J. Non-Newtonian Fluid Mech. 96 (2001) 1–3

Journal of Non-Newtonian Fluid Mechanics

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Editorial

Nonequilibrium thermodynamics and complex fluids

The application of thermodynamics to complex fluids, like polymeric liquids, dispersions, emulsions, etc. is by no means obvious. In fact, there is an overwhelming number of theories and a wide variety of approaches: classical nonequilibrium thermodynamics with internal variables, bracket formulations, continuum or rational thermodynamics, variational formulations, extended irreversible thermodynamics, the matrix model, network thermodynamics, and the general equation for the nonequilibrium reversible–irreversible coupling (GENERIC) formalism. In order to bring together and unify this variety of approaches and to achieve a common framework, suited for applications, a first international workshop was organized in 1996 in Montreal to discuss this matter (see workshop report by M. Grmela [1]). The common opinion was that it should be possible now to combine the various approaches in some kind of common generalized theory. The final goal is to bring nonequilibrium thermodynamics to the same level of clarity and usefulness as equilibrium thermodynamics. In order to achieve this, a second international workshop was organized in Oxford in August 2000.

In view of the promising recent developments in the field of nonequilibrium thermodynamics, a special issue of the *Journal of Non-Newtonian Fluid Mechanics* devoted to this subject was initiated. It is our pleasure, as guest editors of this special issue, to present the result of this initiative. Our intention was to offer a rather complete overview of the current status of the most important approaches to nonequilibrium thermodynamics and some relevant applications and special topics. We asked a number of prominent scientists to write either reviews or more specialized papers. We are glad that many of the requests were honored with valuable contributions, and our impression is that this special issue provides a well balanced introduction and overview of the current status of the various approaches to nonequilibrium thermodynamics in general and its application to complex fluids in particular.

The common root of all approaches to nonequilibrium thermodynamics (with Rational Thermodynamics as a notable exception) is classical *Equilibrium Thermodynamics*. A brief outline of the fundamentals of this subject, following the well-known textbook of Callen [2], is presented in the introductory paper by Jongschaap and Öttinger.

Classical Nonequilibrium Thermodynamics, as described, for instance, in the famous textbook by de Groot and Mazur [3] is still an important starting point for many applications to systems which are in some sense close to equilibrium. The concept of internal variables of state is often crucial in applications. In the paper by Lhuillier an application of this method to colloidal suspensions is described and a link to the two-fluid model of suspensions and the description of molecular mixtures is provided. An application

PII: S0377-0257(00)00185-3

with a diffusive internal variable of state is described in the paper by Drout and Maugin. Also based upon classical nonequilibrium thermodynamics is the paper by Rey on liquid crystal interfaces in which special variables, describing the interfacial dynamics, are discussed in some detail. The so-called *Matrix Model* for driven systems described in the paper by Jongschaap is essentially an extension of Classical Nonequilibrium Thermodynamics with a careful analysis of the role of internal and external variables. The paper gives a review of this method and its relation with other approaches, including control system theory.

The so-called **Extended Irreversible Thermodynamics** (EIT) is an extension of classical nonequilibrium thermodynamics in which the entropy may depend on the dissipative fluxes in addition to the classical hydrodynamic variables. A review of this method is provided in the paper by Jou and Casas-Vázquez. In this paper, EIT is compared to theories with internal variables, the GENERIC approach and the Matrix Model. In the paper by Depireux and Lebon, the problem of non-Fickian thermodynamics in a two component mixture is studied in the framework of EIT.

An important branch of nonequilibrium thermodynamics are methods based upon a *Bracket Formulation* of the underlying convective and dissipative equations. After presenting the basic idea of this method at a conference in Boulder, Colorado in the summer of 1983, M. Grmela explored and developed this field in great depth in many publications, starting with the paper [4]. A review of bracket formulations of nonequilibrium thermodynamics, including also the more recent double-generator formulation, known as GENERIC is provided in the paper by Beris. An atomistic approach to GENERIC, with a statistic mechanical formulation of the basic building blocks of GENERIC, is given in the paper by de Pablo and Öttinger, while Edwards and Dressler describe an application to nonequilibrium molecular dynamics, with emphasis on closure approximations. A further nice example of an application is provided by the paper of Wagner in which the Smoluchowski equation for colloidal suspensions is developed and analyzed through the GENERIC formalism.

Two papers of a fundamental nature are the contribution by Gorban et al., with a thorough discussion of the role of quasi-equilibrium states, and the contribution by Grmela in which a unifying framework for the treatment of externally driven systems in the context of multi-level realizations is presented.

The phenomenological *field* or *continuum formulations* of thermodynamics and the so-called *Rational Thermodynamics* are purely phenomenological. A review on this subject is provided in the paper by Muschick et al., and an extensive review on the inclusion of nonequilibrium thermodynamics into the framework of the Lagrangian formalism is given in the paper of Anthony. Finally, in the paper of Sieniutycz, the optimization of work in systems with complex fluids is discussed as an attempt to relate to the non-Newtonian fluids of particular interest to the readers of this journal.

The combined Workshop and Summer School on Nonequilibrium Thermodynamics and Complex Fluids was arranged as a satellite meeting of the 13th International Congress on Rheology in Cambridge, co-ordinated with the European Society of Rheology as EURORHEO 2000-1, and held at Keble College in Oxford on 14–18 August 2000. The meeting was attended by 62 participants from 16 countries. Offprints of all the papers in the present issue were available for the participants during the meeting. In the *summer school* part of the meeting, the main topics in the field were presented in review papers. New developments were presented in the *workshop* part (several workshop contributions are not included in this special issue). In addition, there was a free forum for discussing future directions.

The recent efforts in nonequilibrium thermodynamics, as for example, presented at the workshops in Montreal and Oxford, are strongly dominated by theoretical developments. For establishing the usefulness of the thermodynamic approach to a wider audience, and for distinguishing between different formalisms, it will be crucial to have experimental results, for example, on the thermal properties and the phase behavior of complex fluids. One of the issues of discussion in the Oxford meeting was the choice of variables in the various approaches. For future success in application to complex fluids, a flexible choice of structural variables is needed. On the one hand, the bracket formulations, including GENERIC, provide a very general framework, and the selection of specific variables clearly requires physical insight into the system of interest, whereas, on the other hand, EIT uses a very restricted set of variables, which seems to be too limited for general application to complex fluids. Another important issue is the inclusion of different levels of description including the atomistic approach. The key to successful future applications, of practical relevance, lies in the inclusion of these levels. This provides a sound foundation of the theories and in addition a connection with existing molecular models of particular systems.

Our impression, at the end of the workshop and concluding the editing of this special issue, is that a significant step forward in the direction of our final goal of unification has been made: a generally accepted consistent formulation of nonequilibrium thermodynamics seems to be emerging. The active researchers in the field become familiar with the different approaches and are seeking integration and combination of their efforts. A full unification in one single framework might not be attainable, and this is probably not even needed. As for instance in classical mechanics, where besides the common Newtonian dynamics also the Hamilton and Lagrangian formulations are available and each of them has specific advantages and disadvantages in particular cases, also in thermodynamics various approaches will remain. We anticipate that there will always be more restrictive formulations for isolated systems and more tractable formulations for driven systems. Most important, however, is that the validity of each of the methods and their interrelations should be investigated thoroughly. The final set of formulations should provide a useful tool for many applications, including the exciting area of complex fluids. Although, this goal has not yet been fully reached, we are glad to see at the workshops in Montreal (1996) and Oxford (2000) that many people are working very hard to approach it, and we hope that the present issue of the *Journal of Non-Newtonian Fluid Mechanics* will also contribute to this effort.

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