JOURNAL OF MECHANICS OF CONTINUA AND
MATHEMATICAL SCIENCES
www.journalimcms.org

ISSN (Online) : 2454 -7190 Vol.-20, No.-8, August (2025) pp 71 - 76 ISSN (Print) 0973-8975

ON THE EQUATION OF STATE IN STRUCTURE WITH ENERGY AND CHEMICAL POTENTIALS - A STATE OF THE ART SHORT COMMUNICATION

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https://doi.org/10.26782/jmcms.2025.08.00005

(Received: May 03, 2025; Revised: July 19, 2025; Accepted: August 04, 2025)

Abstract

This article presents a state of the art of the author's works on problems of energy in structures with thermal and chemical potentials. The theoretical considerations are conducted to present the energy equations in such a structure. The thermodynamics state equations are given.

Keywords: Chemical Potential, Energy Potential, Heat Flow, State Equations, Thermomechanics

I. Introduction

The analysis of the effects of thermal diffusion in solids is important because of its significance for material properties [I]. A thermomechanical model for the equation of energy in a structure with thermal and chemical potentials is presented. This model is based on the author's theoretical investigations of this problem [II-IV]. A general form of the energy balance law incorporating chemical diffusion and present associated dissipation conditions and state equations is derived. The explanation of the issue that inspired this theoretical investigation is that chemical potentials influence materials properties as well as the energy equation.

In the author's model, the analysis is conducted to determine the effects considering gradients in chemical concentration, in composition, in stress, and temperature. There is no specific experimental verification of the model presented, but numerical results from one of the author’s previous works (e.g., [II]) show how the framework was applied to welding and diffusion problems. The potential future applications of the theory can be, for instance, in additive manufacturing, thermal barrier coatings, or reactive transport in porous media. Some diagrams showing how the state variables, i.e., temperature, composition, and strain, relate to material parameters can be found in [II].

II. Energy equation

The physical interpretations and derivations for each introduced here, the quantity can be found in textbook (see [V] for instance). We use the standard notations in the paper for the variables considered.

From the first law of thermodynamics and the kinetic energy theorem, we obtain the relation as to the internal energy variation de during the time interval dt as

$$\Omega\frac{\mathrm{de}}{\mathrm{dt}}+\mathrm{e}\,\mathrm{div}\mathbf{v}=-\mathrm{div}\left(\mathrm{e}_{\mathrm{c}}\mathbf{u}\right)+\boldsymbol{\sigma}\frac{\mathrm{d}\boldsymbol{\varepsilon}}{\mathrm{dt}}+\mathrm{r}-\mathrm{div}\,\mathbf{q} \tag{1}$$

where Ω is the domain considered, $\boldsymbol{\sigma}$ is the stress tensor, $\boldsymbol{\varepsilon}$ is the strain tensor, $\mathbf{q}$ is the heat flow vector, and r represents the volume rate density of the heat provided to the domain Ω, e_c is the internal chemical potential energy, $\mathbf{v}$ is the material velocity, and $\mathbf{u}$ is the diffusion velocity. The total entropy s reads

$$\frac{\mathrm{d}}{\mathrm{dt}}\int_{\Omega}\mathrm{s}\,\mathrm{d}\Omega=\int_{\Omega}\left[\frac{\partial\mathrm{s}}{\partial\mathrm{t}}+\mathrm{div}\left(\mathrm{s}\,\mathbf{v}\right)+\mathrm{div}\left(\mathrm{s}_{\mathrm{c}}\,\mathbf{u}\right)\right]\mathrm{d}\Omega \tag{2}$$

Where s_c is the entropy of the diffusing material.

Since the volume integral must be non-negative for any subsystem Ω.

$$\frac{\mathrm{ds}}{\mathrm{dt}}+\mathrm{s}\,\mathrm{div}\,\mathbf{v}+\mathrm{div}\left(\mathrm{s}_{\mathrm{c}}\,\mathbf{u}\right)+\mathrm{div}\frac{\mathbf{q}}{\mathrm{T}}-\frac{\mathrm{r}}{\mathrm{T}}\geq 0 \tag{3}$$

where T is the absolute temperature.

The above equality, throughout the multiplication it by $d\Omega$, becomes

$$\frac{\mathrm{d}}{\mathrm{dt}}\left(\mathrm{s}\mathrm{d}\Omega\right)+\mathrm{div}\left(\mathrm{s}_{\mathrm{c}}\,\mathbf{u}\right)\mathrm{d}\Omega+\left(\mathrm{div}\frac{\mathbf{q}}{\mathrm{T}}-\frac{\mathrm{r}}{\mathrm{T}}\right)\mathrm{d}\Omega\geq 0 \tag{4}$$

What gives the second law for the elementary material system

Let ψ_c be the free enthalpy of the chemical potential defined by

$$\psi_{\mathrm{c}}=\mathrm{e}_{\mathrm{c}}-\mathrm{T}\mathrm{s}_{\mathrm{c}} \tag{5}$$

where s_c is the entropy of chemical potential.

Let ψ be the free volume energy defined by

$$\psi=\mathrm{e}-\mathrm{Ts} \tag{6}$$

By (4), we have

$$\boldsymbol{\sigma}\frac{d\boldsymbol{\varepsilon}}{dt}-s\frac{dT}{dt}-\frac{d\psi}{dt}-\psi\operatorname{div}\mathbf{v}-s_c\mathbf{u}\operatorname{grad}T-\operatorname{div}(\psi_c\mathbf{u})-\frac{\mathbf{q}}{T}\cdot\operatorname{grad}T\geq 0 \qquad (7)$$

and using the identity

$$\operatorname{div}(\psi_c\,\mathbf{u})=\mathbf{u}\cdot\operatorname{grad}\psi_c+\psi_c\operatorname{div}\mathbf{u} \qquad (8)$$

we get

$$\boldsymbol{\sigma}\frac{d\boldsymbol{\varepsilon}}{dt}-\psi_c\operatorname{div}\mathbf{u}-s\frac{dT}{dt}-\frac{d\psi}{dt}-\psi\operatorname{div}\mathbf{v}-\mathbf{u}[\operatorname{grad}\psi_c+s_c\operatorname{grad}T]-\frac{\mathbf{q}}{T}\cdot\operatorname{grad}T\geq 0 \qquad (9)$$

Eq. (9) is the fundamental inequality extended to thermal and chemical phenomena.

We denote by φ the left-hand side of inequality (9), which is the dissipation per unit initial volume $d\Omega$.

The second law requires the dissipation φ and the associated internal entropy production φ/T to be non-negative

$$\varphi=\varphi_1+\varphi_2+\varphi_3\geq 0 \qquad (10)$$

where

$$\varphi_1=\boldsymbol{\sigma}\frac{d\boldsymbol{\varepsilon}}{dt}-\psi_c\operatorname{div}\mathbf{u}-s\frac{dT}{dt}-\frac{d\psi}{dt}-\psi\operatorname{div}\mathbf{v} \qquad (11)$$

is the intrinsic volume dissipation described in small deformation theory

$$\varphi_2=-\frac{\mathbf{q}}{T}\cdot\operatorname{grad}T \qquad (12)$$

$$\varphi_3=-\mathbf{u}\,[\operatorname{grad}\psi_c+s_c\operatorname{grad}T] \qquad (13)$$

where φ_2 is the thermal dissipation associated with heat conduction and dissipation associated with mass transfer.

If we define $\varphi_m = \varphi_1 + \varphi_3$, then the energy equation (1) can be rewritten as

$$T\left[\frac{ds}{dt}+s\operatorname{div}\mathbf{v}+\operatorname{div}(s_c u)\right]=r-\operatorname{div}\mathbf{q}+\varphi_m \qquad (14)$$

Assume that free energy is a function of variables T, ε_{ij}, C,$\boldsymbol{\kappa}$, where T denotes temperature, C concentration, and ε_{ij} strain components. Assume that the hardening state is characterized by an internal variable $\boldsymbol{\kappa}$ These variables are a set of state variables which characterize the state of the system. If grad T = $\mathbf{u}$ = 0, the non-negativeness of intrinsic dissipation φ_1 is derived independently of the non-negativeness of total dissipation φ

$$\varphi_1 = \boldsymbol{\sigma}\frac{d\boldsymbol{\varepsilon}}{dt} + \psi_c\frac{dC}{dt} - s\frac{dT}{dt} - \frac{d\psi}{dt} \geq 0 \qquad (15)$$

The above results from the second law.
From the intrinsic dissipation (15), we obtain

$$\left(\boldsymbol{\sigma} - \frac{\partial\psi}{\partial\boldsymbol{\varepsilon}}\right)\frac{d\boldsymbol{\varepsilon}}{dt} + \left(\psi_c - \frac{\partial\psi}{\partial C}\right)\frac{dC}{dt} - \frac{\partial\psi}{\partial\boldsymbol{\kappa}}\cdot\frac{\partial\boldsymbol{\kappa}}{dt} - \left(s - \frac{\partial\psi}{\partial T}\right)\frac{dT}{dt} \geq 0 \qquad (16)$$

where

$$\frac{\partial\psi}{\partial\boldsymbol{\kappa}}\cdot\frac{d\boldsymbol{\kappa}}{dt} = \frac{\partial\psi}{\partial\boldsymbol{\kappa}}\cdot\dot{\boldsymbol{\kappa}} \qquad (17)$$

Then the non-negativeness of the intrinsic dissipation gives

$$s = -\frac{\partial\psi}{\partial T} \qquad \boldsymbol{\sigma} = \frac{\partial\psi}{\partial\boldsymbol{\varepsilon}} \qquad \psi_c = -\frac{\partial\psi}{\partial C} \qquad (18)$$

The above equations yield the symmetry relations

$$\frac{\partial s}{d\varepsilon_{ij}} = -\frac{\partial\sigma_{ij}}{\partial T} \quad \frac{\partial s}{\partial C} = -\frac{\partial\psi_c}{\partial T} \quad \frac{\partial\sigma_{ij}}{d\varepsilon_{kl}} = \frac{\partial\sigma_{kl}}{\partial\varepsilon_{ij}} \quad \frac{\partial\psi_c}{d\varepsilon_{ij}} = -\frac{\partial\sigma_{ij}}{\partial C} \qquad (19)$$

The thermodynamic states of a material are characterized by external variables T, ε_{ij}, C, and internal variables ε_{ij}^{p} plastic strain and $\boldsymbol{\kappa}$.
We have

$$\psi = \psi\left(T, \varepsilon_{ij}, C, \varepsilon_{ij}^{p}, \boldsymbol{\kappa}\right) \qquad (20)$$

on account of the local state postulate. The variables appearing in the bracket are a set of state variables that characterize the state of an open system.
The state equations read

$$s = -\frac{\partial\psi}{\partial T} \qquad \boldsymbol{\sigma} = \frac{\partial\psi}{\partial\boldsymbol{\varepsilon}} \qquad \psi_c = -\frac{\partial\psi}{\partial C} \qquad s_c = -\frac{\partial\psi_c}{\partial T} \qquad (21)$$

The above equations are based on the normality of external variables T, ε_{ij} and C with regard to the whole set of state variables.

The expression of free energy ψ with respect to variables T, ε_{ij}, C, and ε_{ij}^{p} can be presented as

$$\begin{aligned}\psi = \boldsymbol{\sigma}^{o}\left(\boldsymbol{\varepsilon}-\boldsymbol{\varepsilon}^{p}\right)-s_{o}T+\frac{1}{2}\left(\boldsymbol{\varepsilon}-\boldsymbol{\varepsilon}^{p}\right)\mathbf{C}\left(\boldsymbol{\varepsilon}-\boldsymbol{\varepsilon}^{p}\right)-C\,\mathbf{B}\left(\boldsymbol{\varepsilon}-\boldsymbol{\varepsilon}^{p}\right)\\ -\theta\,\mathbf{A}\left(\boldsymbol{\varepsilon}-\boldsymbol{\varepsilon}^{p}\right)-\frac{1}{2}\frac{c_{\varepsilon}}{T_{o}}\theta^{2}-Ts_{c}C-\frac{1}{2}\frac{M}{T_{o}}C^{2}+U(\boldsymbol{\kappa})\end{aligned} \tag{22}$$

where $\theta = T - T_o$ and $U(\boldsymbol{\kappa})$ is the frozen energy due to hardening, c_ε is the volume heat capacity, **A**, **B**, **C** and M are material parameters. The thermomechanical state equations are

$$\begin{aligned}\boldsymbol{\sigma} = \boldsymbol{\sigma}_{o}+\mathbf{C}\left(\boldsymbol{\varepsilon}-\boldsymbol{\varepsilon}^{p}\right)-\mathbf{B}\,C-\mathbf{A}\,\theta\\ s = s_{o}+Cs_{c}+\mathbf{A}\left(\boldsymbol{\varepsilon}-\boldsymbol{\varepsilon}^{p}\right)+\frac{MC}{T_{o}}+\frac{c_{\varepsilon}\theta}{T_{o}}\end{aligned} \tag{21}$$

III. Conclusion

This paper shows the state of the art for thermal and chemical problems in structure determining the combined effects of gradients in interstitial concentration, in solvent composition, in stress, and temperature. These results are based on the author's works. There is no specific experimental verification of the model carried out by the author, but numerical results are provided from one of the author’s previous works (e.g., [II]) showing how the framework was applied to welding and diffusion problems. The potential future applications of the theory presented here can be applied in the analysis of additive manufacturing, thermal barrier coatings, and reactive transport in porous media, for instance.

Conflict of Interest:

The author declares that there was no relevant conflict of interest regarding this paper.

References

I. Shewmon P. G.: Diffusion in Solids. McGraw-Hill, New York,1963**.** 10.4236/msce

II. Sluzalec A. Thermoplasticity with diffusion in welding problems, *International Journal for Numerical Methods in Engineering*, 74, 8, 2008, pp 1329-1343. 10.1002/nme.2214

III. Sluzalec A. Materials with Thermo-Diffusive Hardening, *Advanced Materials Research*, 284-286, 2011 pp1643-1646. 10.4028/www.scientific.net/AMR.284-286.1643

IV. Sluzalec A. Introduction to Nonlinear Thermomechanics, Spinger, 1996. 10.1007/978-1-4471-1906-7

V. Sluzalec A. Theory of metal forming plasticity, Springer,2004. 10.1007/978-3-662-10449-1