NONEQUILIBRIUM THERMODYNAMICS – A TOOL FOR APPLIED RHEOLOGISTS

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GENERIC is reviewed not only as a new general framework for modeling nonequilibrium systems, but also as a new way of thinking about nonequilibrium dynamics. This unified framework of nonequilibrium thermodynamics is shown to be deeply rooted in the ample accumulated experience with nonequilibrium systems and, provided that state variables with slow and fast time-evolution can be separated, the framework can actually be derived. In view of its natural capability of modeling systems on different levels of description, GENERIC is ideal for the highly topical attempts of "bridging scales" in science and engineering. The practical usefulness of GENERIC as a powerful tool in the phenomenological and structure-guided modeling of complex fluids is illustrated through two examples.

KEY-WORDS:
GENERIC, thermodynamic modeling, nonequilibrium thermodynamics, emulsions, blends, reptation

GENERIC wird nicht nur als allgemeiner Rahmen zur Modellierung von Nichtgleichgewichtssystemen präsentiert, sondern auch als völlig neuartige Sichtweise von Nichtgleichgewichtsdynamik. Es wird gezeigt, daß dieser vereinheitlichte Rahmen der Thermodynamik des Nichtgleichgewichts tief im umfassenden Erfahrungsschatz über Nichtgleichgewichtssysteme verankert ist und daß er sogar streng abgeleitet werden kann, vorausgesetzt daß die Zustandsvariablen mit langsamer und schneller Zeitentwicklung getrennt werden können. In Anbetracht der Tatsache, daß man mit GENERIC in natürlicher Weise Systeme auf verschiedenen Ebenen mit unterschiedlicher Auflösung beschreiben kann, ist dieser Formalismus ideal für die hochaktuellen Versuche, Skalen zu überbrücken. Die Nützlichkeit von GENERIC bei der phänomenologischen und durch ein molekulares Verständnis geleiteten Modellierung komplexer Flüssigkeiten wird durch zwei Beispiele belegt.

SCHLAGWORTE:
GENERIC, Thermodynamische Modellierung, Nichtgleichgewichts-Thermodynamik, Emulsionen, Mischungen, Reptation

1 INTRODUCTION

Have you ever had any doubts about the usefulness of *equilibrium* thermodynamics? Probably not. Rheologists active in various fields, say from materials science to food technology, are well-aware of the fundamental importance of phase diagrams in designing products with desirable properties, and of the key role played by equilibrium thermodynamics in constructing such phase diagrams.

Less predictable and less straightforward is your answer to the next question: Have you ever had any doubts about the usefulness of *nonequilibrium* thermodynamics? Not unlikely, you have not even been aware of the existence of a unified theory of nonequilibrium systems, comparable in scope and generality to the theory of equilibrium systems. The purpose of this contribution is

- to review the exciting recent developments towards a unified and general framework of nonequilibrium thermodynamics,
- to give a flavor of what this general framework is, of how it works, and of what, in principle and in practice, can or cannot be expected from such a formalism,
- and to illustrate its practical usefulness and potential to applied rheologists through selected examples.

The reward for reading this article should be a basic familiarity with a powerful new tool for modeling complex fluids in processing situations, in particular, under nonisothermal conditions or even when phase transitions, such as phase separation or crystallization, take place under non-quiescent conditions. In the author's opinion, in the next few years, the general tool of nonequilibrium thermodynamics will become increasingly important when treating complex fluids with an increasing number of relevant structural or internal variables.

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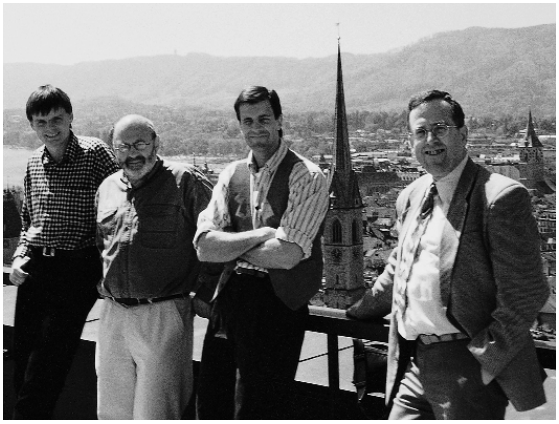
in particular, linear irreversible thermodynamics, was incorporated through the bracket formalism, the description of driven systems became clear through the matrix model, and the role of the degeneracy requirements was elucidated through the modern formulation of classical irreversible thermodynamics and through one-generator theories.

The GENERIC formalism is based on a large state space, that is, the hydrodynamic variables are supplemented by structural variables. This is in clear opposition to the use of functionals in rational thermodynamics or the theory of "simple fluids with fading memory" and, in the author's opinion, an important and necessary step in the right direction. If the total set of hydrodynamic and structural variables comprises all the slow state variables of the system, then the GENERIC formalism can actually be derived by projection-operator methods (while it was originally obtained by analyzing many examples of nonequilibrium systems, and by comparing their formulation on different levels of description).

Nonequilibrium thermodynamics probably is an even more important tool for engineers than equilibrium thermodynamics, for example, in connection with the processing of all kinds of non-Newtonian liquids. Nonequilibrium thermodynamics is obviously important if phase transitions, such as phase separation or crystallization, take place under flow conditions. The successful application of GENERIC to such problems depends on the possibility of obtaining the four building blocks of GENERIC [the two generators energy, E, and entropy, S, and the matrices L and M in Eq. 1)]. Thermodynamic modeling in terms of these basic building blocks is strongly advocated, rather than the direct formulation of time-evolution equations – with the same advantages as gained by working with a thermodynamic potential as a basic building block rather than with several equations of state in equilibrium thermodynamics. Experience with empirical expressions for the GENERIC building blocks needs to be collected by re-formulating and generalizing existing theories.

While microscopic expressions for the building blocks do exist, they will become useful in applications only when the numerical methods for handling these formal expressions



Some of the people interested in foundations of nonequilibrium thermodynamics. From right to left: Rob Jongschaap, Brian Edwards, Miroslav Grmela and Hans Christian Öttinger (Zürich, 2. May 1998)

are developed. In the same spirit as Monte Carlo simulations allow us an atomistic understanding of equilibrium physics, molecular dynamics and Brownian dynamics, as well as other advanced stochastic simulation techniques [29], will be the key to capitalizing on nonequilibrium thermodynamics in industrial applications. The basic tool for understanding structure-properties relationships is now available.

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