Understanding Complex Systems

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Modeling Thermodynamic Distance, Curvature and Fluctuations

A Geometric Approach

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Preface

This textbook aims to briefly outline the main directions in which the geometrization of thermodynamics has been developed in the last decades. The textbook is accessible to the people trained in thermal sciences but not necessarily with solid formation in mathematics. For this, in the first part of the textbook a summary of the main mathematical concepts is made. In some sense, this makes the textbook self-consistent. The rest of the textbook consists of a collection of results previously obtained in this young branch of thermodynamics. The content is organized as follows.

The first part of the textbook, consisting of four chapters, presents the main mathematical tools. Thus, Chap. 1 presents the historical background of the geometrization of mechanics and thermodynamics. In Chap. 2 some basic concepts are briefly reminded, such as the set theory, the relationships theory, and the theory of simple algebraic structures. Then, the essential concepts used in the theory of linear spaces are introduced. The chapter ends by presenting some results concerning the coordinate transformations and the classification of physical quantities in relation with these transformations. Chapter 3 describes the main types of vectors and the standard method of vector geometrization. Then elementary results of vector calculus are presented. The chapter ends with a very brief introduction to the exterior differential calculus, accompanied by some specific useful results. Chapter 4 describes results of Riemann geometry. Two approaches are presented. The first one is the classic approach. The second approach is based on the theory of differential manifolds and tangent spaces. Both approaches allow defining the tensors of different orders, the Riemann metric and the covariant differentiation, among others. The parallel between the two approaches is very useful for a deeper understanding of concepts.

The second part of the textbook, consisting of five chapters, refers to the application of geometric methods in equilibrium thermodynamics. Chapter 5 summarizes some results of equilibrium thermodynamics. The approach based on potentials is presented, including the standard procedures using the energy representation and the entropy representation. Finally, the extreme principles and the mathematical conditions for thermodynamic stability are presented. Chapter 6 briefly shows some results of using tools of contact geometry in thermodynamics. Here only the first law of thermodynamics is geometrized. The chapter ends with a few examples of contact currents in thermodynamics. In Chap. 7 an approach based on statistical methods, which allows defining the notions of thermodynamic metric and thermodynamic distance, is presented. The second law of thermodynamics plays a key role in this context. The relationship between the thermodynamic distance and the entropy production is analyzed and links with the Gouy-Stodola theorem are highlighted. Horse-carrot type theorems are also introduced. The manner in which the thermodynamic curvature can be defined is exposed in Chap. 8. The chapter contains examples of calculation of thermodynamic curvature for simple systems. Chapter 9 presents a covariant theory of the thermodynamic fluctuations and analyzes the level of approximation introduced by the classical theory of fluctuations and its Gaussian approximation.

The textbook is a more extensive version of a section of the course of Advanced Thermodynamics presented for master students at the Faculty of Mechanical Engineering, Polytechnic University of Bucharest, starting from the 2003–2004 academic year. The textbook is presented with an ease of access for the readers with education in natural and technical sciences. Thus, most mathematical demonstrations of the theoretical results with higher degree of difficulty are omitted and references for the relevant literature are provided.

As usual, the preparation of such a work is the result of numerous interactions, discussions, consultations, and collaborations. It is a pleasure to remind here some of them. I received special support from colleagues in the European network CARNET (Carnot Network). This cooperation was institutionalized during the years 1994–1999 by two Copernicus projects on thermodynamic topics funded by the European Commission. In particular, I must thank Prof. Bjarne Andresen (University of Copenhagen), Prof. Ryszard Mrugala (University of Torun, Poland), and Dr. Lajos Diósi (Research Institute for Particle and Nuclear Physics, Budapest) whose publications were massively used in the present work. During the elaboration of the material I received technical support from Prof. Peter Salamon (University of San Diego). Also, discussions with Prof. Constantin Udriste (Polytechnic University of Bucharest) allowed a better understanding of the fundamentals of mathematics.

Viorel Badescu

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Part I
Mathematical Tools

Chapter 1
Introduction

Theoretical thermodynamics has been developed from the practical studies of thermal engines operation. Initially, it was based on the empirical usage of a combination of mechanical and thermal notions. The absence of a sound basis, consisting of well-defined and understood concepts, has often been noticed by personalities who made important contributions in the field, among which we quote Josiah Willard Gibbs, Hermann von Helmholtz, Pierre Duhem and Walther Nernst. They, and many others, have tried to introduce rigor in the theoretical approach by avoiding cyclical logical reasoning and contradictions. Constantin Caratheodory was the first who succeeded to build an axiomatic system for equilibrium thermodynamics (Caratheodory 1909). Thus, notions such as measurable temperature, heat and entropy were defined. Also, empirical assumptions were explained and simplified. From the very beginning, the approach of Caratheodory was analogous in spirit and practice with the axiomatic formulation of Euclidean geometry (Antoniou 2002). The structure of equilibrium thermodynamics, expressed in mathematical terms by Pfaff forms, turns out to be in some sense analogous to the structure of Hamiltonian mechanics and symplectic geometry (Rastal 1970; Peterson 1979).

The criteria proposed by Caratheodory were subsequently used to develop two main lines of research. First, the notion of thermodynamic variable has been clarified, making difference between extensive and intensive variables. Second, the concepts of classical thermodynamics have been extended for non-equilibrium situations.

Equilibrium thermodynamics was formulated based on conjugate pairs of independent variables, known as generalized coordinates (such as volume, area, length, electric charge) and generalized forces (mechanical forces, pressure, surface tension, electric voltage) (Redlich 1968). Generalized coordinates actually correspond to extensive variables because they depend on the size (extension) of the system, while the generalized forces correspond to the intensive variables because they are localized in space and time. This simple observation led to the formulation

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of the fundamental thermodynamic concepts by using the measure theory (Gurtin et al. 1986). In this version, the extensive variables are positive or negative quantities on Euclidean spaces while the intensive variables are associated densities, defined mathematically as Radon-Nykodym derivatives. In case of extensive variables represented by absolute continuous quantities, the corresponding intensive variables are absolute integrable functions. In case of extensive variables represented by singular measures, located on surfaces, curves or fractals, the corresponding intensive variables are generalized functions (Antoniou and Suchanecki 1999). The formulation of classical thermodynamics by using of the measure theory has a number of advantages, among which we can mention the possibility of rigorous generalization to the case of continuous media, to the case of special and general relativity and to non-equilibrium situations, respectively (Antoniou 2002).

The usage of geometrical methods in thermodynamics was inspired by their previous applicability in the field of dynamical systems theory. The idea of approaching the solutions of the dynamic equations from a geometrical point of view is due to Henri Poincaré. However, Nikolay Mitrofanovich Krylov was the first who tried to formulate the statistical mechanics by using the Riemann geometry (see the review by Krylov (1979)). Krylov's ideas were developed by several groups of researchers (see Caiani et al. 1998; Casetti et al. 2000 and references therein). In general, conclusive results have been obtained only for constant negative curvature of the space of configurations. There are attempts to replace the Riemannian manifolds by Finsler manifolds, which have the advantage of allowing the geometrization of the speed dependent potentials (Dryuma 1994). Starting from the identification of the trajectories of a Hamiltonian dynamical system with geodesics in the configuration space equipped with Jacobi or Eisenhart metrics, one can develop a geometric theory of mechanics (Casetti et al. 2000). Interesting results have been obtained, which show, for example, that chaos can be induced not only by negative curvatures but also by positive curvatures of the configuration space, provided that these curvatures oscillate along the geodesics. In case of systems with very large number of particles and having large extension (what is commonly called "the thermodynamic limit") it is possible to describe the dynamical instability by using dynamic models that are independent of the dynamics of microparticles, which allows the analytical estimation of the largest Lyapunov coefficient as a function of the mean value and the fluctuations of the curvature of the configuration space. The main difficulty consists in the extremely complicated form of the geometry of the configuration space, in case of systems with many particles. Therefore, a number of more or less obvious simplifications are used in literature. Usually, these simplifications are a posteriori justified, by comparison with results obtained from computer simulations using statistical physics methods.

Applying geometric methods in thermodynamics was carried out mainly in the classical theory of equilibrium (see Ruppeiner 1991; Gross and Votyakov 2000). In this regard several procedures of geometrization have been proposed. Probably the most popular is the approach developed by Weinhold (1975). It relies on the fact that the differentials of the thermodynamic functions can be interpreted as vectors in a vector space. Then, one can propose a definition of the inner product on that vector space, in connection with the mathematical expression of the second law of thermodynamics, which ultimately leads to the positivity of the metrics attached to the vector space. The procedure initiated by Weinhold experienced many extensions, some of which will be mentioned throughout this book.

On the other hand, some geometrical aspects of the hypersurface of constant energy in the phase space were used in case of the microcanonical ensemble to define the temperature and the specific heat (Rugh 1997; Giardina and Livi 1998). Therefore, one can make distinction between the use of geometrical and topological concepts at the level of the macroscopic phase space (associated with phenomenological thermodynamics) and at the level of the microscopic phase space (associated with statistical thermodynamics), respectively.

When a system undergoes a phase change, fluctuations in the curvature of the phase/configurations space, as a function of temperature or energy, have a singular behavior in the transition point. This singularity can be described using a geometric model. In such a model the singularity of curvature fluctuations originates in the topology of the phase/configurations space. This is the argument leading to the introduction of the so-called topological assumption, which states that phase changes (at least, the continuous ones) are connected to a specific change of the topology of system's space of phase/configurations. This assumption allows the usage within the statistical thermodynamics of existing results in mathematics, such as those obtained in Morse theory. Therefore, one can make such a connection between mathematics (topology) and statistical thermodynamics (the theory of phase change). Existing results in the literature show that from the point of view of Morse theory the essential information is stored in the potential energy function. If the latter depends solely on coordinates, the usage of topological methods can be made by restriction from the phase space to the configurations space.

An important theorem shows the need of topological changes of the hypersurface of constant energy, for the emergence of a first-order or second-order phase change (Casetti et al. 2000). The demonstration is based on several assumptions concerning the diffeomorphicity of the surface and the uniform convergence of the Helmholtz free energy towards the thermodynamic limit for a very large number of particles. The fact that topological changes can occur regardless of the number of particles opens the possibility of describing the phase change in finite systems such as nuclear and atomic clusters, polymers and proteins, as well as nanoscopic and mesoscopic structures.

A geometric theory of thermodynamic fluctuations has already been proposed (for a review see, Ruppeiner 1995). The theory applies to classical, extensive, thermodynamics, in all cases where there are two independent coordinates (identified in that situation with two thermodynamic parameters). Then, a metric is defined on the manifold determined by the two coordinates, which becomes a Riemann manifold. Using known results of Riemann geometry is simplified in case of extensive thermodynamics with positive defined metrics, unlike in the theory of relativity (there, the associated Riemann manifold has four dimensions and its metric is allowed not to be positive definite). Arguments have been provided in support that the theory of fluctuations and, implicitly, the theory of thermodynamic