PREFACE

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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