MECHANO-CHEMISTRY AT DIFFERENT LENGTH SCALES

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Abstract

Following Darken [1], Brenner [2] and Öttinger's [3] theories we recently postulated that the volume velocity defines the local material velocity at nonequilibrium [4]. It allowed fixing the unique frame of reference for all internal transport processes, thermodynamics in general. This frame of reference allows the use of the Navier-Lamé equation of mechanics of solids. Proposed modifications of Navier-Lamé and energy conservation equations are self-consistent with the literature for solid-phase continua dating back to the classical experiments of Kirkendall and their interpretation by Darken. No basic changes are required in the foundations of linear irreversible thermodynamics except recognizing the need to add volume density to the usual list of extensive physical properties undergoing transport in every continuum.

We define the volume density and using the Euler's and Lagrange theorems derive: the volume continuity equation, the equation of motion and energy conservation equations. We present the equivalence of presented and Darken methods when Darken restriction are introduced and the consistency of the Newton laws with thermodynamics. The method fulfills the following conditions:

1. The local acceleration of the mixture depends on its mass, not on its internal energy.
2. The local centre of mass position is not be affected by any diffusion process (mass diffusion, heat transport, internal friction etc.).
3. The volume velocity (υ, i.e., the material velocity) is a unique internal frame of reference for all processes: diffusion, deformation, viscosity, heat transport etc.
4. The nonbalanced diffusion fluxes affect the local volume velocity.

The following equations govern the transport in compressible multicomponent mixtures. The volume continuity equation:

$$\operatorname{div}\left(\sum_{i=1}^{r} c_i \Omega_i \upsilon_i\right) = 0,$$

where $\Omega_i\left(N_1,...,N_r;T,p\right)$ denotes the partial molar volume. The mass conservation law:

$$\frac{\partial c_i}{\partial t} + \operatorname{div}\left(c_i \upsilon_i\right) = 0;$$

the equation of motion:

$$\rho \left.\frac{\mathrm{D}\upsilon}{\mathrm{D}t}\right|_{\upsilon} = \mathrm{Div}\left(\sigma^e + \sigma^p\right) - \sum_{i=1}^{r} c_i \mathrm{grad}\mu_i^{ch} - \rho \mathrm{grad} V^{ext},$$

where μ_i^{ch} is the chemical potential. The mechanical and thermal energy conservation equations:

$$\sum_{i=1}^{r} c_i \left.\frac{\mathrm{D}\mu_i^*}{\mathrm{D}t}\right|_{\upsilon} = \sigma^e : \mathrm{Grad}\,\upsilon + \upsilon \sum_{i=1}^{r} c_i \mathrm{grad}\mu_i^{ch} + \sum_{i=1}^{r} c_i \upsilon_i^d \,\mathrm{grad}\,\mu_i^*,$$

$$\rho \frac{\mathrm{D}Ts}{\mathrm{D}t}\bigg|_{\upsilon} = \sigma^{p} : \mathrm{Grad}\,\upsilon - \mathrm{div}\,J_q - \sum_{i=1}^{r} c_i \upsilon_i^d \,\mathrm{grad}\,\mu_i^* .$$

where μ_i^* is the mechano-chemical potential. The last terms in above equations describe the fact that diffusion (entropy production) does not affect internal energy of the mixture. Namely, that entropy is produced at the expense of mechanical energy of the mixture.

The drift velocity is the unique frame of reference for the diffusion and the volume continuity equation allows defining it quantitatively:

$$\mathrm{div}\left(\sum_{i=1}^{r} c_i \Omega_i \upsilon_i\right) = \mathrm{div}\left(\upsilon^{drift} + \sum_{i=1}^{r} c_i \Omega_i \upsilon_i^d\right) = \mathrm{div}\left(\upsilon^{drift} + \sum_{i=1}^{r} \Omega_i J_i^d\right) = 0 .$$

The local momentum density depends on the diffusion of mass as well as on all other transport processes. The momentum due to the diffusion can be locally compensated by the Darken velocity. In such a case the overall volume velocity in the momentum balance is: $\upsilon = \upsilon^{\sigma} + \upsilon^{tr}$ and complete the condition, that the local acceleration of the body depends on its mass, not on its internal energy and that the local centre of mass position is not affected by diffusion.

The method is applied to investigate the Planck-Kleinert Crystal hypothesis [5]. Crystal is the ideal cubic fcc crystal formed by Planck particles. In this type of quasi-continuum the energy, momentum and mass transport are described by the presented above classical balance equations and volume continuity equation. It will be shown that transverse wave can be interpreted as the electromagnetic wave and its velocity equals the velocity of light. The quasi-stationary collective movement of mass in the crystal is equivalent to the *particle* (body) and such an approach enables derivation of the Schrödinger equation. The interstitial Planck particles (defects) create a deformation that is equivalent to the gravity field and the computed value of G is within the accuracy of experimental data. The model predicts four different force fields in the crystal lattice.

The consequence of the equation of internal energy conservation is the existence of waves involving temperature but not the mechanical potential variations. They are analogous to “the second sound” described by Landau and Lifschitz [6].

References

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