frac{1}{\rho c (1-c)} \mathbf{J}_s \otimes \mathbf{J}_s$$

# Governing equations in "new" variables

$$\rho \frac{de}{dt} = -\operatorname{div} \mathbf{q} + \mathbb{T} : \mathbb{D}(\mathbf{v}) + q$$

where

$$\begin{aligned} \mathbf{q} &:= \mathbf{J}_e + \mathbf{J}_{e_k} + \mathbf{J}_q + \mathbf{J}_T \\ \mathbf{J}_e &:= \rho_s e_s \mathbf{u}_s + \rho_w e_w \mathbf{u}_w \\ \mathbf{J}_{e_k} &:= \frac{1}{2} \rho_s |\mathbf{u}_s|^2 \mathbf{u}_s + \frac{1}{2} \rho_w |\mathbf{u}_w|^2 \mathbf{u}_w \\ \mathbf{J}_q &:= \mathbf{q}_s + \mathbf{q}_w \\ \mathbf{J}_T &:= -T_s \mathbf{u}_s - T_w \mathbf{u}_w \\ q &:= q_s + q_w \end{aligned}$$

# Governing equations in "new" variables

$$\rho \frac{de}{dt} = -\operatorname{div} \mathbf{q} + \mathbb{T} : \mathbb{D}(\mathbf{v}) + q$$

where

$$\begin{aligned} \mathbf{q} &:= \mathbf{J}_e + \mathbf{J}_{ek} + \mathbf{J}_q + \mathbf{J}_T \\ \mathbf{J}_e &:= \mathbf{J}_s(e_s - e_w) \\ \mathbf{J}_{ek} &:= \frac{1}{2} \frac{1 - 2c}{\rho^2 (c(1 - c))^2} (\mathbf{J}_s \bullet \mathbf{J}_s) \mathbf{J}_s \\ \mathbf{J}_q &:= \mathbf{q}_s + \mathbf{q}_w \\ \mathbf{J}_T &:= -((1 - c)\mathbb{T}_s - c\mathbb{T}_w) \left( \frac{\mathbf{J}_s}{\rho c(1 - c)} \right) \\ q &:= q_s + q_w \end{aligned}$$

# Entropy balance

$$\rho_s \frac{d_s \eta_s}{dt} + \operatorname{div} \mathbf{J}_{\eta_s} = \xi_s + \zeta$$

$$\rho_w \frac{d_w \eta_w}{dt} + \operatorname{div} \mathbf{J}_{\eta_w} = \xi_w - \zeta$$

$$\boxed{\rho \frac{d\eta}{dt} + \operatorname{div} \mathbf{J}_\eta = \xi}$$

provided we define

$$\begin{aligned} \rho \eta &:= \rho_s \eta_s + \rho_w \eta_w \\ \mathbf{J}_\eta &:= \mathbf{J}_{\eta_s} + \mathbf{J}_{\eta_w} + (\eta_s - \eta_w) \mathbf{J}_s \\ \xi &:= \xi_s + \xi_w . \end{aligned}$$

# The "minimal" constitutive model

- From the energy and entropy balance

$$\begin{aligned}\rho e &= \rho_s e_s + \rho_w e_w + \frac{1}{2} \rho_s \mathbf{u}_s \bullet \mathbf{u}_s + \frac{1}{2} \rho_w \mathbf{u}_w \bullet \mathbf{u}_w \\ \rho \eta &:= \rho_s \eta_s + \rho_w \eta_w\end{aligned}$$

# The "minimal" constitutive model

- From the energy and entropy balance

$$\begin{aligned}\rho e &= \rho c e_s + \rho(1-c)e_w + \frac{1}{2} \frac{|\mathbf{J}_s|^2}{\rho c(1-c)} \\ \rho \eta &:= \rho c \eta_s + \rho(1-c)\eta_w\end{aligned}$$

# The "minimal" constitutive model

- From the energy and entropy balance

$$\rho e = \rho c e_s + \rho(1-c)e_w + \frac{1}{2} \frac{|\mathbf{J}_s|^2}{\rho c(1-c)}$$

$$\rho \eta := \rho c \eta_s + \rho(1-c)\eta_w$$

- Constitutive assumption:

$$\rho e(\rho, c, \eta, \mathbf{J}_s) = \rho c e_s(\rho, c, \eta) + \rho(1-c)e_w(\rho, c, \eta) + \frac{1}{2} \frac{|\mathbf{J}_s|^2}{\rho c(1-c)}$$

$$\rho \eta(\rho, c, e) := \rho_s \eta_s(\rho, c, e) + \rho_w \eta_w(\rho, c, e)$$

# The "minimal" constitutive model - Helmholtz potential

- Defining absolute temperature

$$\vartheta := \left. \frac{\partial \hat{e}}{\partial \eta} \right|_{c, \rho, \mathbf{J}_s}$$

- Defining the Helmholtz potential

$$\Psi_s := e_s - \vartheta \eta_s$$

$$\Psi_w := e_w - \vartheta \eta_w$$

$$\Psi := e - \vartheta \eta$$

- our constitutive assumptions imply

$$\Psi(\rho, c, \vartheta, \mathbf{J}_s) = c\Psi_s(\rho, c, \vartheta) + (1 - c)\Psi_w(\rho, c, \vartheta) + \frac{1}{2} \frac{|\mathbf{J}_s|^2}{\rho^2 c(1 - c)}$$

- This is one of the results of theory of fluid mixtures of Müller (1968).



# The "minimal" constitutive model

Using

$$\mu := \left( \frac{\partial \Psi}{\partial c} \Big|_{\rho, \vartheta, \mathbf{J}_s} \right) \quad p := \rho^2 \left( \frac{\partial \Psi}{\partial \rho} \Big|_{c, \vartheta, \mathbf{J}_s} \right) \quad \left( \frac{\partial \Psi}{\partial \vartheta} \Big|_{\rho, c, \mathbf{J}_s} \right) = -\eta$$

We may now express

$$\begin{aligned} \rho \vartheta \frac{d\eta}{dt} &= \rho \frac{de}{dt} - \rho \left( \frac{\partial \Psi}{\partial \rho} \frac{d\rho}{dt} + \frac{\partial \Psi}{\partial c} \frac{dc}{dt} + \frac{\partial \Psi}{\partial \mathbf{J}_s} \bullet \frac{d\mathbf{J}_s}{dt} \right) \\ &= -\operatorname{div} \mathbf{q} + \mathbb{T} : \mathbb{D}(\mathbf{v}) + p \operatorname{div} \mathbf{v} + \mu \operatorname{div} \mathbf{J}_s - \frac{\mathbf{J}_s}{\rho c(1-c)} \bullet \frac{d\mathbf{J}_s}{dt}, \end{aligned}$$

$$\begin{aligned}
\rho\vartheta \frac{d\eta}{dt} &= \left( \rho + \frac{4}{3} \frac{|\mathbf{J}_s|^2}{\rho c(1-c)} + \frac{1}{3} \text{tr} \mathbb{T} \right) \text{div} \mathbf{v} + \left( \mathbb{T}^\delta + \left( \frac{\mathbf{J}_s \otimes \mathbf{J}_s}{\rho c(1-c)} \right)^\delta \right) : \mathbb{D}^\delta(\mathbf{v}) \\
&+ \left( ((1-c)\mathbb{T}_s - c\mathbb{T}_w) - \frac{\mathbf{J}_s \otimes \mathbf{J}_s}{\rho} \left( \frac{1}{c} - \frac{1}{1-c} \right) \right) : \nabla \left( \frac{\mathbf{J}_s}{\rho c(1-c)} \right) \\
&- (\boldsymbol{\pi} + \rho c(1-c)\nabla\mu + \mathbb{T}\nabla c) \bullet \left( \frac{\mathbf{J}_s}{\rho c(1-c)} \right) \\
&- \text{div}(\mathbf{J}_q + \mathbf{J}_e - \mu\mathbf{J}_s - \mathbf{J}_{e_k})
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&- (\boldsymbol{\pi} + \rho c(1-c) \nabla \mu + \mathbb{T} \nabla c) \bullet \left( \frac{\mathbf{J}_s}{\rho c(1-c)} \right) \\
&- \text{div} (\mathbf{J}_q + \mathbf{J}_e - \mu \mathbf{J}_s - \mathbf{J}_{ek}) \\
\nabla \mu &= \left( \frac{\partial \mu}{\partial \rho} \Big|_{c, \vartheta, \frac{\mathbf{J}_s}{\rho c(1-c)}} \right) \nabla \rho + \left( \frac{\partial \mu}{\partial c} \Big|_{\rho, \vartheta, \frac{\mathbf{J}_s}{\rho c(1-c)}} \right) \nabla c + \left( \frac{\partial \mu}{\partial \vartheta} \Big|_{c, \rho, \frac{\mathbf{J}_s}{\rho c(1-c)}} \right) \nabla \vartheta \\
&+ \nabla \left( \frac{\mathbf{J}_s}{\rho c(1-c)} \right) \bullet \left( \frac{\partial \mu}{\partial \frac{\mathbf{J}_s}{\rho c(1-c)}} \Big|_{c, \rho, \vartheta} \right)
\end{aligned}$$

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&+ \left( ((1-c)\mathbb{T}_s - c\mathbb{T}_w) - \frac{\mathbf{J}_s \otimes \mathbf{J}_s}{\rho} \left( \frac{1}{c} - \frac{1}{1-c} \right) \right) : \nabla \left( \frac{\mathbf{J}_s}{\rho c(1-c)} \right) \\
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&- \text{div} (\mathbf{J}_q + \mathbf{J}_e - \mu \mathbf{J}_s - \mathbf{J}_{ek}) \\
\nabla \mu &= \left( \frac{\partial \mu}{\partial \rho} \Big|_{c, \vartheta, \frac{\mathbf{J}_s}{\rho c(1-c)}} \right) \nabla \rho + \left( \frac{\partial \mu}{\partial c} \Big|_{\rho, \vartheta, \frac{\mathbf{J}_s}{\rho c(1-c)}} \right) \nabla c + \left( \frac{\partial \mu}{\partial \vartheta} \Big|_{c, \rho, \frac{\mathbf{J}_s}{\rho c(1-c)}} \right) \nabla \vartheta \\
&- \nabla \left( \frac{\mathbf{J}_s}{\rho c(1-c)} \right) \bullet \frac{1-2c}{\rho c(1-c)} \mathbf{J}_s
\end{aligned}$$

Our model thus suggests to identify

$$\begin{aligned}
 \vartheta \xi &= \left( \rho + \frac{4}{3} \frac{|\mathbf{J}_s|^2}{\rho c(1-c)} + \frac{1}{3} \text{tr} \mathbb{T} \right) \text{div} \mathbf{v} + \left( \mathbb{T}^\delta + \left( \frac{\mathbf{J}_s \otimes \mathbf{J}_s}{\rho c(1-c)} \right)^\delta \right) : \mathbb{D}^\delta(\mathbf{v}) \\
 &+ ((1-c)\mathbb{T}_s - c\mathbb{T}_w) : \mathbb{D} \left( \frac{\mathbf{J}_s}{\rho c(1-c)} \right) \\
 &- \left( \boldsymbol{\pi} + \rho c(1-c) \left( \frac{\partial \mu}{\partial \rho} \nabla \rho + \frac{\partial \mu}{\partial c} \nabla c \right) + \mathbb{T} \nabla c \right) \bullet \left( \frac{\mathbf{J}_s}{\rho c(1-c)} \right) \\
 &- \left( \frac{(\mathbf{J}_q + \mathbf{J}_e - \mu \mathbf{J}_s - \mathbf{J}_{e_k})}{\vartheta} \right) \bullet \nabla \vartheta,
 \end{aligned}$$

and

$$\mathbf{J}_\eta = \frac{\mathbf{J}_q + \mathbf{J}_e - \mu \mathbf{J}_s - \mathbf{J}_{e_k}}{\vartheta}.$$

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 &+ ((1-c)\mathbb{T}_s - c\mathbb{T}_w) : \mathbb{D}(\mathbf{u}_s - \mathbf{u}_w) \\
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 &- \left( \frac{(\mathbf{J}_q + \mathbf{J}_e - \mu \mathbf{J}_s - \mathbf{J}_{ek})}{\vartheta} + \rho c(1-c) \frac{\partial \mu}{\partial \vartheta} \frac{\mathbf{J}_s}{\rho c(1-c)} \right) \bullet \nabla \vartheta,
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 &- \left( \frac{(\mathbf{J}_q + \mathbf{J}_e - \mu \mathbf{J}_s - \mathbf{J}_{e_k})}{\vartheta} \right) \bullet \nabla \vartheta,
 \end{aligned}$$

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 &+ ((1-c)\mathbb{T}_s - c\mathbb{T}_w) : \mathbb{D} \left( \frac{\mathbf{J}_s}{\rho c(1-c)} \right) \\
 &- \left( \boldsymbol{\pi} + \rho c(1-c) \left( \frac{\partial \mu}{\partial \rho} \nabla \rho + \frac{\partial \mu}{\partial c} \nabla c + \alpha \frac{\partial \mu}{\partial \vartheta} \nabla \vartheta \right) + \mathbb{T} \nabla c \right) \bullet \left( \frac{\mathbf{J}_s}{\rho c(1-c)} \right) \\
 &- \left( \frac{(\mathbf{J}_q + \mathbf{J}_e - \mu \mathbf{J}_s - \mathbf{J}_{e_k})}{\vartheta} + (1-\alpha) \rho c(1-c) \frac{\partial \mu}{\partial \vartheta} \frac{\mathbf{J}_s}{\rho c(1-c)} \right) \bullet \nabla \vartheta,
 \end{aligned}$$

and

$$\mathbf{J}_\eta = \frac{\mathbf{J}_q + \mathbf{J}_e - \mu \mathbf{J}_s - \mathbf{J}_{e_k}}{\vartheta}.$$

- Let us postulate the rate of entropy production as

$$\begin{aligned} \vartheta \xi &= \frac{2\nu + 3\lambda}{3} (\operatorname{div} \mathbf{v})^2 \\ &+ 2\nu \mathbb{D}^d(\mathbf{v}) : \mathbb{D}^d(\mathbf{v}) + 2\tilde{\nu} \mathbb{D} \left( \frac{\mathbf{J}_s}{\rho c(1-c)} \right) : \mathbb{D} \left( \frac{\mathbf{J}_s}{\rho c(1-c)} \right) \\ &+ k \left( \frac{\mathbf{J}_s}{\rho c(1-c)} \right) \bullet \left( \frac{\mathbf{J}_s}{\rho c(1-c)} \right) + \frac{\kappa}{\vartheta} \nabla \vartheta \bullet \nabla \vartheta \geq 0 \end{aligned}$$

for  $\nu, \tilde{\nu} \geq 0, 2\nu + 3\lambda \geq 0, k \geq 0, \kappa \geq 0$ .

- Let us employ the postulate of maximization of rate of entropy production with respect to the thermodynamic affinities (see e.g. Rajagopal & Srinivasa (2004))  $\left( \operatorname{div} \mathbf{v}, \mathbb{D}^d(\mathbf{v}), \mathbb{D} \left( \frac{\mathbf{J}_s}{\rho c(1-c)} \right), \frac{\mathbf{J}_s}{\rho c(1-c)}, \nabla \vartheta \right)$

## Final constitutive relations

$$\rho + \frac{4}{3} \frac{|\mathbf{J}_s|^2}{\rho c(1-c)} + \frac{1}{3} \text{tr} \mathbb{T} = \frac{2\nu + 3\lambda}{3} \text{div } \mathbf{v}$$

$$\mathbb{T}^\delta + \left( \frac{\mathbf{J}_s \otimes \mathbf{J}_s}{\rho c(1-c)} \right)^\delta = 2\nu \mathbb{D}^\delta(\mathbf{v})$$

$$((1-c)\mathbb{T}_s - c\mathbb{T}_w) = 2\tilde{\nu} \mathbb{D} \left( \frac{\mathbf{J}_s}{\rho c(1-c)} \right)$$

$$\pi + \rho c(1-c) \left( \frac{\partial \mu}{\partial \rho} \nabla \rho + \frac{\partial \mu}{\partial c} \nabla c + \alpha \frac{\partial \mu}{\partial \vartheta} \nabla \vartheta \right) + \mathbb{T} \nabla c = -k \mathbf{J}_s$$

$$\frac{(\mathbf{J}_q + \mathbf{J}_e - \mu \mathbf{J}_s - \mathbf{J}_{ek})}{\vartheta} + (1-\alpha) \rho c(1-c) \frac{\partial \mu}{\partial \vartheta} \frac{\mathbf{J}_s}{\rho c(1-c)} = -\frac{\kappa}{\vartheta} \nabla \vartheta$$

## Final constitutive relations

$$\rho + \frac{4}{3} \frac{|\mathbf{J}_s|^2}{\rho c(1-c)} + \frac{1}{3} \text{tr} \mathbb{T} = \frac{2\nu + 3\lambda}{3} \text{div } \mathbf{v}$$

$$\mathbb{T}_s^\delta + \mathbb{T}_w^\delta = 2\nu \mathbb{D}^\delta(\mathbf{v})$$

$$((1-c)\mathbb{T}_s - c\mathbb{T}_w) = 2\tilde{\nu} \mathbb{D}(\mathbf{u}_s - \mathbf{u}_w)$$

$$\pi + \rho c(1-c) \left( \frac{\partial \mu}{\partial \rho} \nabla \rho + \frac{\partial \mu}{\partial c} \nabla c + \alpha \frac{\partial \mu}{\partial \vartheta} \nabla \vartheta \right) + \mathbb{T} \nabla c = -k \mathbf{J}_s$$

$$\frac{(\mathbf{J}_q + \mathbf{J}_e - \mu \mathbf{J}_s - \mathbf{J}_{e_k})}{\vartheta} + (1-\alpha) \rho c(1-c) \frac{\partial \mu}{\partial \vartheta} \frac{\mathbf{J}_s}{\rho c(1-c)} = -\frac{\kappa}{\vartheta} \nabla \vartheta$$

# Heat and entropy fluxes

- Let us inspect the final form of heat flux  $\mathbf{q}$  and entropy flux  $\mathbf{J}_\eta$

$$\begin{aligned}\mathbf{q} &= -\kappa \nabla \vartheta + \mathbf{J}_e + \mathbf{J}_{e_k} + \mathbf{J}_T \\ &+ \left( c \frac{\partial e_s}{\partial c} + (1-c) \frac{\partial e_w}{\partial c} - \alpha \vartheta \frac{\partial}{\partial c} (c \eta_s + (1-c) \eta_w) \right) \mathbf{J}_s \\ \mathbf{J}_\eta &= \frac{1}{\vartheta} (\mathbf{q} - 2\mathbf{J}_{e_k} - \mathbf{J}_T - \mu \mathbf{J}_s) \\ &= -\frac{\kappa}{\vartheta} \nabla \vartheta - (1-\alpha) \frac{\partial \mu}{\partial \vartheta} \mathbf{J}_s\end{aligned}$$

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- Choice of  $\alpha$ ?:  $\alpha = 0$

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$$\begin{aligned}\mathbf{J}_\eta &= \frac{1}{\vartheta} (\mathbf{q} - 2\mathbf{J}_{e_k} - \mathbf{J}_T - \mu \mathbf{J}_s) \\ &= -\frac{\kappa}{\vartheta} \nabla \vartheta + (\eta_s - \eta_w) \mathbf{J}_s + \left( c \frac{\partial \eta_s}{\partial c} + (1-c) \frac{\partial \eta_w}{\partial c} \right) \mathbf{J}_s\end{aligned}$$

- Choice of  $\alpha$ ?:  $\alpha = 0$
- satisfactory - no entropy contribution in heat flux  $\mathbf{q}$  + correct diffusive term present in entropy flux  $\mathbf{J}_\eta$



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- Of particular interest is the quantity  $\vartheta \mathbf{J}_\eta - \mathbf{q}$

# Comparison $\vartheta \mathbf{J}_\eta - \mathbf{q}$

- Our result

$$\vartheta \mathbf{J}_\eta - \mathbf{q} = -\mathbf{J}_{\text{ek}} - \mathbf{J}_\mathbb{T} - \frac{\partial}{\partial c}(c\Psi_s + (1-c)\Psi_w)\mathbf{J}_s$$

- Fluid Mixture theory of Bowen (1976) (entropy flux postulated)

$$\vartheta \mathbf{J}_\eta - \mathbf{q} = -\mathbf{J}_{\text{ek}} - \mathbf{J}_\mathbb{T} - (\Psi_s - \Psi_w)\mathbf{J}_s$$

- Müller (1984) theory for mixtures of non-viscous fluids (entropy flux derived)

$$\vartheta \mathbf{J}_\eta - \mathbf{q} = -\mathbf{J}_{\text{ek}} - \mathbf{J}_\mathbb{T} - (\Psi_s - \Psi_w)\mathbf{J}_s$$

# Evolution equation for $\mathbf{J}_s$

$$\begin{aligned} \frac{d\mathbf{J}_s}{dt} &= -\mathbf{J}_s \bullet (\nabla \mathbf{v} - (\operatorname{div} \mathbf{v}) \mathbb{I}) - \operatorname{div} \left( \frac{1}{\rho} \left( \frac{1}{c} - \frac{1}{1-c} \right) \mathbf{J}_s \otimes \mathbf{J}_s \right) \\ &+ \operatorname{div} ((1-c) \mathbb{T}_s - c \mathbb{T}_w) + \mathbb{T} \nabla c + \boldsymbol{\pi} \end{aligned}$$

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Using the constitutive relations for  $\boldsymbol{\pi} + \mathbb{T} \nabla c$  and  $(1-c) \mathbb{T}_s - c \mathbb{T}_w$ :

$$\begin{aligned} \frac{d\mathbf{J}_s}{dt} &= -\mathbf{J}_s \bullet (\nabla \mathbf{v} - (\operatorname{div} \mathbf{v}) \mathbb{I}) + \operatorname{div} \left( \frac{1}{\rho} \left( \frac{1}{c} - \frac{1}{1-c} \right) \mathbf{J}_s \otimes \mathbf{J}_s \right) \\ &+ \operatorname{div} \left( 2\tilde{\nu} \nabla_{\operatorname{sym}} \left( \frac{\mathbf{J}_s}{\rho c(1-c)} \right) \right) - \rho c(1-c) \left( \frac{\partial \mu}{\partial \rho} \nabla \rho + \frac{\partial \mu}{\partial c} \nabla c \right) - k \mathbf{J}_s \end{aligned}$$

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Provided fast relaxation  $\frac{d\mathbf{J}_s}{dt} \sim 0$  and neglecting non-linear terms in  $\mathbf{v}, \mathbf{J}_s$ , and assuming  $\tilde{\nu} \sim 0$ , one obtains

$$k \mathbf{J}_s \sim -\rho c(1-c) \left( \frac{\partial \mu}{\partial \rho} \nabla \rho + \frac{\partial \mu}{\partial c} \nabla c \right)$$

# Conclusions

- Key features of the presented model: reformulation in traditional variables  $\rho$ ,  $c$ ,  $\mathbf{v}$ ,  $\vartheta$  and also  $\mathbf{J}_s$ , for all of them evolution equations are available - equivalent to 2 mass balances, 2 momentum balances and single energy balance (class II mixtures (Hutter))
- Minimal scenario for Helmholtz potential implied by balance eq.

$$\Psi(\rho, c, \vartheta, \mathbf{J}_s) = c\Psi_s(\rho, c, \vartheta) + (1 - c)\Psi_w(\rho, c, \vartheta) + \frac{1}{2} \frac{|\mathbf{J}_s|^2}{\rho^2 c(1 - c)}$$

fits well the framework of earlier mixture theories.

- Choice of rate of entropy production - satisfaction of 2nd law of thermodynamics
- Maximization of r.e.p.  $\rightarrow$  constitutive equations

## Conclusions II

- Classical viscous-fluid relations for fluid part  $\mathbb{T}_s + \mathbb{T}_w \sim \mathbb{D}(\mathbf{v})$
- Additional relation for  $(1 - c)\mathbb{T}_s - c\mathbb{T}_w \sim \mathbb{D}(\mathbf{u}_s - \mathbf{u}_w)$
- Interaction force  $\boldsymbol{\pi}$  contains all relevant (for diffusion) mechanisms.
- Energy and entropy flux consistent extensions of theories of Müller and Bowen.
- "Physical" limit of evolution eq. for diff. flux  $\mathbf{J}_s$  yields classical Fick's diffusion.

Thank you for your attention!