

Mathematical Engineering

Yuri B. Zudin

Non-equilibrium Evaporation and Condensation Processes

Analytical Solutions

Third Edition



Springer

Mathematical Engineering

Series Editors

Jörg Schröder, Institute of Mechanics, University of Duisburg-Essen, Essen, Germany

Bernhard Weigand, Institute of Aerospace Thermodynamics, University of Stuttgart, Stuttgart, Germany

Today, the development of high-tech systems is unthinkable without mathematical modeling and analysis of system behavior. As such, many fields in the modern engineering sciences (e.g. control engineering, communications engineering, mechanical engineering, and robotics) call for sophisticated mathematical methods in order to solve the tasks at hand.

The series Mathematical Engineering presents new or heretofore little-known methods to support engineers in finding suitable answers to their questions, presenting those methods in such manner as to make them ideally comprehensible and applicable in practice.

Therefore, the primary focus is—without neglecting mathematical accuracy—on comprehensibility and real-world applicability.

To submit a proposal or request further information, please use the PDF Proposal Form or contact directly: Dr. Thomas Ditzinger (thomas.ditzinger@springer.com)

Indexed by SCOPUS, zbMATH, SCImago.

More information about this series at <http://www.springer.com/series/8445>

Yuri B. Zudin

Non-equilibrium Evaporation and Condensation Processes

Analytical Solutions

Third Edition

 Springer

Yuri B. Zudin
National Research Center
Kurchatov Institute
Moscow, Russia

ISSN 2192-4732

ISSN 2192-4740 (electronic)

Mathematical Engineering

ISBN 978-3-030-67552-3

ISBN 978-3-030-67553-0 (eBook)

<https://doi.org/10.1007/978-3-030-67553-0>

1st edition: © Springer International Publishing AG 2018

2nd edition: © Springer Nature Switzerland AG 2019

3rd edition: © The Editor(s) (if applicable) and The Author(s), under exclusive license to Springer Nature Switzerland AG 2021

This work is subject to copyright. All rights are solely and exclusively licensed by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed.

The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

The publisher, the authors and the editors are safe to assume that the advice and information in this book are believed to be true and accurate at the date of publication. Neither the publisher nor the authors or the editors give a warranty, expressed or implied, with respect to the material contained herein or for any errors or omissions that may have been made. The publisher remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

This Springer imprint is published by the registered company Springer Nature Switzerland AG
The registered company address is: Gewerbestrasse 11, 6330 Cham, Switzerland

*To my beloved wife Tatiana,
who has always been my source of
inspiration,
to my children Maxim and Natalya,
and to my grandchildren Alexey and Darya*

Preface

The present third edition substantially augments the second edition of the book (Non-equilibrium Evaporation and Condensation Processes. Analytical Solutions, Springer, 2019) by the author. Non-equilibrium evaporation and condensation processes play an important role in a number of fundamental and applied problems. When using laser methods for the processing of materials, it is important to know the laws of both evaporation (for thermal laser ablation from the target surface) and condensation (for the interaction with the target of an expanding vapor cloud). Some accident situations in the energetic industry develop from a sudden contact of bulks of cold liquid and hot vapor. Shock interaction of two phases produces a pulse rarefaction wave in vapor accompanied by an abrupt variation of pressure in vapor and intense condensation. Spacecraft thermal protection design calls for the modeling of the depressurization of the protection cover of nuclear propulsion units. To this end, one should be capable of calculating the parameter of intense evaporation of the heat transfer medium as it discharges into vacuum. Solar radiation on a comet surface causes evaporation of its ice core with the formation of the atmosphere. Depending on the distance to the Sun, the intensity of evaporation varies widely and can be immense. The process of evaporation, which varies abruptly in time, has a substantial effect on the density of the comet atmosphere and the character of its motion.

The specific feature of intense phase transitions is the formation of the non-equilibrium Knudsen layer near the surface. In this setting, the standard gas-dynamic description within the Knudsen layer becomes illegitimate: the phenomenological parameters of the gas, as determined by statistical averaging rules, cease to have their macroscopic sense. Under non-equilibrium conditions, the joining conditions of the condensed and gaseous phases turn out to be much more involved than those adopted in the equilibrium approximation. From the consistent consideration of molecular-kinetic effects on the phase boundary, one can get important nontrivial information about the thermodynamic state of vapor under phase transitions.

An important problem of safety assurance in nuclear power plants is the calculation of the process of discharge of the heat transfer medium through pipeline ruptures. This can be accompanied by the explosive boiling of superheated liquid resulting in the substantial restructuring of the flow structure. The explosive boiling regime

is manifested most vividly when the liquid attains the limit thermodynamic temperature (the spinodal temperature). This is accompanied by homogeneous nucleation (fluctuation generation of vapor bubbles in the mother phase).

Despite the fluctuation character of nucleation and the short lifetime of vapor bubbles, the phenomenon of gaseous (vapor) bubbles in liquid has many manifestations: underwater acoustics, sonoluminescence, ultrasonic diagnosis, reduction of friction by surface nanobubbles, and bubble boiling. In applications pertaining to the physics of boiling, it is required to know the dependence of the growth rate of a vapor bubble on a number of parameters: thermophysical properties of liquid and vapor, capillary, viscous, and inertial forces, and molecular-kinetic laws on the phase boundary.

Modern progress in microelectronics and nanotechnologies calls for further analysis of the behavior of the phase boundary in microscopic objects, and in particular, the behavior of the liquid–gas boundary. Here, of great value is the study of the joint action of intermolecular and surface forces, which control the motion of evaporating microscopically thin films.

The cooling of heated surfaces by droplet jets is widely spread in various engineering applications: energy industry, metallurgy, cryogenics, space engineering, and firefighting. The progress in this area is hindered by the insufficient comprehension of all the phenomena accompanying the impingement of a jet on a surface. The key problem here is the study of the interaction of liquid droplets with a rigid surface.

The problem of vapor condensation in a transverse flow past a horizontal cylinder (in contrast to the “classical” case of stationary steam on a vertical plate) is much more involved, which requires a comprehensive analysis, including the correct consideration of all forces acting on a falling condensate film. With film condensation of vapor, even a small portion of noncondensable gas can significantly reduce the intensity of heat- and mass transfers. Due to the loss of vapor due to condensation, the velocity of the steam–gas flow decreases downstream, while the concentration of the noncondensable gas increases. Therefore, the negative effect of noncondensable gas can be quite substantial, even though its initial content could be small. In contrast to the case of pure vapor condensation, it is necessary to calculate the local characteristics of the heat- and mass transfer.

Bubble boiling, which is an integral part of various techniques, is an extremely effective method for cooling solid surfaces exposed to high-intensity thermal effects (structural elements of thermonuclear fusion plants, high-power lasers, physical targets, etc.). The very strong dependence of the heat flux density on the wall overheating makes it possible to divert energy flows of huge density at a relatively small temperature difference. The unique combination of the resistance to “strong” and the instability to “weak” external influences provides a fundamental obstacle to creating a consistent theory of bubble boiling. Special attention should be paid to the debatable issue of the influence of thermophysical characteristics of a heat-transmitting wall on the characteristics of bubble boiling.

Exotic non-equilibrium effects accompany the boiling of liquid helium in the state of superfluidity, which is a macroscopic quantum state. Of fundamental interest here is the analysis of thermodynamic principles of superfluid helium from two

alternative positions: the macroscopic approach, which is based on the two-fluid model, and the microscopic analysis, which depends on the quantum-mechanical model of quasi-particles.

Of special interest is also the physical concept of pseudoboiling, which describes the laws of heat exchange in the range of supercritical pressures of a single-phase liquid. The model of pseudoboiling enables one to calculate the heat exchange with turbulent flow in a channel of medium with highly variable thermophysical properties.

Gas bubbles that rise in a stationary liquid under the action of the gravity force can have shapes of a sphere, an ellipsoid of rotation flattened in the direction of the pop-up, and a spherical cap. Depending on the volume of the bubble, the trajectory of its motion can be straight, zigzag, or helical. The unusual shape and trajectory of gas bubbles have been the subject of a huge number of studies starting with Leonardo da Vinci. Experimental studies of rising bubbles cover the last 120 years. The only exact solution to the problem of rising bubbles in a liquid volume was obtained by Hadamard and Rybczynski in the case of very small bubbles. At present, the dependence of the rise velocity on the size of moderate and large gas bubbles is described by semi-empirical and empirical relations.

Helium at supercritical pressures is used as a coolant for cryogenic superconductivity-based objects. Pulsations of flow rate and temperature may develop in a flow of supercritical helium under certain combinations of regime parameters. Due to the strong dependence of the thermophysical properties of supercritical helium on the temperature during its flow in the channels, a thermohydraulic instability of the “density wave” type can occur. The theoretical analysis of this specific instability requires a physical model which is fundamentally different from the standard method of small oscillations.

In the case of a turbulent flow in channels of two-phase flows, the effect of dispersed inclusions (bubbles, droplets, etc.) on the thermal hydrodynamics of the continuous phase plays an important role. To correctly account for this effect, it is necessary to conduct a theoretical study of the process of bubble and droplet breakup as they interact with the turbulent continuous medium.

The present book is solely concerned with analytical approaches to the statement and solution of problems of this kind. The analytical approach is capable of providing a solution to the mathematical model of a physical problem in the form of compact formulas, expansions into series, and integrals over a complete family of eigenfunctions of a certain operator. The study involves the application of the available methods and the discovery of new methods of solutions of a given mathematical model of a real process, given as a differential or integral equation or a system of differential or integro-differential equations. The resulting analytical relation provides an adequate description (even for a simplified model) of the essence of a physical phenomenon. From analytical solutions, one is capable to understand and represent in a transparent form the principal laws, especially in the study of a new phenomenon or a process. This is why analytical methods are always employed in the first stage of mathematical modeling. Analytical solutions are also used as test models for the validation of results of numerical solutions.

In Chap. 1, the molecular-kinetic theory is looked upon as a link between the microscopic and macroscopic levels of the description of the structure of the material. Historical aspects of the creation by Ludwig Eduard Boltzmann of his seminal equation are discussed; we also dwell upon the discussions following this discovery. We give a precise solution to the Boltzmann equation in the case of space-homogeneous relaxation. Applied problems of intense phase transition are discussed. The problem of specifying boundary conditions on the phase interface of the condensed and gaseous phases is discussed. Methods of kinetic analysis of evaporation and condensation processes are discussed.

Chapter 2 is concerned with the non-equilibrium effects on the phase interface. We give the conservation equations of molecular flows of mass, momentum, and energy, and describe the classical problem of evaporation into a vacuum. Actual and extrapolated boundary conditions are analyzed for the gas-dynamic equations in the external domain. It is shown that in the non-equilibrium Knudsen layer (adjacent to the phase boundary), the velocity distribution function of molecules can be conventionally split into two parts. We also discuss the problem of determination of the accommodation coefficients of mass, momentum, and energy. We present the fundamentals of the linear kinetic theory. Approximate kinetic models of the strong evaporation problem are described.

Chapter 3 is devoted to the approximate kinetic analysis of strong evaporation. On basis of the mixing model, we give analytical solutions for temperatures, pressures, and mass velocities of vapor and match them with the available numerical and analytical solutions. The mechanism of reflection of molecules from the condensed-phase surface is analyzed. The effect of the condensation coefficient on the conservation equations of molecular flows of mass, momentum, and energy, and also on the thermodynamic state of the resulting vapor is studied. “Thermal conductivity in target-intensive evaporation” conjugate problem is calculated. The asymptotic behavior of the solutions in terms of the key parameters of the systems is obtained and analyzed from the physical viewpoint. The conjugate problem for the hyperbolic heat conduction equation was considered. The integral Laplace transform was applied to find an analytical solution of the hyperbolic heat conduction equation in the general case when the temperature and the heat flux on the body surface are arbitrary time functions. A general solution to the problem is constructed using the concept of the relative HTC. A two-zone approximation of the solution was given, using which the following characteristic parameters of the conjugate problem were identified: the delay time, the height of the hyperbolic shelf, and the hyperbolic and parabolic zones of the evaporation process.

Chapter 4 proposes a semi-empirical model of strong evaporation based on the linear kinetic theory. Extrapolated jumps of density and temperature on the condensed-phase surface are obtained by summing the linear and quadratic components. The expressions for the linear jumps are taken from the linear kinetic theory of evaporation. The nonlinear terms are calculated from the relations for a rarefaction shock wave with due account of the corrections for the acceleration of the egressing flow of gas. Analytical dependences of the vapor parameters in the gas-dynamic region on the Mach number, the condensation coefficient, and the number of degrees

of freedom of gas molecules are put forward. For a kinetic shock evaporation wave, its model is proposed based on the composition of classical results of the linear kinetic evaporation theory and the theory of gas-dynamic shock rarefaction wave. A kinetic shock wave is shown to be stable based on the second law of thermodynamics. It is proved that the maximum entropy principle, which follows from Prigogine's theorem, is satisfied during transonic evaporation. A highly unstable solution of the inverse problem of intense evaporation is obtained. It is shown that the solution of the intense evaporation problem is conservative with respect to the method of approximation of the distribution function.

In Chap. 5, the approximate kinetic analysis of strong condensation is developed. The "mixing model" is used to calculate regimes of subsonic and supersonic condensation. Peculiarities of supersonic condensation with increased Mach number are studied: inversion of the solution, bifurcation of the solution, transition to two-valued solutions, and the limit Mach number, for which a solution exists. The effect of the condensation coefficient on the conservation equations for mass, the normal component of the momentum, and the energy of molecular flows is studied. The "condensation lock" phenomenon due to the reduced permeability of the condensed-phase surface is examined.

In Chap. 6, the mixing model is used for the analysis of linear kinetic problems of phase transition. The asymmetry of evaporation and condensation, which occurs for intensive processes, remains even for the case of linear approximation. The expressions for pressure and temperature jumps are obtained for the evaporation problem: these results almost coincide with those of the classical linear theory. The dependence of the vapor pressure on its temperature is shown as having a minimum near the margin between the anomalous and normal regimes of condensation. The results are extended to the case of diffusion reflection of molecules from the phase boundary.

Chapter 7 is concerned with the spherically symmetric growth of a vapor bubble in an infinite volume of a uniformly superheated liquid. We consider the influence of each effect within the framework of the limiting schemes. A detailed analysis of the energetic thermal scheme of a bubble is carried out. As the next step, we come to the "binary" schemes of growth that describe the simultaneous effect of two factors on the growth of a bubble. The evaporation–condensation coefficient was estimated by comparing the theoretical solution with experimental data on the growth of a vapor bubble under reduced gravity conditions. The growth mechanism of bubbles formed as a result of the homogeneous bubble nucleation is studied.

Chapter 8 is concerned with the study of the growth of a vapor bubble in the case when the superheating enthalpy exceeds the phase transition heat is considered. The Plesset–Zwick formula was extended to the region of strong superheating. It was that when the Stefan number exceeds 1 there arises a feature of the mechanism of heat input from the liquid to the vapor leading to the effect of pressure blocking in the vapor phase. To calculate the Stefan number in the metastable region, we use the scaling law of change in the isobar heat capacity. The problem of the effect of the experimental conditions on the effervescence of the butane drop is solved. An algorithm was proposed for constructing an approximate analytical solution for the range of Stefan numbers greater than unity.

Chapter 9 provides an evaporating meniscus on the interface of three phases. An approximate solution method is presented capable of finding the influence of the kinetic molecular effects on the geometric parameter of the meniscus and on the heat transfer intensity. The method depends substantially on the change of the boundary-value problem for the fourth-order differential equation (describing the thermo-hydrodynamics of the meniscus) by the Cauchy problem for a second-order equation. Analytical expressions for the evaporating meniscus parameters are obtained from the analysis of the interaction of the intermolecular, capillary, and viscous forces, and the study of the kinetic molecular effects. The latter effects are shown to depend substantially on the evaporation–condensation coefficient.

Chapter 10 is concerned with the kinetic effects for a spheroidal state. The question on the influence of the kinetic molecular effects on the drop equilibrium conditions is considered for the first time. Results of the linear kinetic theory of evaporation are used to evaluate the kinetic pressure difference due to the non-equilibrium conditions of the evaporation process. It is shown that, depending on the value of the evaporation/condensation coefficient, the kinetic pressure with respect to a drop may have either repulsing or attracting character. The analytical dependence for the thickness of the vapor film for a wide range of evaporation/condensation coefficients is found.

Chapter 11 provides vapor condensation upon the transversal flow around a cylinder. The analytical solutions for the limiting heat-exchange laws, which correspond to the effect of only one factor, are obtained under the assumption that there is no effect of the remaining factors. The results of the solution are presented as relative (with respect to the case of steady-state vapor) heat-exchange laws. The qualitative analysis of the effect of mode parameters on heat transfer upon condensation is carried out. The analysis of the limiting heat-exchange laws demonstrates their mutual interdependence, which impedes the isolation of simple asymptotics of the problem under consideration with respect to individual parameters. The mechanistic model of condensation from a vapor–gas mixture is considered. We propose an iteration-free procedure of the solution of the main equation of the mechanistic model, from which parametrical analysis with arbitrary different mass contents of the inert gas can be carried out. For high gas contents, the mechanistic model is shown to be unphysical, which is manifested in the inversion of the diffusion component of the heat flow (the diffusion paradox) and vanishing of the total heat flow (the condensation lock paradox). We develop a modified mechanistic model of condensation from a vapor–gas mixture based on the introduction of the effective heat of phase transition.

Chapter 12 describes the principal constituents of the general problem of the boiling phenomenon: conditions for the inception of boiling, formation of nucleation sites, and boiling regimes. Growth laws of a vapor bubble in a bulk of liquid and on a rigid surface are described. A microlayer of liquid under a vapor bubble, a macrolayer under vapor conglomerates, and dry spots on the heat surfaces are studied. A brief description of heat-exchange models for nucleate boiling is given; these models are based on the bubble dynamics and integral characteristics of the process. Special attention is given to a debating problem on the effect of thermophysical characteristics

of a heat-transmitting wall. An approximate model for the periodic conjugate heat-exchange problem for boiling is given. The calculation results of the conjugation factor for boiling and transition boiling regimes are given.

Chapter 13 describes the superfluidity phenomenon due to the formation of “particle condensate” in one quantum state. Here, we consider specific peculiarities of heat exchange with film boiling of superfluid helium (He-II) related to molecular-kinetic effects on the phase boundary. The analysis of thermodynamic principles of He-II in the framework of the two-fluid model is carried out. A method of construction of thermodynamics from the first principles is considered. The use of the quantum-mechanical conception of quasi-particles enables us to prove the equivalence of the macroscopic and microscopic levels of He-II thermodynamics analysis.

Chapter 14 describes the heat transfer problem under a turbulent flow in a coolant channel in the zone of supercritical pressures. The modified surface renewal model was developed capable of calculating the effect of variable thermophysical properties on the friction and heat exchange. The approximation solution is shown as being legitimate in describing the general case of variation of thermophysical properties. The model was validated on problems with available solutions: flow in a turbulent boundary layer of a viscous compressible gas, a permeable wall past incompressible fluid, etc. The law of heat transfer for the turbulent flow in the channel in the zone of supercritical pressures was calculated.

In Chap. 15, the derivation of the problem of gas bubble rise in a liquid at rest under the action of the gravity force is given. We present a model of bubble rise for the region free from the effect of viscosity (moderately large and large bubbles). In the model based on the “base underpressure” concept, a bubble is assumed to be composed of two parts. The analysis of the “traditional” and “capillary” asymptotics of the dependence of the rise velocity on the equivalent radius is given. A general analytical solution of the problem is put forward, which holds for the “inviscid range” of the bubble rise velocity. The problem of the rise of the Taylor bubble in a round tube is considered. An analytical solution of the problem is obtained based on the collocation method and the asymptotical analysis of the solution to the Laplace equation. The method employed was validated on an example of the solution of the corresponding flat problem. As a result, a correct approximate solution of the rise problem of a Taylor bubble in a round tube is presented.

Chapter 16 describes the problem of the dynamics of gas bubbles in a liquid under various conditions. Based on the analysis of the Laplace equation for the velocity potential in an ideal fluid, a generalized Rayleigh equation is proposed for the dynamics of a bubble in a circular pipe. The spherical and cylindrical asymptotics are analyzed. An exact analytical solution of the bubble collapse problem in a tube is obtained. A critical analysis of the problem of homogeneous nucleation of vapor bubbles in an unlimited volume of liquid is given. A quantum-mechanical model of homogeneous nucleation is proposed. The problem of bubble size in a turbulent fluid flow is considered. A description of the Kolmogorov–Hinze model of bubble breakup, which is based on the balance of capillary and inertial forces, is given. The modified Kolmogorov–Hinze model eliminating the above paradox is presented.

The main idea of the modified model is the consideration of the balance of the forces acting on the bubble of liquid pulsations caused by the gravitational of bubble rise.

In Chap. 17, we study how the heat-exchange characteristics depend on the droplets dispersed in a turbulent steam flow in a channel. The process of droplet breakup is investigated on the basis of a semi-empirical resonance model. A final relation for the maximum stable droplet diameter is obtained. The classical Prandtl turbulence model was used to study the effect of droplets on the heat exchange. An analytical solution of the energy equation with thermal effluents caused by the droplet evaporation is obtained. The relative law of heat transfer is calculated, allowing one to determine the quantitative measure of the effect of the droplets on the heat exchange with a dispersed flow. The asymptotic variants of the analytical solution thus obtained are analyzed.

In Chap. 18, the derivation of the thermal-hydraulic “density wave”-type instability occurring in flows of supercritical helium in channels is given. It is shown that this instability is described by three dimensionless quantities: the extension parameter, the pressure parameter, and the homochronicity parameter. We consider two problems described by two parameters and distinguished by the type of pressure losses over the channel length. The Maple computer algebra software system was used to derive the exact analytical solutions determining the stability boundary, the frequency of developed perturbations, and the characteristics of growth increment and damping decrement. The asymptotical behavior of the analytical solution is studied and its approximations are constructed. It is shown that with increasing extension parameter the system crosses in succession new stability boundaries, as a result, high-frequency exponentially increasing perturbations of more and more increasing frequency come into play.

Chapter 19 presents the results of an experimental investigation of heat transfer in a pebble bed for flows of single-phase boiling liquid. The experiments involved the measurements of the temperature of a heated wall, as well as of the temperature distribution over the channel cross section at the outlet from the pebble bed. Use was made of a method of processing of experimental data, which enables one to determine the turbulent thermal conductivity without differentiation of the experimentally obtained temperature profile. The solution of unsteady-state heat equation, obtained for the conditions of the initial thermal segment, is used for this purpose. The experimental data for single-phase flow are described using the mathematical model of the process with two free parameters (the temperature on the boundary of the flow core and the turbulent thermal conductivity) and then processed by numerical optimization methods.

Appendix A considers the problem of heat transfer under film boiling. We obtain analytical solutions capable of taking into account the effects of vapor superheat in a film and the influence of the convection on the effective values of thermal conductivity and heat of phase transition of superheated vapor. Universal calculation formulas are presented describing the dependence of these values on the Stefan number for the cases of linear and parabolic distributions of velocities in the vapor film.

Appendix B analyzes the physical relation of the hydrodynamic model of pool boiling crisis and the development of instability for evaporation from the interphase

boundary (the Landau instability). It is shown that in both cases, the resulting dependences for the limit heat flow are identical in both cases and differ only by a numerical coefficient. An analogy with the development of the Kelvin–Helmholtz instability is given. Calculations of the critical heat flow at liquid boiling in a pipe under conditions of a turbulent flow in a channel are performed. It is found that the use of the centrifugal acceleration in Kutateladze’s formula provides a satisfactory agreement with the experimental data.

I would like to deeply thank the Director of ITLR, Series Editor Mathematical Engineering of Springer-Verlag, Prof. Dr.-Ing. habil. B. Weigand, for his strong support for my aspiration to successfully accomplish this work, as well as for his valuable advice and numerous fruitful discussions concerning all aspects of the analytical solution methods. Prof. B. Weigand repeatedly invited me to visit Institute of Aerospace Thermodynamics to perform joint research. Our collaboration was of great help to me in the preparation of this book. I am deeply indebted to Dr. T. Ditzinger, Editor of Springer-Verlag, for his interest in the publication and very good cooperation during the preparation of this manuscript.

The work on this book would be impossible without the long-term financial support of my activity at German universities (Uni Stuttgart, TU München, Uni Paderborn, HSU/UniBw Hamburg) from the German Academic Exchange Service (DAAD), from which for quarter of century I was awarded eight (!) grants. I also wish to express my sincere thanks to Dr. P. Hiller, Dr. W. Trenn, Dr. H. Finken, Dr. T. Prahl, Dr. G. Berghorn, Dr. M. Krispin, Dr. A. Hoeschen, M. Linden-Schneider, and also to all other DAAD employees both, in Bonn and in Moscow.

I would like to thank my dear wife Tatiana for her invaluable moral support for my work, especially in these tough and challenging times.

I am also thankful to Dr. A. Alimov (Moscow State University) for his very useful comments, which contributed much toward the considerable improvement of the English translation of this book.

In conclusion, I cannot but stress the most crucial role played in my career by the prominent Russian scientist Prof. Labuntsov who was my scientific advisor. I would consider my task accomplished if in this book, I was able to develop some of Prof. Labuntsov’s ideas that could lead to some new modest results.

Stuttgart, Germany
November 2020

Yuri B. Zudin

Contents

1	Introduction to the Problem	1
1.1	Kinetic Molecular Theory	1
1.2	Discussing the Boltzmann Equation	4
1.3	Precise Solution to the Boltzmann Equation	7
1.4	Intensive Phase Change	10
	References	14
2	Non-equilibrium Effects on the Phase Interface	17
2.1	Conservation Equations of Molecular Flows	18
2.2	Evaporation into Vacuum	22
2.3	Extrapolated Boundary Conditions	25
2.4	Accommodation Coefficients	27
2.5	Linear Kinetic Theory	29
2.6	Introduction to the Problem of Strong Evaporation	35
	2.6.1 Conservation Equations	35
	2.6.2 The Model of Crout	39
	2.6.3 The Model of Anisimov	40
	2.6.4 The Model of Rose	42
	2.6.5 The Mixing Model	42
	References	43
3	Approximate Kinetic Analysis of Strong Evaporation	47
3.1	Introduction	48
3.2	Conservation Equations	50
3.3	Mixing Surface	52
3.4	Limiting Mass Flux	54
3.5	Reflection of Molecules from the Surface	57
	3.5.1 Condensation Coefficient	57
	3.5.2 Diffusion Scheme for Reflection of Molecules	60
3.6	Thermodynamic State of Vapor	62
3.7	Laser Irradiation of Surface	66

3.8	Integral Heat Balance Method	67
3.8.1	Analytical Solutions	67
3.8.2	Heat Perturbation Front	69
3.9	Heat Conduction Equation in the Target	70
3.10	The “Thermal Conductivity–Evaporation” Conjugate Problem	72
3.11	Linear Evaporation Problem	75
3.12	Nonlinear Evaporation Problem	78
3.13	Irradiation of Saturated Fluid	83
3.14	Conjugate Problem for Hyperbolic Heat Conduction Equation	85
3.14.1	Generalized Form for the Solution	85
3.14.2	Fourier’s Heat Conduction Hypothesis	86
3.14.3	Cattaneo–Vernotte’s Heat Conduction Hypothesis	89
3.14.4	Spatially Inhomogeneous Structures	89
3.14.5	Estimate of the Relaxation Time	91
3.15	General Analytical Solution of the Conjugate Problem	92
3.15.1	Integral Laplace Transform	92
3.15.2	Relative Heat Transfer Coefficient	95
3.15.3	Dimensionless Heat Transfer Coefficients	97
3.15.4	Two-Zone Approximation of the Solution	100
3.15.5	Algorithm of Solution of the Conjugate Problem	102
3.16	Conclusions	104
	References	105
4	Semi-Empirical Model of Strong Evaporation	109
4.1	Strong Evaporation	110
4.2	Approximate Analytical Models	113
4.3	Analysis of the Available Approaches	115
4.4	The Semi-Empirical Model	116
4.5	Validation of the Semi-Empirical Model	120
4.5.1	Monatomic Gas	120
4.5.2	Sonic Evaporation	123
4.5.3	Polyatomic Gas	126
4.5.4	Maximum Mass Flow	126
4.6	Hydrodynamic Instability	129
4.6.1	Small Disturbance Method	129
4.6.2	Kelvin–Helmholtz Instability	130
4.6.3	Kinetic Shock Wave	133
4.6.4	Thermodynamic System	134
4.6.5	Onsager Reciprocal Relation	136
4.6.6	Prigogine Theorem	138
4.6.7	Change of the Entropy	140

4.7	Inverse and Ill-Posed Problems	142
4.7.1	Conditions for Well-Posedness	142
4.7.2	Numerical Methods	145
4.8	Direct and Inverse Problems of Strong Evaporation	145
4.8.1	Strong Evaporation	145
4.8.2	Macroscopic Models of Strong Evaporation	148
4.8.3	Solution of Inverse Problem	150
4.9	Conclusions	153
	References	154
5	Approximate Kinetic Analysis of Strong Condensation	157
5.1	Introduction	158
5.2	Macroscopic Models	159
5.3	Strong Evaporation	161
5.4	Strong Condensation	163
5.5	The Mixing Model	163
5.6	Solution Results	167
5.7	Sonic Condensation	169
5.8	Approximate Solution	171
5.9	Supersonic Condensation Regimes	174
5.9.1	Introduction	174
5.9.2	Calculation Results	175
5.10	Diffusion Scheme of Reflection of Molecules	179
5.11	The General Case of Boundary Conditions	182
5.12	The Effect of β on the Condensation Process	185
5.13	Conclusions	186
	References	187
6	Linear Kinetic Analysis of Evaporation and Condensation	189
6.1	Introduction	190
6.2	Conservation Equations	192
6.3	Equilibrium Coupling Conditions	196
6.4	Linear Kinetic Analysis	197
6.4.1	Linearized System of Equations	197
6.4.2	Symmetric and Asymmetric Cases	199
6.4.3	Kinetic Jumps	201
6.4.4	Effect of Condensation Coefficient	203
6.4.5	Short Description	207
6.5	Conclusions	207
	References	208
7	Binary Schemes of Vapor Bubble Growth	209
7.1	Introduction	210
7.2	Limiting Schemes of Growth	210
7.3	The Energetic Thermal Scheme	213
7.4	Binary Schemes of Growth	218

7.4.1	The Viscous–Inertial Scheme	218
7.4.2	The Inertial–Thermal Scheme	219
7.4.3	The Region of High Superheatings	220
7.4.4	The Non-equilibrium-Thermal Scheme	223
7.5	Conclusions	225
	References	226
8	Pressure Blocking Effect in a Growing Vapor Bubble	229
8.1	Introduction	230
8.2	The Inertial-Thermal Scheme	231
8.3	The Pressure Blocking Effect	234
8.4	The Stefan Number in the Metastable Region	236
8.5	Effervescence of the Butane Drop	238
8.6	Seeking an Analytical Solution	242
8.6.1	Qualitative Analysis	242
8.6.2	Asymptotically Analytical Solution	243
8.7	Conclusions	245
	References	245
9	Evaporating Meniscus on the Interface of Three Phases	247
9.1	Introduction	248
9.2	Evaporating Meniscus	251
9.3	Approximate Analytical Solution	253
9.4	Nanoscale Film	257
9.5	The Averaged Heat Transfer Coefficient	258
9.6	The Kinetic Molecular Effects	259
9.7	Conclusions	262
	References	263
10	Kinetic Molecular Effects with Spheroidal State	265
10.1	Introduction	266
10.2	Assumptions in the Problem Description	267
10.3	Hydrodynamics of Flow	268
10.4	Equilibrium of Drop	271
10.5	Conclusions	277
	References	278
11	Solution of Special Problems of Film Condensation	279
11.1	Condensation of Vapor Flowing around a Cylinder	280
11.1.1	Introduction	280
11.1.2	Limiting Heat Transfer Laws	282
11.1.3	Asymptotics of Immobile Vapor	284
11.1.4	Pressure Asymptotics	285
11.1.5	Tangential Stresses at the Interface Boundary	286
11.1.6	Analysis of the Results	288

11.2	Condensation from a Vapor-Gas Mixture	293
11.2.1	Survey of the Literature	293
11.2.2	The Mechanistic Model	295
11.2.3	The Chilton–Colburn Analogy	298
11.2.4	The Principal Equation of the Mechanistic Model	299
11.2.5	Iteration-Free Solution Procedure	302
11.2.6	Evaluation by the Mechanistic Model	303
11.2.7	The Modified Mechanistic Model	305
11.2.8	Asymptotic Analysis of Mechanistic Model	307
11.3	Conclusions	309
	References	309
12	Nucleate Pool Boiling	313
12.1	Metastable Liquid	314
12.2	Conditions for the Onset of Boiling	316
12.3	Nucleation Sites	317
12.4	Boiling Regimes	318
12.4.1	Boiling Curve	318
12.4.2	Nucleate Boiling	319
12.4.3	Film Boiling	320
12.4.4	Transition Boiling	321
12.5	Vapor Bubble Growth Laws	322
12.5.1	Bubble Growth in a Bulk Liquid	322
12.5.2	Bubble Growth on a Rigid Surface	324
12.6	Mechanisms of Nucleate Boiling Heat Transfer	329
12.6.1	Applied Significance of Nucleate Boiling	329
12.6.2	Classification of Utilized Liquids	330
12.6.3	Heat Transfer Modeling (Dynamics of Bubbles)	331
12.6.4	Heat Transfer Modeling (Integral Characteristics)	332
12.6.5	Difficulties of Theoretical Descriptions	336
12.7	Periodic Model of Nucleate Boiling	337
12.7.1	Oscillations of the Thickness of a Liquid Film	337
12.7.2	Nucleation Site Density	339
12.8	Effect of Thermophysical Characteristics of Wall Materials	342
12.9	Effect of Oscillating Interface on Heat Transfer	343
12.9.1	Oscillation Structure of Convective Heat Transfer	343
12.9.2	Correct Averaging of the Heat Transfer Coefficient	345
12.9.3	Model of Periodical Contacts	348

12.10	Conjugate Heat Transfer Problem in Boiling	350
12.10.1	Nucleate Boiling	350
12.10.2	Transition Boiling	354
12.11	Conclusions	356
	References	356
13	Heat Transfer in Superfluid Helium	359
13.1	Introduction	359
13.2	Practical Applications of Superfluidity	361
13.3	Two-Fluid Model of Superfluid Helium	361
13.4	Peculiarities of “Boiling” of Superfluid Helium	362
13.4.1	Some Properties of Superfluid Helium	362
13.4.2	Heat Transfer in Superfluid Helium	363
13.4.3	Kapitza Resistance	365
13.5	Theory of Laminar Film Boiling of Superfluid Helium	367
13.5.1	Laminar Film Boiling	367
13.5.2	Cylinder	373
13.5.3	Plate	374
13.6	Thermodynamic Principles of Superfluid Helium	375
13.6.1	Two-Fluid Model	375
13.6.2	Microscopic Analysis	378
	References	382
14	Pseudoboiling	383
14.1	Area of Supercritical Pressures	384
14.1.1	The Relevance of the Problem	384
14.1.2	Theoretical Studies of Heat Transfer	387
14.2	Surface Renewal Model	388
14.2.1	Periodic Structure of Near-Wall Turbulent Flow	388
14.2.2	Relative Correspondence Method	389
14.3	Mathematical Description	390
14.3.1	Conservation Equations	390
14.3.2	Boundary Conditions	392
14.3.3	Dimensionless Variables	393
14.4	Solution of the Main Equation	394
14.4.1	Exact Solution	394
14.4.2	Approximate Solution	397
14.5	Heat Transfer and Friction in the Turbulent Boundary Layer	398
14.5.1	Mathematical Description	398
14.5.2	Effect of Variable Thermophysical Properties	400
14.5.3	Effect of Thermal Expansion/Contraction	402
14.6	Wall Blowing/Suction	406
14.7	Heat Transfer Evaluation	409
14.7.1	Relative Law of Heat Transfer	409
14.7.2	Deteriorated and Improved Regimes	409

14.7.3	Comparison with Experimental Data	411
14.8	Conclusions	413
	References	413
15	Bubble Rising in a Liquid	415
15.1	Bubble Rising in Liquid Column	415
15.1.1	Spherical Bubbles	415
15.1.2	Force Balance	420
15.1.3	Energy Balance	421
15.1.4	Semiempirical Models	423
15.1.5	Empirical Models	425
15.1.6	Instability of Buoyancy Trajectory for a Bubble	427
15.1.7	Base Underpressure Model	429
15.1.8	Gravitational Asymptotics	434
15.1.9	Capillary Asymptotics	435
15.2	Taylor Bubble Rising in Vertical Tube	438
15.2.1	Theoretical Solutions	438
15.2.2	Correct Statement of the Problem	440
15.2.3	Stagnation Point	444
15.2.4	Method of Collocations	446
15.2.5	Asymptotical Solution	448
15.2.6	Plane Taylor Bubble	451
15.2.7	Non-uniqueness of the Solution	453
15.3	Conclusions	454
	References	454
16	Bubbles Dynamics in Liquid	457
16.1	Bubble Dynamics in a Tube	458
16.1.1	The Generalized Rayleigh Equation	458
16.1.2	The General Case	462
16.1.3	Collapse of a Bubble in a Tube	464
16.2	Homogeneous Nucleation	465
16.2.1	Introduction	465
16.2.2	Classical Theory	466
16.2.3	Quantum Mechanical Model	468
16.3	Bubble Size in a Turbulent Fluid Flow	470
16.3.1	Structure of Turbulent Vortices	470
16.3.2	Richardson–Kolmogorov Cascade	472
16.3.3	Models of Turbulence	475
16.3.4	Bubbles Breakup	478
16.3.5	Local Isotropic Turbulence	479
16.3.6	Empirical Formulas and Experimental Data	480
16.3.7	Calculation of Turbulence Energy Dissipation	481
16.3.8	Modified Kolmogorov–Hinze Model	482
16.4	Conclusions	484
	References	485

17	Heat Transfer to a Disperse Two-Phase Flow	487
17.1	Droplet Size in Dispersed Two-Phase Flow	488
17.1.1	Free Oscillations of Droplet	488
17.1.2	Analysis of the Solution	490
17.1.3	Theory of Locally Isotropic Turbulence	492
17.1.4	Resonance Model of Droplets Breakup	493
17.2	Effect of Droplets on Heat Transfer to a Disperse Two-Phase Flow	495
17.2.1	Analytical Solutions	495
17.2.2	Energy Equation for Dispersed Two-Phase Flow	496
17.2.3	Analytical Solution	498
17.2.4	Relative Law of Heat Transfer	499
17.3	Conclusions	501
	References	501
18	Thermal–Hydraulic Stability Analysis of Supercritical Fluid	503
18.1	Thermal–Hydraulic Instability	503
18.2	Small Variations Method	505
18.3	Density Wave Instability	506
18.3.1	Physical Analysis	506
18.3.2	Mathematical Description	508
18.4	Problem 1. Pressure Losses in Throttles	512
18.4.1	The Process of Solution	512
18.4.2	Approximation of the Solution	515
18.5	Problem 2. Pressure Losses Over the Channel Length	516
18.5.1	Construction of the General Solution	516
18.5.2	Analytical Solution	518
18.5.3	Instability Region	519
18.5.4	Stability Region	520
18.6	Conclusions	521
	References	522
19	Heat Transfer in a Pebble Bed	523
19.1	Introduction	523
19.2	Experimental Facility	524
19.3	Measurement Results	526
19.4	Processing of the Results	530
19.5	Conclusions	536
	References	536
	Appendix A: Film Boiling Heat Transfer	539
	Appendix B: Critical Heat Flux and Landau Instability	549

Chapter 1

Introduction to the Problem



Abbreviations

BC	Boundary condition
KL	Knudsen layer

Symbols

f	Distribution function
I	Collision integral
$\mathbf{n}$	Unit vector
t	Time
r	Distance between particles
u	Argument
$\mathbf{v}$	Molecular velocity
w	Volume element
x	Spatial coordinate

Greek Letter Symbols

μ	Argument
ϕ	Fourier transform of a distribution function

1.1 Kinetic Molecular Theory

Statistical mechanics (at present, the statistical physics), which is considered as a new trend in theoretical physics and is based on the description of involved systems with an infinite number of molecules, was created by Maxwell, Boltzmann, and Gibbs. An important constituent of statistical mechanics is the kinetic molecular theory, which resides on the Boltzmann integral-differential equation. In 1872, Ludwig Boltzmann published his epoch-making paper [1], in which, on the basis of his Boltzmann equation, he described the statistical distribution of the molecules of gas. The equilibrium

distribution function of molecules with respect to velocities, as derived by Maxwell in 1860, is a particular solution to the Boltzmann equation in the case of statistical equilibrium in the absence of external forces. The famous H-theorem, which theoretically justifies that the gas growth irreversibly in time, was formulated in [1].

Metaphysically, the kinetic molecular theory promoted the decisive choice between two alternative methods of describing the structure of matter: the continual and discrete ones. The continual approach operates with continuous medium and by no means is concerned with the detailed inner structure of matter. The system of Navier–Stokes equations is considered as its specific tool in the application to liquids. The discrete approach traditionally originates from the antique atomistic structure of matter. By the end of the nineteenth century, it was already generally adopted in chemistry. However, in the time of Boltzmann no final decision in theoretical physics was made. It may be said that Boltzmann’s theory played a crucial role in the solution of this central problem: the description of the structure and properties of a substance should be based on the discrete kinetic approach.

The time period at the end of the nineteenth century is noticeable in European science by notorious philosophical discussions between the leading natural scientist. Wilhelm Ostwald, the author of “energy theory” in the natural philosophy considered energy as the only reality, while matter is only a form of its manifestation. Being skeptical about the atomic–molecular view, Ostwald interpreted all natural phenomena as various forms of energy transformation and thus brought the laws of thermodynamics to the level of philosophic generalizations. Ernst Mach, a positivist philosopher and the founder of the theory of shock waves in gas dynamics, was a great opponent of atomism. Since at his times, atoms were unobservable, Mach considered the “atomistic theory” of matter as a working hypothesis for explaining physical and chemical phenomena.

Disagreeing with the “energists” (Ostwald) and “phenomenologists” (Mach), Boltzmann, nevertheless tried to find in their approaches a positive component and sometimes spoke almost in the spirit of Max’s positivism. In his paper [2], he wrote: “I felt that the controversy about whether matter or energy was the truly existent constituted a relapse into the old metaphysics which people thought had been overcome, an offence against the insight that all theoretical concepts are mental pictures”.

Irrespective of the fact that Boltzmann’s theory depends on the simple kinetic molecular model (which now seems quite transparent), it looked fairly challenging for many physicists 150 years ago. The principal moment of the theory is the following postulate: all phenomena in gases can be completely described in terms of interactions of elementary particles: atoms and molecules. Consideration of the motion and interaction of such particles had enabled to put forward a general conception combining the first and the second laws of thermodynamics. The crux of Boltzmann’s perceptions can be expressed in a somewhat simplified form as follows [3]: atoms and molecules do really exist as elements in the outside world, and hence there is no need to artificially “generate” them from hypothetical equations. The study of the interaction of molecules on the basis of the kinetic molecular theory provides comprehensive information about gas behavior.

It is also worth pointing out that until the mid-1950s, theoretical physics contained the “caloric theory”, which looked quite good from the application point of view. This theory was capable of adequately describing a number of facts, but was incapable of correctly describing transitions of various forms of energy into each other. It was the kinetic molecular theory that made it possible to ultimately and correctly solve the problem of the description of the heat phenomenon. So, from the metaphysical point of view, the kinetic molecular theory is an antithesis to both the “energetic” and the “phenomenological” approaches.

Boltzmann introduced into science the concept of the “statistical entropy”, which later played a crucial role in the development of quantum theory [4]. When Planck was deriving his well-known formula on the spectral density of radiation, he first wrote it down from empirical considerations. Later, Planck obtained this formula by theoretical considerations with the help of the statistical concept of entropy. In extending this concept for the radiation of a black body, he required the conjecture of discrete portions of energy. As a result, Planck had arrived at the definition of an elementary quantum of energy with a fixed frequency. This being so, quantum theory in its modern form could not in principle be formulated without an appeal to statistical entropy [5]. A few years after Einstein, Planck introduced the concept of a quantum of light. The Bose–Einstein statistics and the Fermi–Dirac statistics both have their roots in Boltzmann’s statistical method. Finally, the second law of thermodynamics (an increase of the entropy for a closed system) is obtained as an equivalent of the H-theorem.

The Boltzmann equation, which was obtained, strictly speaking, for rarefied gases, proved applicable also to the problem of the description of a dense medium. Succeeding generations of scientists investigated in this way plasmas and mixtures of gases (simple and polyatomic ones), and molecules were being considered as small solid balls. It is worth observing here that the kinetic molecular theory was a link between the microscopic and macroscopic levels of the description of matter. The solution to the Boltzmann equation by Chapman–Enskog’s method of successive approximations (expansion in terms of a small parameter near the equilibrium) had enabled one to directly calculate the heat conduction and the viscosity coefficients of gases.

For many years, due to its very involved structure, the Boltzmann equation had been looked upon as a mathematical abstraction. It suffices here to mention that the Boltzmann equation involves a fivefold integral collision integral and that in it the distribution function varies in the seven-dimensional space: time, three coordinates, and three velocities. From the applied point of view, the need for solving the Boltzmann equation was at first unclear. Various continual-based approximations proved quite successful for near-equilibrium situations.

However, in the 1950s, with the appearance of high-altitude aviation and the launch of the first artificial satellite, it became eventually clear that the description of motion in the upper atmosphere is only possible in the framework of the kinetic molecular theory. The Boltzmann equation also proved to be indispensable in vacuum-engineering applications and in the study of the motion of gases under low-pressure conditions. Later it seemed opportune to develop methods of the kinetic

molecular theory in far-from-equilibrium situations (that is, for processes of high intensity).

It appeared later that the Boltzmann equation can give much more than it was expected 100 years ago. The Boltzmann equation proved capable of describing involved nonlinear far-from-equilibrium new type phenomena. It is worth noting that such phenomena were formulated originally from pure theoretical considerations as a result of the solution of some problems for the Boltzmann equation.

1.2 Discussing the Boltzmann Equation

The kinetic molecular theory depends chiefly on Boltzmann's H-theorem, which underlies the thermodynamics of irreversible processes. According to this theorem, the mean logarithm of the distribution function (the H-function) for an isolated system decreases monotonically in time. By relating the H-function to the statistical weight, Boltzmann showed that the state of heat equilibrium in a system will be the most probable. Considering as an example a perfect monatomic gas, he showed the H-function as being proportional to the entropy and derived a formula relating the entropy to the probability of a macroscopic state (Boltzmann's formula).

Boltzmann's formula directly yields the statistical interpretation of the second law of thermodynamics based on the generalized definition of the entropy. This relation unites in fact classical Carnot–Clausius thermodynamics and the kinetic molecular theory of matter. It is the probabilistic interpretation of the second law of thermodynamics that manages to reconcile the property reversibility of mechanical phenomena with the irreversible character of thermal processes. However, at first this most important location provision of statistical thermodynamics was vigorously opposed by fundamentalist scientists.

The first objections against the new Boltzmann's theory had appeared already in 1872 right after the appearance of the paper [1]. With some simplification, these objections can be phrased as follows [3].

- why do the reversible laws of mechanics (the Liouville equation) allow the irreversible evolution of a system (Boltzmann's H-theorem)?
- does the Boltzmann equation contradict classical dynamics?
- why does the symmetry of the Boltzmann equation not agree with that of the Liouville equation?

The Liouville equation, which is of primary importance for classical dynamics, features the fundamental symmetry property: the reversion of velocity leads to the same result as that for time. In contrast to this, the Boltzmann equation, which describes the evolution of the distribution function, does not have the symmetry property. The reason for this is the invariance of the collision integral in the Boltzmann equation with respect to the reversion of velocity: Boltzmann's theory does not distinguish between the collisions reversed in the positive or negative directions of time (that is, "in the past or in the future").

This remarkable property of the Boltzmann equation had led Poincaré to the conclusion that the trend in the entropy growth contradicts the fundamental laws of classical mechanics. Indeed, according to the well-known Poincaré recurrence theorem (1890) [3], after some finite time interval, any system should return to a state which is arbitrarily close to the initial one. This means that to each possible increase of the entropy (when leaving the initial state), there should correspond a decrease of the entropy (when returning to the initial state).

In 1896, Zermelo, a pupil of Planck, derived the following corollary to the Poincaré recurrence theorem: no single-valued continuous and differentiable state function (in particular, the entropy) may increase monotonically in time. It turns out that irreversible processes in classical dynamics are impossible in principle when excluding the singular initial states. Boltzmann, when raising objections to Zermelo, pointed out the statistical basis of the kinetic molecular theory, which operates with probabilistic quantities. For a statistical system, which is composed of a huge number of molecules, the recurrence time should be astronomically large and hence has negligible probability.

So, the Poincaré recurrence theorem remains valid, but in the context of a gas system it acquires the abstract sense: in reality, only irreversible processes with finite probability are realized. In 1918 Caratheodory claimed that the proof of the Poincaré recurrence theorem is insufficient, for it does not make use of Lebesgue's (1902) concept of a "measure of a set point". In reply to Zermelo's criticism, Boltzmann wrote: "Already Clausius, Maxwell and others have shown that the laws of gases have statistical character. Very frequently and with the best possible clarity I have been emphasizing that Maxwell's law of distribution of velocities of gas molecules is not the law of conventional mechanics, but rather a probabilistic law. In this connection, I also pointed out that from the viewpoint of molecular theory the second law is only a probability law...". In 1895, in reply to Kelvin's strong criticism, Boltzmann wrote: "My theorem on the minimum (or the H-theorem) and the second law of thermodynamics are only probabilistic assertions".

The discussion on the H-theorem was concluded by Boltzmann in his last lifetime publication [6]: "Even though these objections are very potent in explaining theorems of kinetic theory of gases, they by no means disprove the simple theorems of probability ... The state of thermal equilibrium differs only in that that to it there correspond the most frequent distributions of vis viva between mechanical elements, whereas other states are rare, exceptional. Only by this reason, an isolated gas quantum which is in a state different from thermal equilibrium will go over into thermal equilibrium and will permanently stay there...".

In 1876 Loschmidt put forward the following fundamental objection to the kinetic molecular theory: the time-symmetric dynamic equations exclude in principle any irreversible process. Indeed, reverse collisions of molecules "mitigate" the consequences of direct collisions, and hence in theory the system should return to the initial state. Hence, following its decrease, the H-function (or the inverse entropy) must again increase from a finite value to the initial value. Correspondingly, following its growth the must again decrease. Boltzmann in his polemics with Loschmidt pointed out the conjecture of "molecular chaos", underlying his statistical approach.

According to this conjecture, in a real situation there is no correlation of any pair of molecules prior to their collision. In a simplified form, the line of Boltzmann's reasoning is as follows.

Loschmidt's idea of intermolecular interaction postulates the existence of some "storage of information" for gas molecules in which they "store" their previous collisions. In the framework of classical dynamics, the role of such storage should be played by correlations between molecules. Let us now trace the consequences of a "time-backward" evolution of a system which is accepted by the Liouville equation. It turns out that certain molecules (however far they were at the time of velocities reversion) are "doomed" to meet at a predetermined time instant and be subject to a predetermined transformation of velocities. But this immediately implies that the reversion of velocities in time generates a highly organized system, which is antipodal to the state of molecular chaos.

This being so, Boltzmann's elegant physical considerations formally disprove Loschmidt's rigorous observation. As a result, the kinetic molecular theory had enabled to justify a passage from classical dynamics to statistical thermodynamics or, figuratively speaking, "from order to chaos". Such a passage is most natural in rarefied gases, which determined the main domain of applicability of the Boltzmann equation.

Boltzmann's legacy is extremely broad and very deep in its contents. The philosophical idea of the atomic structure matter weaves through his work in a striking manner. He uncompromisingly defended this idea from Mach and Ostwald as representatives of the phenomenological (or "pure") description of natural phenomena. In his polemics with Ostwald, who stated that any attempts of the mechanistic interpretation of energetic laws should be rejected, Boltzmann wrote: "From the fact that the differential equations of mechanics are left unchanged by reversing the sign of time without changing anything else, Ostwald concludes that the mechanical view of the world cannot explain why natural processes already run preferentially in a definite direction. But such a view appears to me to overlook that mechanical events are determined not only by differential equations, but also by initial conditions". In his numerous speeches and popular talks, Boltzmann always pointed out the real existence of atoms and molecules: "Thus he, who believes he can free himself from atomism by differential equations, does not see the wood for the trees... We cannot doubt that the scheme of the world, that is assumed with it, is in essence and structure atomistic".

One should also mention the original Boltzmann's idea pertaining to the time nature, which he did not succeed in bringing in the scientific form. A year before his tragic death, he wrote to the philosopher von Brentano: "I am just now occupied with determining the number which plays the same role for time as the Loschmidt number for matter, the number of time-atoms = discrete moments of time, which make up a second of time".

The synthesis between classical dynamics and the kinetic molecular theory was achieved in the 1930s. Bogolyubov [7] gave an elegant derivation of the Boltzmann equation from the Liouville equation. This derivation, which depends on the "hierarchy of characteristic times", takes into account binary collisions of molecules.

Later, Bogolyubov in collaboration with other researchers developed systematic methods capable of producing more general equations (which take into account triple and multiple collisions). These methods were subsequently used as a basis for the derivation of equations describing dense gases. According to Ruel [8]: “... La vie de Boltzmann a quelque chose de romantique. Il s’est donné la mort parce qu’il était, dans un certain sens, un raté. Et pourtant nous le considérons maintenant comme un des grands savants de son époque, bien plus grand que ceux qui furent ses opposants scientifiques. Il a vu clair avant les autres, et il a eu raison trop tôt...”.

1.3 Precise Solution to the Boltzmann Equation

Numerous studies show that considerable mathematical difficulties are encountered trying to solve precisely the Boltzmann equation. Bobylev [9] seems to be the first to obtain the only known particular precise solution to the Boltzmann equation. Below we shall briefly enlarge on the results of the pioneering work [9]. In the classical kinetic theory of monatomic gases, the gas state at time $t \geq 0$ is characterized by one-particle distribution function of molecules over spatial coordinates $\mathbf{x}$ and velocities $\mathbf{v}$ in the three-dimensional Euclidean space: $f(\mathbf{x}, \mathbf{v}, t)$. With some simplification, this function can be looked upon as the number of particles (molecules) per unit volume of the velocity-configuration phase space at a time t . Its space-time evolution is described by the Boltzmann equation

$$\frac{\partial f}{\partial t} + \mathbf{v} \frac{\partial f}{\partial \mathbf{x}} = I[f, f]. \quad (1.1)$$

The right-hand side of (1.1), the collision integral, this is the nonlinear integral operator, which can be represented as

$$I[f, f] = \int d\mathbf{w} d\mathbf{n} g\left(u, \frac{\mathbf{u}\mathbf{n}}{u}\right) \{f(\mathbf{v}')f(\mathbf{w}') - f(\mathbf{v})f(\mathbf{w})\}. \quad (1.2)$$

Here, $\mathbf{w}$ is the volume element, $\mathbf{n}$ is the unit vector, and $|\mathbf{n}| = 1$, $d\mathbf{n}$ is the unit sphere surface element; the integration is taken over the entire five-dimensional space of molecular velocities. In (1.2), we used the following notation

$$\begin{aligned} \mathbf{u} &= \mathbf{v} - \mathbf{w}, u = |\mathbf{u}|, g(u, \boldsymbol{\mu}) = u\sigma(u, \boldsymbol{\mu}), \\ \mathbf{v}' &= 1/2(\mathbf{v} + \mathbf{w} + \mathbf{u}\mathbf{n}), \mathbf{w}' = 1/2(\mathbf{v} + \mathbf{w} - \mathbf{u}\mathbf{n}). \end{aligned} \quad (1.3)$$

We shall assume that the collision of molecules follow the laws of the classical mechanics of particles, which interact with the pair potential $U(r)$ where r is the distance between particles. The function $\sigma(u, \boldsymbol{\mu})$ in (1.3) is the differential scattering cross section for the angle $0 < \theta < \pi$ in the center-of-mass system of colliding molecules, where $u > 0$, $\boldsymbol{\mu} = \cos \theta$ are the arguments. The quantity