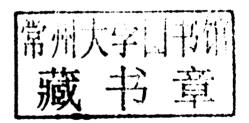*Advances in*
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## THERMODYNAMICS AND KINETICS OF COMPLEX SYSTEMS

## SYSTEMS

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*Thermodynamics* and *kinetics* can surely be counted—along with transport phenomena, chemistry, unit operations, and advanced mathematics—as subjects that form the foundation of Chemical Engineering education and practice. Thermodynamics is of course a very old subject. For example, it was the same Rudolf Clausius, who in 1865 coined two immortal sentences (1) "The energy of the universe is constant" and (2) "The entropy of the universe tends to a maximum," that developed the famous Clausius–Clapeyron equation, one of the most basic physico-chemical relationships. Classical thermodynamics was largely complete in the 19th century, before even the basic structure of the atom was understood.

The early 20th century saw the development of a statistical description of thermodynamics which successfully explained the macroscopically observable thermodynamic relations in terms of the statistical behavior of ensembles of atoms or molecules. By the late 1920s the statistical treatment of molecular thermodynamics was starting to connect chemical thermodynamics to chemical kinetics through the development of transition state theory. Consequently, in 1930–1950 the pioneers of chemical engineering science had most of what they needed to begin putting chemical engineering on a firm mathematical foundation. That was indeed the focus of theoretical research in chemical engineering for the next 30 years or more.

Since about 1970, chemical engineering has diversified and bifurcated into practically every adjacent area of science including polymer chemistry, materials science, molecular biology, microelectronics, nanotechnology, and biomedical engineering. What has enabled chemical engineers to infiltrate these adjacent fields so successfully? We believe part of the answer is that chemical engineers are well equipped by their education to analyze systems in terms of the governing equations of thermodynamics and kinetics. Whether the system is composed of fluids, molecules, unit operations, cells, repeat units, micro-electronic devices, or organisms, we wish to know the possible states of the system, their stability, the relationships between them, and the rate of change from one state to another. Whether at the basic scientific level or the practical technological level, such questions are essentially thermodynamic and kinetic questions.

From the very beginning Gibbs formulation of thermodynamics was highly mathematical, in particular geometrical. In accordance with this tradition, several scientific schools have applied modern geometrical methods to continue progress in chemical thermodynamics and chemical kinetics. Three schools have to mentioned: the Belgian school of non-equilibrium thermodynamics (de Donder, De Groot, Mazur, Defay, and the Nobel laureate Prigogine), the American Minnesota School (Amundson, Aris, Horn, Feinberg), and the Russian Siberian School (Gorban *et al.*). In this book we present two new examples of this chemo-geometrical activity.

First, Miroslav Grmela from the Montreal Ecole Polytechnique (Montreal, Canada), in the paper "Multiscale Equilibrium and Nonequilibrium Thermodynamics in Chemical Engineering," develops a unifying thermodynamic framework for multiscale investigations of complex macroscopic systems. In this new theoretical paradigm, the key conceptual role is played by the *Legendre transformation*, and the time evolution representing the approach to a more macroscopic level of description is introduced as a continuous sequence of Legendre transformations. This method is developed for chemically reacting multilevel systems. It can be considered as one of the cornerstones of the emerging multiscale engineering, which seeks to combine nano-, micro-, and macroscales.

In the paper "Equilibrium Thermodynamic Modeling of Dissipative Macroscopic Systems" by Boris Kaganovich, Alexander Keiko, and Vitaliy Shamansky (Melentiev Energy Institute, Irkutsk, Russia), the authors present updated information regarding the model of extreme intermediate states. The authors build up this approach which started in the mid-1980s based on the chemo-geometrical ideas of Russian and American colleagues (Russian Siberian Team—Gorban, Yablonsky, and Bykov and US schools—Horn, Feinberg and Shinnar, respectively). However, during more than two decades they developed this model significantly, transforming it into the original and powerful tool for analysis of many processes of chemical engineering (flows in hydraulic circuits, coal combustion, isomerization, etc.).

The phase equilibrium of materials is an inherently multiscale phenomenon which spans from the functional group (or atomic) scale through the morphological-structure scale to the macroscopic scale. Two texts presented in this volume are devoted to this problem.

The contribution "Application of Meso-Scale Field-based Models to Predict Stability of Particle Dispersions in Polymer Melts" by Prasanna Jog, Valeriy Ginzburg, Rakesh Srivastava, Jeffrey Weinhold, Shekhar Jain, and Walter Chapman examines and compares Self Consistent Field Theory and interfacial Statistical Associating Fluid Theory for use in predicting the thermodynamic phase behavior of dispersions in polymer melts. Such dispersions are of quite some technological importance in the

plastics, materials, and electronics industries. This contribution highlights a recent advance by some of the authors: the inclusion of compressibility in the thermodynamics of nanoparticle dispersion. This is an important advance in mesoscale simulation which correctly expands the region of intercalated microstructures. The chapter demonstrates that mesoscale field-based simulation is finding practical applications for industrial nano-material development.

In the final chapter "Principles of Statistical Chemistry as Applied to Kinetic Modeling of Polymer Obtaining Processes" by Semion Kuchanov (Lomonosov Moscow State University, Moscow, Russia), the contemporary problems of bridging models of micro- and macrostructure are discussed. The hierarchical analysis of chemical correlation functions (so-called *chemical correlators*) is a subject of the author's special interest. These problems are presented conceptually stressing that the problem of crucial importance is revealing the relation between the process mode and the chemical structure of polymer products obtained.

We conclude with a famous quotation attributed to the great theoretical physicist, Arnold Sommerfeld

> *Thermodynamics is a funny subject. The first time you go through it, you don't understand it at all. The second time you go through it, you think you understand it, except for one or two small points. The third time you go through it, you know you don't understand it, but by that time you are so used to it, it doesn't bother you any more.*

This quotation is referred to often, maybe too often. Nevertheless, its lasting truth suggests that it makes sense to check from time to time the progress of chemical thermodynamics and kinetics, despite how old are the subjects, in particular as it concerns areas adjacent to chemical engineering.

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# CONTENTS

# Equilibrium Thermodynamic Modeling of Dissipative Macroscopic Systems

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**Abstract**     The possibility is substantiated to model open and closed systems as well as reversible and irreversible processes on the basis of classic equilibrium thermodynamics statements. The consideration is given to new modifications of the model of extreme intermediate states (MEIS) built originally in the mid-1980s. They include constraints on irreversible macroscopic kinetics presented in a thermodynamic form, i.e., without the time variable. MEIS is compared with models of chemical kinetics and irreversible thermodynamics from two viewpoints: (1) the range and versatility of application areas, and (2) the simplicity and self-descriptiveness of computational experiments. The potential of equilibrium modeling is explained on the examples of analysis of chemical systems and hydraulic circuits.

# 1. INTRODUCTION

The subject of the studies to be discussed is modeling of macroscopic dissipative systems on the basis of the classical equilibrium thermodynamics principles. The modeling tool is the model of extreme intermediate states (MEIS) suggested in the mid-1980s at the Melentiev Energy Systems Institute of Siberian Branch of Russian Academy of Sciences (Antsiferov et al., 1987; Gorban et al., 2001, 2006; Kaganovich et al., 1989, 1993, 1995) and which, unlike the traditional thermodynamic models intended for search of the final equilibrium point, allows one to study the entire attainability region from a given initial state of the studied system and find a point of partial or complete equilibrium that corresponds to the extreme value of a property the researcher is interested in (for example, concentration of target or harmful products of the processes that may

occur in the system). Various modifications of MEIS have been created over the past years. They include the constraints on irreversible macroscopic kinetics that are written in thermodynamic form (without time variable) (Gorban et al., 2006; Kaganovich, 2002; Kaganovich et al., 2004, 2005a, 2005b, 2006a, 2006b, 2006c).

The equilibrium modeling of reversible and irreversible processes has been a traditional approach for studies in the natural science (and since the mid-19th century in the social and economic sciences as well). The theoretical foundations of this approach were laid by Galileo whose principles of equilibrium, relativity, and inertia showed that the motion could be represented as a sequence of states of rest (equilibrium). The formalized analysis of equilibrium models was mostly carried out in the 18th century, first of all in the works by Euler and Lagrange. Lagrange using his equilibrium equation gave a single mathematical description for the entire Newton mechanics (Lagrange, 1997). Revealing the interrelations between the models of motion and rest resulted in creation of mathematical disciplines and methods related to the solution of variational and extreme problems: the method of multipliers, the theory of optimal equilibrium trajectories—calculus of variations and, later, the modern mathematical theory of extreme equilibrium states—mathematical programming (MP).

In the 19th century the variational principles of mechanics were extended to the analysis of nonconservative, nonholonomic, and nonscleronomous systems. However, the greatest progress in equilibrium modeling in the century before last is certainly connected with the science about equilibrium—the thermodynamics—created by Clausius, Helmholtz, Maxwell, Boltzmann, and Gibbs. Owing to thermodynamics the extreme principle—the principle of entropy increase (the second law of thermodynamics) came into physics. It is more general compared with the principles of virtual work and of least action that were formulated in mechanics. Boltzmann explained this law in two ways (Boltzmann, 1878; Polak, 1987): (1) from the motion trajectory analysis (kinetic) formulated as the H-theorem and (2) from the immediate consideration of possible states of a system and determination of the most probable among them. This explanation facilitated further analysis of interrelations between the models of motion and rest as interrelations between kinetics and thermodynamics. The assumptions on the Markov random behavior of processes of motion toward entropy maximum and on existence of the thermodynamic Lyapunov functions (without using the corresponding terms, of course), which had been made by Boltzmann in his research even before Markov and Lyapunov, became the foundation for the development of equilibrium modeling of diverse processes including irreversible natural ones.

However, with successful penetration of equilibrium models into physics, chemistry, biology, and social sciences in the 20th century, largely because of the need to study various nonlinear effects (self-oscillations,

self-organization), special sciences started to develop: the theory of dynamic systems (Arnold, 1989; Katok and Hasselblatt, 1997), nonequilibrium thermodynamics (Glansdorff et al., 1971; Kondepudi et al., 2000; Prigogine, 1967), synergetics (Haken, 1983, 1988) and others which are intended either completely or partly for the analysis of nonequilibrium irreversible processes. The "seizure" of a considerable part of the application area of equilibrium thermodynamics by other sciences was fostered by two conditions: First, is it due to the contradiction in the Boltzmann explanation of the second law which lies between the following suppositions: on the one hand, reversibility of the individual interactions among micro particles and, on the other hand, irreversibility of the final result of all these interactions in the aggregate (the Boltzmann paradox). Second, it is because of a wide discussion of the mentioned contradiction which unfolded at the turn of the 20th century. Now the opinion that "Classical thermodynamics gives a complete quantitative description of equilibrium (reversible) processes,… for nonequilibrium processes it establishes only the inequalities which indicate the direction of these processes (for example, the Clausius inequality)" (Zubarev, 1998) has become widespread.

The MEIS developers relying on the capabilities of modern computers and computational mathematics started the work whichresulted in an essential expansion of the application area of "good, old" classical thermodynamics and in the possibility to study (using thermodynamics) any states on all possible motion trajectories of a nonequilibrium system. In other words, they put forward the goal to use the models of equilibrium not only to determine the directions of irreversible processes but to estimate the attainability of desired and undesired states on these directions.

The works on equilibrium modeling of dissipative systems include four natural components:

1.  substantiation of the possibility to describe irreversible processes in terms of equilibrium;
2.  creation of quite a representative set of models (modifications of a general equilibrium model) to enable the analysis of a wide range of problems interesting in terms of theory and application;
3.  comparison of advantages and disadvantages of equilibrium and nonequilibrium models and differentiation of the areas of their effective applications;
4.  solving as many as possible specific problems and analysis of the modeling experience gained.

The above four topics of studies are subsequently discussed below. In creation of MEIS its authors have used as a base the ideas of their colleagues in studies of equilibria—those by Bykov, Gorban, and Yablonsky (Gorban, 1979, 1984, 1986; Yablonsky et al., 1991), as well as works by Horn (1964; Horn and Jackson, 1972), Feinberg (1972, 1999; Feinberg and

Hildebrant, 1997; Feinberg and Horn, 1974), Shinnar (1988; Shinnar and Feng, 1985) and other scientists who dealt with thermodynamic analysis of macroscopic systems kinetics and attainable states and areas research. In development of the latest MEIS modifications intended for modeling of irreversible processes we have utilized the equilibrium trajectory interpretations suggested by Gorban (2007; Gorban and Karlin, 2005; Gorban et al., 2001), which in turn are based on elaboration of Erenfests' idea on coarse-graining phase spaces (Ehrenfest, 1959). Besides, the study being presented has been strongly influenced by the works by Gorban on "Model Engineering"—a new scientific discipline formulated in Gorban and Karlin (2005) and further unfolded in Gorban (2007; Gorban et al., 2007). Whereas mathematicians often use formalized statements of problems that were suggested in other sciences and, then, based on the study of mathematical features develop the methods of their solution, the "Model Engineering" supposes the choice of the initial models which are most suitable in terms of both analysis and computation. The research area presented below fits naturally into this new discipline and represents a limit case of reduction, i.e., the transformation of models of motion into models of rest (equilibrium).

## 2. SUBSTANTIATION OF THE EQUILIBRIUM THERMODYNAMICS CAPABILITIES FOR DESCRIBING IRREVERSIBLE PROCESSES

### 2.1 The experience of classics

Great experience in equilibrium modeling of irreversible processes was gained even in the classical mechanics. Lagrange, analyzing the specific features of the equilibrium search problems (Lagrange, 1997), stated that if the left-hand side of his equation of the mechanical system equilibrium represents a total differential of some function, then the solution to the problem of determining the equilibrium corresponds to the solution to the problem of finding the extremum of this function. Thus, he assumed that the cases were possible where the equilibria are attained between non-differentiable variables. The assumption on the equilibrium of mechanical systems that was made by him in a formalized description of the Newton mechanics appeared to be more general than the assumption on the conservatism of these systems that was in fact used by Newton and Leibniz for creation of the differential calculus. While the conservatism is a sufficient but not necessary condition of the possibility to describe the system behavior with the help of differential equations, the equilibrium is a necessary condition for admissibility of such a description. Indeed, the nonequilibrium systems cannot be described by intensive macroscopic

parameters which are the functions of states and the notion of the function differential for such systems loses its sense.

In the 19th century the variational principles of mechanics that allow one to determine the extreme equilibrium (passing through the continuous sequence of equilibrium states) trajectories, as was noted in the introduction, were extended to the description of nonconservative systems (Polak, 1960), i.e., the systems in which irreversibility of the processes occurs. However, the analysis of interrelations between the notions of "equilibrium" and "reversibility," "equilibrium processes" and "reversible processes" started only during the period when the classical equilibrium thermodynamics was created by Clausius, Helmholtz, Maxwell, Boltzmann, and Gibbs. Boltzmann (1878) and Gibbs (1876, 1878, 1902) started to use the terms of equilibria to describe the processes that satisfy the entropy increase principle and follow the "time arrow."

The principle of entropy increase was explained by Boltzmann in two ways: (1) by analyzing the feasible paths (H-theorem) and (2) by considering the possible attainable states of thermodynamic system and searching for the most probable ones among them. In both explanations he made assumptions on the independence of the considered states from the attainment prehistory and the possibility of their full description on the basis of functions, determined exclusively by the probability of fulfillment, and changing monotonously in the process of transitions from state to state. Using modern terms we can say that Boltzmann presupposed the Markov behavior of processes taking place and the existence of the Lyapunov functions. In turn the possibility to represent the states by a set of quantity related only to the probability of attainment implies that such a state can be interpreted as partial or complete equilibria. Indeed, fixing some quantity (function) can be easily explained by equilibrium of the forces tending to change it. This makes clear both the equilibrium of the Boltzmann trajectories of attaining the entropy maximum and the "equilibrium" of the Boltzmann descriptions of irreversible processes. Boltzmann's explanations reveal to a great extent the interrelations between thermodynamics and kinetics and the possibilities of thermodynamic equilibrium analysis of kinetic equations, i.e., the equations of motion.

Gibbs in his system explanation of macroscopic thermodynamics (Gibbs, 1876), which had been made before he and Boltzmann formulated the principles of statistical mechanics, relied on the Lagrange equilibrium description of mechanical systems. However, instead of the single Lagrange equilibrium equation, which, according to Krylov, included all Newton mechanics, Gibbs, in order to derive all thermodynamic relationships, used four fundamental equations written for different combinations of independent parameters. Thus, not ordinary but partial differential equations became the mathematical apparatus of thermodynamics unlike mechanics. Owing to thermodynamics, a more general, compared with the

mechanical principles, the extreme principle, i.e., the second law of thermodynamics, appeared in the science. For trajectories it determined the entropy nondecrease instead of action minimization (according to the least action principle) and for states—instead of the virtual work principle the entropy maximum: global for complete equilibrium and conditional (under the condition of braking all the processes that can continue after the given state is attained)—for partial equilibria.

Gibbs conducted the specific studies on the basis of mathematical relations obtained. These studies focused on the complex systems, subjected to the action of various forces (chemical, electrical, gravitational, surface tension, and elastic), and the systems in which there can be substance transformations and phase transitions along with energy transformations. In these studies Gibbs used the method of potentials which supposed equilibrium trajectories of attaining the sought equilibrium states. Gibbs, without using time variable, distinguished the approximate equilibria which settle fast and the final equilibrium which is slowly attained. Not considering the computational problems proper he foresaw the relations between physical stability and uniqueness of the final equilibrium point. In terms of the art of equilibrium modeling of irreversible processes the analysis of the process of hydrogen burning in oxygen (Gibbs, 1876) is particularly impressive. Gibbs, without information on thermodynamic properties of substances and without computers, managed to draw a complete qualitative picture of this process. Discussing potential solutions to the system of equations he explained the decrease in reaction temperature due to water dissociation and the presence of constrained explosibility and ignition regions. Certainly, he could not find the chain mechanism of the considered reaction but the probable results of the studied processes for different conditions under which these processes occur Gibbs showed absolutely correctly.

Discussing the period when the thermodynamic equilibrium descriptions of various irreversible phenomena started one cannot but point out the papers on the theory of electric circuits that are of explicitly thermodynamic character. These had been written by Kirchhoff (1848, 1882) before the works by Clausius and Boltzmann, which made the second law the property of science. In his work (Kirchhoff, 1848)(yet in 1848!) Kirchhoff proved the theorem on minimum heat production in the open passive (without electromotive force sources) electric circuit for the case of isothermal motion of charges. It is easy to ascertain that this theorem represents a particular case of the nonequilibrium thermodynamics theorem on minimum entropy production that was proved by Onsager and Prigogine approximately 100 years after Kirchhoff. In the 1870s Rayleigh suggested the principle of the least energy dissipation (Rayleigh, 1873).

Following the founders of thermodynamics, Planck and Einstein presented vivid illustrations of the possibilities to analyze irreversible

processes in terms of equilibrium. Taking into consideration the condition
of equilibrium between substance and radiation and the condition of
equilibrium energy transfer, they derived the laws of light radiation,
propagation, and absorption. As is known their works were the develop-
ment and brilliant completion of the radiation thermodynamics works by
Kirchhoff and Boltzmann. In the papers dedicated to the Brownian motion
Einstein, proceeding from the equations of equilibrium between the
Brownian particle and carrying fluid, derived the law of Fick for a princi-
pally irreversible process, i.e., diffusion. In the theories of fluctuations and
opalescence Einstein "broke into" the fields of applications of modern
nonequilibrium thermodynamics. He introduced the notion of partial
equilibria (in his terms "incompletely determined in the phenomenologi-
cal sense of the word") in the analysis of opalescence phenomenon and
used this notion to explain the irreversible process of light diffusion,
considering, in fact, a set of attainable states.

In the second half of the 20th century it is precisely the classical
equilibrium thermodynamics that became a basis for the creation of
numerous computing systems for analysis of irreversible processes in
complex open technical and natural systems as applied to the solution of
theoretical and applied problems in various fields. The methods of MP,
i.e., the mathematical discipline that emerged from the Lagrange interpre-
tation of the equilibrium state, were a main computational tool employed
for the studies.

## 2.2 New interpretations of equilibrium and reversibility

In order to clearly explain the possibilities of describing nonequlibrium
irreversible processes in terms of equilibrium it is certainly necessary
to define quite accurately the notions of equilibrium and reversibility,
nonequilibrium and irreversibility. It is clear that their interpretation, as
well as the interpretation of other scientific notions, changes with the
development of respective theories, models, and methods. Since the
work touches upon the issues of interrelations between the competing
models in a historical profile it is desirable that the appropriateness of
various interpretations of the said notions be assessed in this profile.
Making no pretence of the systematic presentation of the issue we will
only touch upon some points that are important for understanding the
text[1] below.

Mechanics emerged as a science studying reversible processes that are
symmetrical relative to time. Euler, in his "thesis" on the least action

[1] A rich material for the comprehension of the evolution of basic notions in the course of development of
variational principles and principles of equilibrium and extremality in physics can be found in remarkable
books by L.S. Polak (1987, 1960).