

Continuum Mesoscopic Thermodynamics applied to Chemical Reacting Systems

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Introdução

This work intends to propose a mesoscopic continuum model to describe simple chemical reactions that depend solely on the particles orientations. The results of this project could be of interest for the development of chemical reactors, and modeling the thermochemical behavior of geological fluids. Furthermore, this work could be a reference one for the development of continuous mesoscopic models for more complex materials, such as polymers, metal, alloys, and crystalline solids, among others.

Resultados e Discussão

Characteristics of the system:

1. The model reaction taken into account in this study is $A+A \rightarrow B+B$, where the constituents A and B are considered rigid, and they possess a planar shape, or they are needle-shaped.
2. One assumes that the solution (mixture) consists of a heat conducting Newtonian fluid in which the concentration of A is much higher than that of the constituent B . This consideration is a theoretical artifice to ensure that the solution thermodynamics is described as that of the main fluid.
3. The chemical reactions are influenced by possibility of preferential orientation of the system particles only. This orientations is determined by the microscopic director $\mathbf{n} \in S^2$ (see figure 1), where S^2 is unit sphere manifold.

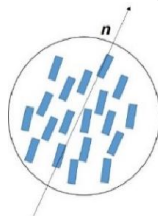


Figure 1. The arrangement (a sketch) of rod-like particles at a region of system under consideration.

Balance equations

In this work, just the balance equations in the mesoscopic space for solution are outlined:

- ✓ **Mass:** $\frac{d\rho}{dt} + \rho \operatorname{div}(\mathbf{v}) + \rho \nabla_n \cdot (\mathbf{w}) = 0$.
- ✓ **Linear Momentum:** $\rho \frac{d\mathbf{v}}{dt} - \operatorname{div}(\mathbf{T}^T) - \nabla_n \cdot (\mathbf{J}^T) - \rho \mathbf{k} = 0$.
- ✓ **Angular velocity:** $\rho \mathbf{I} \frac{d\bar{\mathbf{w}}}{dt} - \operatorname{div}(\mathbf{W}^T) - \nabla_n \cdot (\mathbf{W}^T) - \hat{\mathbf{t}} - \check{\mathbf{t}} - \rho \mathbf{g} = 0$.

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✓ **Energy:** $\rho \frac{d\varepsilon}{dt} + \operatorname{div}(\boldsymbol{\phi}) - \nabla_n \cdot (\hat{\boldsymbol{\phi}}) - \mathbf{T} : \operatorname{grad}(\mathbf{v}) - \mathbf{W} : \operatorname{grad}(\mathbf{w}) - \mathcal{T} : \nabla(\mathbf{v}) - \mathcal{W} : \nabla(\mathbf{w}) + \mathbf{w} \cdot (2\hat{\mathbf{t}} + 2\check{\mathbf{t}}) - \rho r = 0$.

✓ **Entropy:** $\rho \sigma = \rho \frac{ds}{dt} - \operatorname{div}(\boldsymbol{\varphi}) - \nabla_n \cdot (\boldsymbol{\varphi}) - \rho \eta \geq 0$.

Constitutive model

In this work, the constitutive model employs the following sets of independent (\mathcal{J}) and dependent (\mathcal{G}) constitutive variables

$$\mathcal{J} \in [\rho, c_\alpha, \operatorname{grad}(c_\beta), \mathbf{D}, \mathbf{A}, \operatorname{grad}(\mathbf{w}), \theta, \operatorname{grad}(\theta)]$$

$$\mathcal{G} \in [\mathbf{J}_\alpha, \chi_\alpha, \varepsilon, s, \boldsymbol{\phi}, \mathbf{T}, \mathbf{W}, \boldsymbol{\varphi}]$$

To create a link between the balance of entropy and the remaining balances, the method of Lagrange multipliers is employed, as proposed by Liu [1]. By using this method, we obtain some results:

1. Definition of chemical potential μ_α and hydrostatic pressure p in terms of the Lagrange multipliers,

$$\mu_\alpha = -\frac{\Lambda^{c_\alpha}}{\Lambda^\varepsilon} \quad e \quad p = -\rho \frac{\Lambda^p}{\Lambda^\varepsilon}$$

2. The thermodynamic potential $\psi = \varepsilon - \theta s$, which in differential form is

$$d\psi = \frac{p}{\rho^2} d\rho + \sum_{\alpha=1}^{v-1} \mu_\alpha dc_\alpha - s d\theta$$

3. The extra entropy flux vector, $\mathbf{h} = \boldsymbol{\varphi} - \sum_{\alpha=1}^{v-1} \Lambda^{c_\alpha} \mathbf{J}_\alpha - \Lambda^\varepsilon \boldsymbol{\phi}$, which takes into account all deviations of the entropy flux vector in relation to the heat and diffusive flux vectors, does not amount to a restriction.

Conclusões

The equation for the thermodynamic potential coincides with the Helmholtz relation of the classical thermostatics. However, the former is more comprehensive than that of classical thermostatics because it holds for any point of the solution and it is valid under equilibrium and non-equilibrium conditions. Furthermore, the thermodynamic potential ψ takes into account the microscopic structure of the particles of the considered system.

In order to investigate the validity of the thermodynamic potential, the integrability conditions obtained from the Lagrange multipliers are used. However, such investigation is not presented in this text.

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¹Liu, I. S., *Arch. Rat. Mech. Anal.* 1972, 46, 131.