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Fundamental Aspects of Plasma Chemical Physics

Thermodynamics

With 110 Figures

Springer

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I busied myself, from then on, that is,
from the day of its establishment,
with the task of elucidating a true physical
character for the formula, and this problem
led me automatically to a consideration of the
connection between entropy and probability,
that is, Boltzmann's trend of ideas;
until after some weeks of the most strenuous
work of my life, light came into the darkness,
and a new undreamed-of perspective
opened up before me.
– Max Planck – Nobel Lecture

Preface

In this book, we develop basic and advanced concepts of plasma thermodynamics from both classical and statistical points of view. After a refreshment of classical thermodynamics applied to the dissociation and ionization regimes, the book introduces the reader, since the very beginning, to discover the role of electronic excitation in affecting the properties of plasmas, a topic often overlooked by the thermal (equilibrium) plasma community. This point is usually disregarded in the existing textbooks of statistical mechanics and thermodynamics mainly devoted to temperature ranges much lower than those covered in this book.

Concepts, such as translational and internal partition functions of atomic and molecular species, are introduced and discussed with different degrees of accuracy. Particular attention is paid to the problem of the divergence of partition function of atomic species as well as to the *state-to-state* approach for calculating the partition function of diatomic and polyatomic molecules, going beyond the well-known harmonic oscillator and rigid rotor approximations. The limit of the ideal gas approximation is then discussed by presenting non-ideal effects including Debye-Hückel and virial corrections. Plasma properties for one and multi-temperature situations are then discussed presenting in the last chapter tables of thermodynamic properties of high temperature planetary atmosphere (Earth, Mars, Jupiter) plasmas.

The book is intended as a graduate-level textbook as well as a monograph on high temperature statistical thermodynamics useful for thermal plasma researchers. The first four chapters are being used for undergraduate students of Physics and Chemistry of the University of Bari (Italy).

Bari

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Many thanks to Annarita Laricchiuta for a careful review of the Appendix and for useful suggestions.

The authors dedicate this book to their wives Giuliana, Grazia and Marianna, the sons and daughters Paolo, Francesco and Cinzia, Mariachiara, Michelangelo, Gerardina, Maria Teresa and the grandsons Alberto and Stefano.

Contents

Introduction

Plasma technology is an emerging multidisciplinary topics widely studied worldwide due to its relevance in many applications. The plasma, also called the fourth state of matter, is a mixture of molecules, atoms, ions and electrons, which can be described by the laws of classical and statistical mechanics.

Usually, plasma technology distinguishes between thermal and cold plasmas, the first characterized by the equilibrium between the different degrees of freedom including the chemical ones, and the second characterized by thermal and chemical non-equilibrium.

Thermal plasmas are usually characterized by a single temperature determining the distribution of internal states and the chemical composition through dissociation and ionization (Saha) equilibria. Boltzmann distributions hold for vibrationally, rotationally and electronically excited states of heavy particles, while Maxwell distributions characterize the velocity distribution of free electrons. On the contrary, thermal plasmas with different temperatures are still accepted in this kind of literature, the different temperatures being related to the corresponding reservoirs of energy. The internal distributions are still Boltzmann at a given (different) temperature. Also in this case chemical equilibrium characterizes the plasma properties even though caution must be exercised in using it. Typical conditions for thermal plasmas are temperatures in the range of 5,000–50,000 K, pressure in the range 10^{-2}–10^{-3} bar and ionization degree larger than 10^{-3}.

In technological applications, thermal plasmas are considered as high enthalpy combustion flames, which can be used for cutting, welding, coating spray and waste removal. Thermal plasmas are also those faced by hypersonic flying objects (e.g. reentering shuttles or meteorites) impacting Earth or planetary atmospheres. Thermal plasma conditions are also generated in Laser Induced Breakdown Spectroscopy (LIBS) and Inductive Coupled Plasmas (ICP) plasmas, two analytical tools widely used to determine metal concentrations in complex matrices. For all these applications, the knowledge of high temperature thermodynamic properties becomes of paramount importance.

In this book, we develop the basic ideas for plasma thermodynamics trying to link the new arguments with the concepts that Science and Engineering students have already learned during physics and chemistry courses. Emphasis will be in particular given to the role of electronic excitation in affecting the thermodynamic properties, a topic often overlooked by the thermal plasma community.

Chapter 1 of the book is dedicated to the use of classical thermodynamics to derive the equations of a reacting mixture by using the equipartition energy theorem for translational, vibrational and rotational energies, the electronic term being inserted in parametric form. In this chapter are also presented the corrections of ideal equations due to real effects, in particular emphasing the classical virial approach from Van der Waals equation.

Chapter 2 is dedicated to the development of two- or three-level models to estimate the electronic contribution for atoms and ions under plasma conditions. These models are based on grouping levels such to reproduce the thermodynamic behaviour of thousand and thousand electronic excited levels. As an example the nitrogen atom is reduced to a three-level system composed by the ground state (^{4}S), a second level which coalesces with appropriate energy and multiplicity the two low lying excited states ^2P and ^2D and a third level which accounts for the huge number of electronically excited states coming from the interaction of the most important nitrogen core (^3P) with the optical level jumping on the 3s, 3p, 3d, 4s, 4p, 4d, 4f,... electronic states. These first two chapters can be used to teach plasma thermodynamics to graduated students avoiding the massive use of statistical thermodynamics and quantum mechanics.

Chapter 3 presents statistical thermodynamics of the perfect gas by introducing the concept of partition function and its linking to the thermodynamic properties of single species and of mixture. The chapter uses the Boltzmann approach introducing molecule and system partition function approaches.

Chapter 4 deals with the calculation of the partition function of atomic species (translational and electronic) and its use in deriving plasma properties considering atomic hydrogen plasma as a case study. In this chapter, we also introduce the importance of imposing an upper limit of principal quantum number to avoid the divergence of partition function, a problem reconsidered in Chap. 8.

Chapters 5 introduces the reader to the partition function of molecular species by using closed forms and state-to-state approaches for the vibro-rotational partition functions of several electronic states. Results are presented and discussed to understand how the standard approach of harmonic oscillator and rigid rotor for a diatomic species deviates from the state-to-state approach emphasizing the role of electronic excitation in affecting the partition function and thermodynamic properties of diatomic molecules. This chapter also introduces the linking between the symmetry of rotational wavefunctions and nuclear spin discussing the ortho–para hydrogen case.

Chapter 6 develops Debye–Hückel equations for correcting the thermodynamic properties of an ideal mixture and for better understanding the problem of the divergence of partition function. In addition, developments to go beyond the Debye–Hückel approach are presented and quantified.

Chapter 7 discusses real gas effects on plasma thermodynamics either applying the virial approach or by using the Reaction Ensemble Monte Carlo (REMC) technique. In this chapter, the grand-partition function is introduced which is then used in the REMC. Problems associated with the calculations of virial coefficients of atom–atom open shell interactions are also presented.

Chapter 8 is dedicated to the study of the influence of the cutoff of partition functions on the thermodynamic properties of thermal plasmas. The most used cutoff criteria derived from Debye–Hückel and confined atom approaches are introduced. These approaches are rationalized on the basis of results obtained by solving the Schrödinger equation of atomic hydrogen in a box. Many results for high temperature-high pressure Oxygen plasmas are presented emphasizing the role of electronic excitation in affecting the frozen properties of a plasma as well as the total ones. The effects of electronic excitation on the global thermodynamic properties of a mixture is hidden, in some cases, by the onset of the reactive contributions due to the ionization reactions.

Chapter 9 describes plasma thermodynamics for multi-temperature systems describing the onset of a multitude of Saha equations coming from the maximization of the total entropy and by minimization of Gibbs potential taking into account different constraints. Results for hydrogen plasmas, again considered as a case study, are reported.

Chapter 10 finally discusses the thermodynamic properties of high temperature planetary atmospheres (Earth, Jupiter, Mars) either in graphical or in tabular form. The accuracy of the used data is discussed in the case of the air plasma by comparing with results existing in literature.

An useful appendix is dedicated to the calculation of energy levels and degeneracies of complex atoms/ions as well as of diatomic molecules.