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NONEQUILIBRIUM THERMODYNAMICS: A POWERFUL TOOL FOR SCIENTISTS AND ENGINEERS

TERMODINÁMICA DE NO EQUILIBRIO: UNA PODEROSA HERRAMIENTA PARA CIENTÍFICOS E INGENIEROS

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RESUMEN: Se presenta el marco general de referencia de la termodinámica fuera de equilibrio con énfasis en los conceptos fundamentales en lugar de detalles matemáticos. Se centra la atención en la mecánica estadística subyacente y en las consecuencias para las técnicas de simulación termodinámicamente guiadas. La utilidad y la madurez de este marco general se ilustran mediante la revisión de un gran número de aplicaciones recientes lejos del equilibrio, donde se aplican las reglas de no linealidad. Por último, se ofrecen algunas perspectivas prometedoras para el futuro de la termodinámica de no equilibrio.

ABSTRACT: We present the two-generator framework of nonequilibrium thermodynamics with a strong emphasis on fundamental notions rather than mathematical details. The underlying statistical mechanics and the implications for thermodynamically guided simulation techniques are sketched briefly. The usefulness and maturity of the framework are illustrated by reviewing a large number of recent far-from-equilibrium applications, where nonlinearity rules. Finally, we offer some promising perspectives for the future of nonequilibrium thermodynamics.

1. INTRODUCTION

Thermodynamics occurs in the curriculum of every scientist or engineer. A typical course on thermodynamics is restricted to equilibrium phenomena. In most modern courses, thermodynamics is presented together with statistical mechanics; in many cases, statistical mechanics is even presented in the beginning of the course, as if thermodynamics could be derived from statistical mechanics. Historically, thermodynamics has of course been developed well before statistical mechanics, based on a multitude of experimental observations condensed into the fundamental laws of equilibrium thermodynamics. Moreover, thermodynamics has the beautiful geometric structure associated with Legendre transformations between pairs of conjugate extensive and intensive variables (“contact structure”) and is a full-fledged theory in its own right.

Whereas thermodynamics usually is not among the most popular courses, its laws and tools eventually prove useful to most scientists and engineers. In many applications, however, one would like to go beyond equilibrium thermodynamics. A typical example is provided by transport phenomena [1] which play a most important role in biology, chemical engineering, materials processing, mechanical engineering, and many other fields. Relaxation phenomena occurring

in many areas of application also belong to the world of nonequilibrium thermodynamics. Simplification by coarse-graining the description and focusing on the essence of a problem is an important key to successful engineering. A general course on statistical nonequilibrium thermodynamics would hence be at least as useful as a course on equilibrium thermodynamics.

The purpose of this article is to address the question “is nonequilibrium thermodynamics ready for scientists and engineers?” Should a corresponding course occur in a state-of-the-art curriculum in science and engineering? To answer these questions we describe a lucid framework of nonequilibrium thermodynamics and its statistical-mechanical foundations. We then provide a number of recent applications of this framework. We finally offer some conclusions and an outlook.

This article may be considered as a continuation of the compact review [2] presenting modern nonequilibrium thermodynamics to applied scientists and engineers. We hence focus on collecting the literature on the new developments mainly of the last 10 years.

2. GENERIC FRAMEWORK

Time-evolution equations for nonequilibrium systems possess a well-defined thermodynamic structure in

which reversible and irreversible contributions are constructed separately. The reversible contribution is assumed to be of the Hamiltonian form (driven by the gradient of energy) and hence requires an underlying geometric structure which reflects the idea that the reversible time evolution should be “under mechanistic control.” The remaining irreversible contribution is assumed to be driven by the gradient of a nonequilibrium entropy. Our discussion is based on the GENERIC (“general equation for the nonequilibrium reversible-irreversible coupling”) framework for closed nonequilibrium systems [3-5] (see also the brief summary in [6] adapted for our purposes here),

$$\frac{dx}{dt} = L \cdot \frac{\delta E}{\delta x} + M \cdot \frac{\delta S}{\delta x}, \quad (1)$$

where x represents the set of independent variables required for a complete description of a given closed nonequilibrium system, E and S are the total energy and entropy expressed in terms of the system variables x , and L and M are certain linear operators, or matrices. The so-called Poisson matrix L and the friction matrix M can also depend on x so that the fundamental evolution equation (1) can be highly nonlinear. The two contributions to the time evolution of x generated by the total energy E and the entropy S in (1) are the reversible and irreversible contributions to dynamics, respectively. Because x typically contains position-dependent fields, such as the local mass, momentum and energy densities of hydrodynamics, the state variables are usually labeled by continuous (position) labels in addition to discrete ones. A matrix multiplication, which can alternatively be considered as the application of a linear operator, hence implies not only summations over discrete indices but also integrations over continuous labels, and the gradient $\delta/\delta x$ typically implies functional rather than partial derivatives. Equation (1) is supplemented by the complementary degeneracy requirements

$$L \cdot \frac{\delta S}{\delta x} = 0 \quad (2)$$

and

$$M \cdot \frac{\delta E}{\delta x} = 0. \quad (3)$$

The requirement that the entropy gradient $\delta S/\delta x$ is in the null-space of the Poisson matrix L in (2) expresses the reversible nature of the first contribution to the

dynamics, irrespective of the particular form of the Hamiltonian. The requirement that the energy gradient $\delta E/\delta x$ is in the null-space of the friction matrix M in (3) expresses the conservation of the total energy in a closed system by the irreversible contribution to the dynamics. Furthermore, it is required that the matrix L is antisymmetric, whereas M is Onsager-Casimir symmetric (see Section 3.2 of [5] for details) and positive-semidefinite. Finally, the Poisson bracket that can be associated with the antisymmetric matrix L is assumed to satisfy the Jacobi identity, which expresses the time-structure invariance of the reversible dynamics [7] and can be conveniently and rigorously tested by using symbolic mathematical tools [8,9].

Equations (1)-(3) lay the foundations of nonequilibrium thermodynamics. These equations can be obtained along three different lines of thinking.

(i) One possibility is to start from the wealth of problems and systems that have been treated successfully since the early work of Newton (1687), Fourier (1822), Ohm (1826), and Fick (1855) on the transport of momentum, energy, charge, and mass, respectively. In particular, all the knowledge of linear irreversible thermodynamics [10] must be contained in the fundamental evolution equation (1). Moreover, the highly nonlinear processes in chemical reactions and the Boltzmann equation should also be described by (1)-(3).

(ii) An important guideline in the formulation of (1)-(3) in [3,4] was the elegance of geometric structures. From the landscapes of energy and entropy, reversible and irreversible contributions to dynamics are obtained by converting gradient vectors of the landscapes into tangent vectors of trajectories. As the existence of a general variational principle seems to conflict with the degeneracy of the Poisson matrix implied by (2) (according to the mathematical theory behind variational principles [11]), the GENERIC structure (1)-(3) seems to provide the appropriately strong and general setting of nonequilibrium thermodynamics.

(iii) The separation of reversible and irreversible contributions to nonequilibrium dynamics reflects a separation of slow and fast degrees of freedom. The projection-operator formalism carrying out the latter separation [12-16] provides the proper tool for laying the statistical foundations of nonequilibrium

thermodynamics. Indeed, our fundamental equations (1)-(3) arise naturally from projection-operator techniques.

Whereas each of the above arguments may be plausible or appealing, the combination of the arguments (i), (ii), and (iii) makes the GENERIC framework fully convincing. Note that energy and entropy are the fundamental concepts of nonequilibrium thermodynamics. In cases where a nonequilibrium temperature can be introduced in a meaningful way, at least locally, one may be able to combine the two generators E and S into a single one (a “nonequilibrium free energy”). The possibilities and limitations of the single-generator approach have been discussed in the textbook [17] and in the detailed comparison to the double-generator approach [18-20].

3. SECOND LAW

“Does your theory fulfill the second law of thermodynamics?” is a famous killer question. In modeling dynamic systems, it may not always be clear what exactly this question means. The GENERIC framework offers a very clear and simple formulation of the second law valid for nonequilibrium thermodynamics,

$$\frac{dS}{dt} = \frac{\delta S}{\delta x} \cdot M \cdot \frac{\delta S}{\delta x} \geq 0, \quad (4)$$

which follows directly from the chain rule by using (1) and (2).

Equation (4) shows clearly that all entropy production arises from irreversible dynamics and that a nonnegative entropy production is a simple consequence of the positive-semidefiniteness of the friction matrix. Note that this is a very strong version of the second law because it does not make any use of a particular functional form of the entropy. The second law (4) holds on the time scales of the slow variables and, in view of the assumption of a clear separation of time scales, is not affected by the fluctuation theorem which relates positive and negative entropy fluctuations on much shorter time scales [21].

4. NONEQUILIBRIUM STATISTICAL MECHANICS

By eliminating the fast degrees of freedom, the projection-operator formalism [12-16] produces

equations of the GENERIC form (1)-(3) (see Chapter 6 of [5] and [22-24]). The fast degrees result in noise and friction felt by the slow variables, where these two effects are found to be intimately related according to the fluctuation-dissipation theorem (see Section 1.6 of [25]). As a result of the projection procedure, well-defined statistical expressions for the thermodynamic building blocks E , S , L , M in (1)-(3) arise (see Section 6.1.4 of [5]). Evaluation of these expressions should be the Holy Grail of computer simulations for nonequilibrium systems [24]. The counterpart in equilibrium statistical thermodynamics is the determination of partition functions (or their partial derivatives) by Monte Carlo simulations to obtain thermodynamic information in terms of the free energy.

A cornerstone of nonequilibrium statistical mechanics is the nonequilibrium ensemble. It is a probability density on the larger space of more microscopic states, parametrized by the more macroscopic state variables taking values from a smaller space (to avoid awkward formulations, we simply refer to microscopic and macroscopic states from now on). The ideas of microcanonical, canonical, and mixed ensembles are taken over from equilibrium statistical mechanics, but now with a much larger and less universal set of thermodynamic nonequilibrium variables. The energy E and the Poisson matrix L of the coarse-grained description can be obtained by simply averaging their microscopic counterparts by means of the nonequilibrium ensemble. As at equilibrium, the evaluation of the entropy S is a matter of counting microscopic states or, more generally, of properly normalizing the ensemble.

The friction matrix M is the only building block that requires dynamic material information. According to the fluctuation-dissipation theorem, it can be obtained from the time-correlation functions of fluctuations. More precisely, one needs to evaluate the time-integral of two-time correlations of the fluctuations of the macroscopic variables resulting from the elimination of fast microscopic degrees of freedom. The explicit expression for the friction matrix is known as the Green-Kubo formula (see, for example, (3.47) or (6.73) of [5] or (3) of [24]).

The respective role and potential of Monte Carlo, molecular dynamics, and Brownian dynamics

simulations in thermodynamically guided simulations for nonequilibrium systems has been elaborated in [24]. Dynamic simulations should run only over a fraction of the characteristic slow time scales, just sufficiently long to evaluate the decay of two-time correlations on the fast time scales. Initial conditions should be obtained by Monte Carlo sampling from nonequilibrium ensembles. Thermostats and similar devices should be unnecessary for such short simulations.

5. RIGOR AND LIMITATIONS

Equilibrium thermodynamics is a theory of remarkable rigor and generality. Can a similar statement be made about nonequilibrium thermodynamics?

The rigor of equilibrium thermodynamics stems from the fact that it deals with infinitely slow variables. The fact that certain variables do not change in time is related to fundamental symmetries (see Chapter 21 of [26]). In nonequilibrium thermodynamics, slow and fast variables are separated only by a finite factor, which makes nonequilibrium thermodynamics less rigorous than its equilibrium counterpart for the infinitely slow variables and the choice of good variables much less clear-cut. In terms of elegance and generality of the geometric approach, however, nonequilibrium thermodynamics is by no means inferior to the famous equilibrium theory.

It may be worthwhile to point out that nonequilibrium thermodynamics is *not* the theory of everything that is not at equilibrium. To justify the use of nonequilibrium thermodynamics for a particular problem, one needs to identify a proper set of slow variables (a system) that can be employed to describe the problem in a self-contained way. In other words, the problem must be amenable to coarse graining. From a statistical mechanics point of view, the same problem occurs as the need to justify the existence of a proper nonequilibrium ensemble and the applicability of the Green-Kubo formula. By insisting on accounting for increasingly finer details, or when processes on the shortest time and length scales have a crucial impact on the large-scale features of a problem, the use of nonequilibrium thermodynamics becomes impossible. For problems related to the deepest understanding of life it may even be philosophically desirable that any attempt of a thermodynamic description is doomed to failure.

6. APPLICATIONS

In addition to the many famous applications of linear irreversible thermodynamics (such as chemical reactions, diffusion, osmotic pressure, heat conduction, propagation of sound, electrokinetic effects, thermoelectric effects, thermokinetic effects, dielectric relaxation, polarizable media in electromagnetic fields, magneto-plasmas, superfluids, and viscoelastic fluids), a number of applications of nonlinear irreversible thermodynamics have been compiled in Appendix E of the textbook [5]. Those advanced applications are from the fields of complex fluids (reptation model for entangled linear polymers [27-31], pompon model for branched polymers [32,33], polymer blends [34-39], colloidal suspensions [40-42], and two-phase systems [43-46]), relativistic hydrodynamics [47-51], discrete formulations of hydrodynamics for simulations [52-55], and thermodynamically guided simulations [56-65] (see also the review article [24] offering “four lessons and a caveat” for good simulations in the context of nonequilibrium statistical mechanics).

Several basic transport phenomena have been generalized to the nonlinear regime. For example, diffusion through polymeric and nanocomposite membranes has been modeled by means of the GENERIC framework [66,67]. Also a comprehensive discussion of the multiscale thermodynamics and mechanics of heat flow goes beyond linear irreversible thermodynamics [68]. Significant progress in applying nonequilibrium thermodynamics to increasingly more complex fluids has, for example, been made with rheological modeling of suspensions of red blood cells [69], a biological problem of obvious importance. Thermodynamics has also contributed to the understanding of gas flow in the smallest of channels, as in microfluidics, and of aerodynamics of satellites and space stations in the outer limits of our atmosphere [70-72].

Whereas the original development of nonequilibrium thermodynamics has mainly been pushed in the context of complex fluids, the general framework is by no means restricted to fluids. Also crystallization phenomena, including polymer crystallization, have been better understood with the help of the methods of modern nonequilibrium thermodynamics and statistical mechanics [73-80]. Plasticity and viscoplastic solids

are further topics in which important issues have been clarified by means of thermodynamics [81-87]. By combining thermodynamics with a thoughtful characterization of the microstructure, valuable insight into continuum damage mechanics has been gained [88]. Structural glasses are another challenging problem in physics and materials science for which nonequilibrium phenomena are widely believed to play an important role. Promising new ways to approach this long-standing challenge are suggested by the GENERIC framework [6,89,90].

Most of the applications of nonequilibrium thermodynamics deal with the modeling of bulk systems. To solve the resulting bulk equations one typically needs boundary conditions. The usefulness of linear irreversible thermodynamics for obtaining boundary conditions has been shown by Waldmann in his famous 1967 article [91]. Brenner and Ganesan [92] asked the very deep question “Are conditions at a boundary ‘boundary conditions’?” Nonequilibrium thermodynamics actually provides the powerful language for expressing the physics at the boundary consistently [93,94], thus going well beyond the mathematics of boundary conditions. An illustrative example is provided by the thermodynamic formulation of wall slip [95]. Within linear irreversible thermodynamics, a general description of the dynamics of interfaces has been developed by Bedeaux and coworkers [96-98]. The main challenge is to generalize the concept of local equilibrium, which is known to be a key ingredient to the nonequilibrium thermodynamics of bulk systems, to lower-dimensional interfaces [99-101]. The analysis of the fully nonlinear thermodynamic behavior of complex interfaces within modern nonequilibrium thermodynamics is a very active field of research [102-106].

7. FUTURE

The previous section gives many important applications of the modern framework of nonequilibrium thermodynamics. The following two predictions for a promising future of nonequilibrium thermodynamics seem to be rather safe:

Prediction 1: The more complex the problems of interest become, the more useful the framework of nonequilibrium thermodynamics will turn out to be. In the presence of many structural variables and

many transport and relaxation processes, the focus on the basic thermodynamic building blocks (E , S , L , M), including consistency conditions such as (2) and (3), and the possibility to use well-defined tools of statistical mechanics to obtain these building blocks render modeling efforts much more efficient and help to avoid inconsistencies.

Prediction 2: The theory of quantum dissipation [107,108] will play an increasing role in various branches of quantum technology, such as quantum computing, quantum information processing, quantum communication, quantum cryptography, quantum simulation, quantum metrology, quantum sensing, and quantum imaging. After gaining a deep understanding of its geometric structure, modern nonequilibrium thermodynamics suggests the proper form of the equations also for coupling quantum systems to classical environments [109-112]. A most remarkable result is that thermodynamics imposes nonlinearity on quantum master equations, contrary to the almost universal presupposition of linear quantum master equations in present-day applications.

8. CONCLUSION

We have sketched the GENERIC framework of nonequilibrium thermodynamics and its statistical foundations, emphasizing the geometric structure of the approach. This short exposition shows that there exists an elegant unified approach to nonequilibrium systems. The power of the framework is demonstrated by sketching a variety of applications in which nonequilibrium thermodynamics contributes significantly to our state-of-the-art knowledge.

In short, the question asked in the introduction can now be answered very convincingly: “Nonequilibrium thermodynamics is definitely ready for scientists and engineers!” The more interesting question now is: “Are scientists and engineers ready for nonequilibrium thermodynamics?” I hope that this article shows them why they should be. Researchers in academia should be increasingly motivated to use the tools of statistical nonequilibrium thermodynamics to gain understanding by coarse graining. These researchers should then become the pioneering teachers of inspiring courses on nonequilibrium thermodynamics for the next generation of scientists and engineers.

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