

Thermodynamics of mixtures with internal variables

Mauro Francaviglia

Dipartimento di Matematica , Università di Torino

Via C. Alberto

`mauro.francaviglia@unito.it`

Annunziata Palumbo

Dipartimento di Matematica , Università di Messina

Contrada Papardo, Salita Sperone

`apalumbo@unime.it`

Patrizia Rogolino

Dipartimento di Matematica , Università di Messina

Contrada Papardo, Salita Sperone

`patrizia@dipmat.unime.it`

In a number of applications, models of fluid continua are assumed to be represented by **mixtures**, i.e. the continua are supposed to be microscopically formed by two or more separate components having different specific physical properties. These models are particularly effective when they are used to describe the thermodynamical behaviour of composite materials, e.g. polymers, as well as fluxes through porous media and in presence of liquid Helium. In these situations the classical diffusion laws of Fick and Fourier, that relate linearly the mass gradient and the temperature to fluxes of mass and heat, respectively, are in general no longer applicable. Although these laws are valid under normal conditions, they do not lead to acceptable results since, e.g., they do not imply the propagation of perturbations with a finite velocity. Several models have been proposed in the past in literature but they turn out to be valid only in particular situations. More recently some theories have been proposed with the aim of extending the classical description: Extended Thermodynamics, Extended Irreversible Thermodynamics, General Equation for the Non-Equilibrium Reversible-Irreversible Coupling. This problem of mixtures has been also studied in the framework of mesoscopic theory; in particular, some of us (A.P.,P.R.) deduced in the evolution equations for dissipative fluxes characterizing hyperbolicity for the fundamental systems of differential equations.

Whenever a continuum is composed as two or more "internal phases", the properties are in general known not as single deterministic components but rather as suitable averages of microlocal phenomena, a convenient modelization technique may pass through the use of so-called "*internal variables*". These represent phenomena occurring at the microscopic or at the mesoscopic level that cannot be controlled in their full detail but only in average over small portions of the continuum. These microlocal phenomena (which are typical of non-equilibrium and dissipation processes) are thus summarized into a set of extra variables, the so-called "internal variables" which depend on the model chosen and obey a number of phenomenological equations. Usually, the internal variables enter directly the state functions and the constitutive laws, but it is sometimes convenient to adopt more general models in which these averages are non-uniform in space so that the internal variables appear together with their space gradients.

In the framework of thermodynamics of continua with internal variables one is often able to better understand the overall behaviour of the continuum in situations far from equilibrium and in the presence of dissipative phenomena. A recent line of research initiated by two of us (M. F. and P. R.) in collaboration with others has provided a systematic suitable geometrized method for deducing the entropy production, the thermodynamical restrictions on free energy, the so-called extra flux of entropy due to internal variables, the Clausius-Duhem inequality and the evolution equations for the heat flux \mathbf{q} . The method applies at least whenever a material is considered to be a simple material in the sense of Coleman and Noll endowed with a number of internal variables representing micro- or mesoscopic phenomena to be controlled as a whole on the basis of phenomenological evolutive equations.

The general theory - which allows to generate the entropy function, the extra flux and all other relevant quantities out of the "process method" by mean of integrals which contain from the very beginning terms in dt (t being Galilean time) - has been applied to a number of physically relevant continua with internal variables, like e.g. polarizable and magnetizable media, materials with an internal metric or materials with grain or other microlocal structures.

Our purpose is to extend the application of this method to the study of mixtures under the hypothesis that the single components are treated as internal variables (out of equilibrium). The method is thence applied to the case of a mixture with N internal scalar components ($N \geq 2$). General thermodynamical restrictions are obtained for the extra flux of entropy and the relevant residual dissipation inequality is derived both in presence or absence of viscosity. Moreover we will apply these results to simple case of a binary mixtures under linear constitutive hypothesis.

References

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