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Yuri B. Zudin

Non-equilibrium Evaporation and Condensation Processes

Analytical Solutions

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Non-equilibrium Evaporation and Condensation Processes

Analytical Solutions

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ISSN 2192-4732 ISSN 2192-4740 (electronic)
Mathematical Engineering
ISBN 978-3-319-67151-2 ISBN 978-3-319-67306-6 (eBook)
<https://doi.org/10.1007/978-3-319-67306-6>

Library of Congress Control Number: 2017952021

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The registered company is Springer International Publishing AG
The registered company address is: Gewerbestrasse 11, 6330 Cham, Switzerland

For Tatiana, my beloved wife

Preface

This present book is concerned with two important aspects of non-equilibrium evaporation and condensation processes: the molecular kinetic theory of phase transition and the dynamics of a vapor bubble in a superheated liquid.

The problems pertaining to the processes of intense phase change (evaporation and condensation) are of great interest both from a theoretical and from a practical point of view. Exposure of materials to laser radiation may lead to strong evaporation from the heated sections, which is accompanied by active condensation on the cooled parts. Development of space hardware calls for the study of singularities of flows that may appear in the evaporation of a coolant or as a consequence of its leak. A hypothetical root cause may be the loss of leak integrity of the containment shell of a nuclear engine due to thermal overloads in the course of a spaceflight. Exposure to the solar radiation on a comet surface results in the evaporation of its ice nucleus with the formation of atmosphere. Depending on the distance to the Sun, the intensity of evaporation varies a great deal and may reach huge values. The process of evaporation, which is sharply varying with time, has a great effect on the density of the comet atmosphere and the character of its motion.

The majority of phase change problems are studied within the approximation to thermodynamic equilibrium. However, in a number of cases, one has to take into account gas-phase non-equilibrium phenomena on the phase interface consequent on molecular kinetic effects. Theoretical analysis of non-equilibrium phenomena depends on the Boltzmann equation, which for many years, due to its very involved structure, had been looked upon as a mathematical abstraction. Labuntsov [1] laid the foundation of the linear kinetic theory and studied for the first time the phase changes from the theoretical point of view on the basis of the Boltzmann equation. This theory was further developed by Loyalka [2] and Siewert [3].

A phase change in which the flow velocity is comparable with the sonic one is called the strong evaporation or strong condensation. Theoretical studies of such processes may be conventionally subdivided into two directions. In the strong (“microscopic”) approach, one solves numerically the Boltzmann equation (or its simplified “relaxation” analogues) to determine the distribution function of its molecules in velocities. Using the distribution function, one calculates the

distributions of the velocity, pressure, and temperature in the vapor near the phase interface. Among recent studies in this direction, we mention the papers by Gusarov and Smurov [4], Frezzotti and Ytrehus [5], and Frezzotti [6]. In turn, the approximation (“macroscopic”) approach calls for the solution of the system of mass, momentum, and energy conservation equations of the molecular fluxes, which is augmented by various approximations of the distribution function. As a result, one obtains general analytical expressions for the distributions of gas-dynamic parameters away from the phase interface. Here, one may mention the studies by Anisimov [7], Labuntsov and Kryukov [8], Ytrehus [9], Rose [10], as well as the studies by the author of this present book.

The phenomenon of gas (vapor) bubbles in a liquid, in spite of the fluctuation character of their nucleation and short lifetime, has a wide spectrum of manifestations: underwater acoustics, sonoluminescence, ultrasonic diagnostics, decreasing friction by surface nanobubbles, nucleate boiling, etc. The most important application of the bubble dynamics is the effervescence of a liquid superheated with respect to the saturation temperature. This results in the initiation and growth of nuclei of a new (vapor) phase in liquid. An ideal subject of investigation of this phenomenon is the spherically asymmetric growth of the vapor bubble in the volume of a uniformly superheated liquid.

Labuntsov proposed a systematic approach to the problem of the vapor bubble growth in a superheated liquid. The growth rate in the general case was shown as being dependent on four physical effects: (a) viscous resistance of the medium displaced by the bubble; (b) inertial reaction of the liquid to the swelling of the bubble in it; (c) non-equilibrium effects at the interface; and (d) the mechanism of heat transfer from the superheated liquid to the bubble boundary. Taking into account the action of each of the factors under the assumption that the influence of the others is absent leads to “limiting schemes” of the bubble growth.

In this present book, we perform the next step by changing to “binary” schemes of growth that describe the simultaneous effect of two principal factors on the growth of a bubble: inertial reaction of the liquid and heat transfer from the superheated liquid. We describe the effect of “pressure blocking” in the vapor phase, when the superheating enthalpy exceeds the phase transition heat.

The problem of non-equilibrium evaporation and condensation processes will be the underlying theme of this entire book. Moreover, each chapter, which will be concerned with some or other aspects of this general problem, is practically self-contained and can be studied independently. The author has deliberately followed this approach in the organization of this book, which leads to certain “self-intersection” of some chapters and, as a consequence, to some “overweighting” of this book. However, here I am convinced that in the present digital era the reader ought to be given a possibility of the independent familiarization with the chosen topic. Such a presentation of the material is aimed at releasing the reader from wearisome paging through this book in searching for references scattered over the entire volume of this book. This is why each chapter contains a separate reference list and a separate list of symbols (in case their number is fairly large).

The title of the books suggests that it is concerned solely with analytical methods of solution. Analytical solutions of the fluid flow and heat transfer problems play a significant role even in the current computer age:

- The value of the analytical approach consists in the opportunity of the closed qualitative description of the process, revealing the full list of dimensionless characteristic parameters and their hierarchical classification based on the criteria of their importance.
- Analytical solutions possess a necessary generality, so that a variation of the boundary and inlet conditions allows one to carry out parametrical investigations.
- In order to validate numerical solutions of the full differential equations, it is necessary to have basic analytical solutions of the equations for some obviously simplified cases after an estimation and omission of negligible terms.

Chapter 1 provides a short introduction to the topic. We give a short history of the development of the molecular kinetic theory and the discussion around the Boltzmann equation. An exact solution of the Boltzmann equation is presented. Processes of intensive phase change are briefly discussed.

Chapter 2 is concerned with 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. We present the fundamentals of the linear kinetic theory and give a short introduction to the problem of strong evaporation.

Chapter 3 is devoted to the approximate kinetic analysis of strong evaporation. The author's mixing model is presented. On this basis, we give analytical solutions for temperatures, pressures, and mass velocities of vapor and match them with the available numerical and analytical solutions. We also calculate the evaporation limiting mass velocity.

Chapter 4 proposed a semiempirical model of strong evaporation based on the linear kinetic theory. Here, it proved possible to achieve a pretty good agreement with the results of numerical and approximate analytical solutions for monatomic and polyatomic gas and also for the limit mass flux.

In Chap. 5, the approximate kinetic analysis of strong condensation is considered. As in Chap. 3 we shall use the mixing model of strong condensation. We give solutions for the sonic and supersonic condensations. The analytical solution demonstrates a good agreement with available simulation data.

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 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.

Chapter 7 is concerned with the spherically symmetric growth of a vapor bubble in an infinite volume of a uniformly superheated liquid. Following Labuntsov, we considered the influence of each effect within the framework of the following four

“limiting schemes”: (a) dynamic viscous; (b) dynamic inertial; (c) energetic molecular kinetic (non-equilibrium); and (d) energetic thermal. A problem on the description of the limiting schemes of bubble growth is presented. As the next step, we come to “binary” schemes of growth that describe the simultaneous effect of two factors on the growth of a bubble.

Chapter 8 proposed a “pressure blocking effect” in the growing vapor bubble in a highly superheated liquid. The known Plesset–Zwick formula has been generalized to the region of strong superheating. The problem for the conditions of the experiment on the effervescence of the butane drop has been solved. An algorithm for calculating was proposed for constructing an approximate analytical solution under conditions when the enthalpy of the superheating of which exceeds the phase transition heat.

Chapter 9 provides an evaporating meniscus on the interface of three phases. An approximate solving method is presented capable of finding the influence of the molecular kinetic effects on the geometric parameter of the meniscus and on the heat transfer intensity. Analytical expressions for the evaporating meniscus parameters are obtained from the analysis of interaction of the intermolecular, capillary, and viscous forces, and the study of the molecular kinetic effects.

Chapter 10 is concerned with kinetic effects for a spheroidal state. The kinetic pressure with respect to a levitating droplet is shown to have either “repulsing” or “attracting” character depending on the value of the coefficient of evaporation/condensation. We also put forward an analytical dependence for the vapor film thickness with the consideration of molecular kinetic effects. The asymptotic formula for the solution is written down for the exotic case when the coefficient of evaporation/condensation tends to zero.

Chapter 11 provides a vapor condensation upon transversal flow around a cylinder. An analysis of the limiting heat exchange laws is given. Analytical solutions for the laws were obtained, which correspond to the effect of only one factor: gravity, longitudinal pressure gradient, interfacial friction. The results of the solution were presented as relative heat exchange laws with respect to the case of steady-state vapor.

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.

Appendix B presents the results of experimental investigation of heat transfer in a pebble bed for flows of single-phase boiling liquid. Use was made of a method of processing of experimental data, which enables one to determine the coefficient of “pseudo-turbulent” thermal conductivity without differentiation of the experimentally obtained temperature profile. Temperature profiles were obtained for the case of boiling on the pebble bed wall, and qualitative analysis of these profiles was performed.

I would like to deeply thank the Director of the ITLR, Series Editor Mathematical Engineering of Springer-Verlag, Prof. Dr.-Ing. habil. Bernhard Weigand for his strong support of my aspiration to successfully accomplish this

work, as well as for his numerous valuable advice and fruitful discussions concerning all aspects of the analytical solution methods. Prof. Bernhard Weigand repeatedly invited me to visit the Institute of Aerospace Thermodynamics to perform joint research. Our collaboration was of great help for me in the preparation of this book.

I am deeply indebted to Dr. Jan-Philip Schmidt, 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 (TU München, Uni Paderborn, HSU/UniBw Hamburg, Uni Stuttgart) from the German Academic Exchange Service (DAAD), from which for twenty years I was awarded seven grants. I also wish to express my sincere thanks to Dr. T. Pahl, Dr. G. Berghorn, Dr. P. Hiller, Dr. H. Finken, Dr. W. Trenn, 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 of my work, especially in these tough and challenging times.

I am also thankful to Dr. Alexey Alimov (Moscow State University) for his very useful comments, which contributed much toward 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
October 2017

Yuri B. Zudin

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Contents

1	Introduction to the Problem	1
1.1	Kinetic Molecular Theory	1
1.2	Discussing the Boltzmann Equation	3
1.3	Precise Solution to the Boltzmann Equation	6
1.4	Intensive Phase Change	10
	References	14
2	Nonequilibrium Effects on the Phase Interface	17
2.1	Conservation Equations of Molecular Flows	17
2.1.1	The Distribution Function	17
2.1.2	Molecular Flows	19
2.2	Evaporation into Vacuum	21
2.2.1	The Hertz–Knudsen Equation	22
2.2.2	Modifications of the Hertz–Knudsen Equation	23
2.3	Extrapolated Boundary Conditions	25
2.4	Accommodation Coefficients	26
2.5	Linear Kinetic Theory	29
2.5.1	Low Intensity Processes	29
2.5.2	Impermeable Interface (Heat Transport)	30
2.5.3	Impermeable Interface (Momentum Transport)	31
2.5.4	Phase Change	32
2.5.5	Special Boundary Conditions	33
2.6	Introduction into 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	Conservation Equations	49
3.2	Mixing Surface	52
3.3	Limiting Mass Flux	54
3.4	Conclusions	56
	References	57
4	Semi-empirical Model of Strong Evaporation	59
4.1	Strong Evaporation	59
4.2	Approximate Analytical Models	62
4.3	Analysis of the Available Approaches	64
4.4	The Semi-empirical Model	65
4.4.1	Linear Jumps	65
4.4.2	Nonlinear Jumps	66
4.4.3	Summarized Jumps	67
4.4.4	Design Relations	68
4.5	Validation of the Semi-empirical Model	69
4.5.1	Monatomic Gas ($\beta = 1$)	69
4.5.2	Monatomic Gas ($0 < \beta \leq 1$)	72
4.5.3	Sonic Evaporation ($0 < \beta \leq 1$)	72
4.5.4	Polyatomic Gas ($\beta = 1$)	73
4.5.5	Maximum Mass Flow	74
4.6	Final Remarks	76
4.7	Conclusions	77
	References	77
5	Approximate Kinetic Analysis of Strong Condensation	79
5.1	Macroscopic Models	81
5.2	Strong Evaporation	83
5.3	Strong Condensation	85
5.4	The Mixing Model	85
5.5	Solution Results	89
5.6	Sonic Condensation	90
5.7	Supersonic Condensation	93
5.8	Conclusions	93
	References	95
6	Linear Kinetic Analysis of Evaporation and Condensation	97
6.1	Conservation Equations	100
6.2	Equilibrium Coupling Conditions	104
6.3	Linear Kinetic Analysis	105
6.3.1	Linearized System of Equations	105
6.3.2	Symmetric and Asymmetric Cases	107
6.3.3	Kinetic Jumps	109
6.3.4	Short Description	111

6.4	Conclusions	112
	References	113
7	Binary Schemes of Vapor Bubble Growth	115
7.1	Limiting Schemes of Growth	116
7.2	The Energetic Thermal Scheme	118
7.2.1	The Jakob Number	118
7.2.2	The Plesset-Zwick Formula	119
7.2.3	Solution of Scriven	120
7.2.4	Approximations	122
7.3	Binary Schemes of Growth	125
7.3.1	The Viscous-Inertial Scheme	125
7.3.2	The Nonequilibrium-Thermal Scheme	125
7.3.3	The Inertial-Thermal Scheme	126
7.3.4	The Region of High Superheatings	126
7.4	Conclusions	130
	References	130
8	The Pressure Blocking Effect in a Growing Vapor Bubble	133
8.1	The Inertial-Thermal Scheme	134
8.2	Pressure Blocking Effect	138
8.3	The Stefan Number in the Metastable Region	140
8.4	Effervescence of the Butane Drop	142
8.5	Seeking an Analytical Solution	145
8.6	Conclusions	148
	References	148
9	Evaporating Meniscus on the Interface of Three Phases	151
9.1	Evaporating Meniscus	154
9.2	Approximate Analytical Solution	156
9.3	Nanoscale Film	160
9.4	The Averaged Heat Transfer Coefficient	161
9.5	The Kinetic Molecular Effects	162
9.6	Conclusions	165
	References	165
10	Kinetic Molecular Effects with Spheroidal State	167
10.1	Assumptions in the Analysis	168
10.2	Hydrodynamics of Flow	169
10.3	Equilibrium of Drop	173
10.4	Conclusions	179
	References	179
11	Flow Around a Cylinder (Vapor Condensation)	181
11.1	Limiting Heat Exchange Laws	183
11.2	Asymptotics of Immobile Vapor	184

11.3	Pressure Asymptotics	185
11.4	Tangential Stresses at the Interface Boundary.	186
11.5	Results and Discussion	188
11.6	Conclusions	193
	References.	193
	Appendix A: Heat Transfer During Film Boiling	195
	Appendix B: Heat Transfer in a Pebble Bed	203
	Index	217

Chapter 1

Introduction to the Problem

1.1 Kinetic Molecular Theory

The 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 infinite number of molecules, was created by Maxwell, Boltzmann, and Gibbs. An important constituent of the 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 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 the 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 the 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 Mach’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* depend 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 the 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 to the definition of an elementary quantum of energy with a fixed frequency. This being so, the quantum theory in its modern form could not in principle be formulated without an appeal to statistical entropy [5]. Few years after Einstein, Planck introduced the concept of a quantum of light. The Bose–Einstein statistics and Fermi–Dirac statistics both have their roots in Boltzmann’s statistical method. Finally, the second law of

thermodynamics (increase of the entropy for a closed system) is obtained as an equivalent of the H-theorem.

Boltzmann equation, which was obtained, strictly speaking, for rarefied gases, proved applicable also to the problem of description of a dense medium. Succeeding generations of scientists investigated in this way plasmas and mixtures of gases (simple and polyatomic ones), 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 5-fold 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 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 motion of gases under low pressure conditions. Later it seemed opportune to develop methods of 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 the pure theoretical considerations as a result of solution of some problems for the Boltzmann equation.

1.2 Discussing the Boltzmann Equation

The kinetic molecular theory depends chiefly on the 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 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 the reversible laws of mechanics (the Liouville equation) allow irreversible evolution of a system (Boltzmann’s H-theorem)?
- Whether the Boltzmann equation contradicts the classical dynamics?
- Why the symmetry of the Boltzmann equation does not agree with that of the Liouville equation?

The Liouville equation, which is of primary importance for the 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: the *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 back 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 deconfiguration 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 the 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 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 in 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 s 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 a 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 the classical dynamics to the 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 her work in a striking manner; he uncompromisingly defended this idea from Mach and Ostwald as representatives of phenomenological (or "pure") description of natural phenomena. In his polemics with Ostwald, who stated that any attempts of 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 the 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 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 part of (1.1) the collision integral—this is the nonlinear integral operator, which can be represented as

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

Here, $\mathbf{w}$ is the volume element, $\mathbf{n}$ is the unit vector, $|\mathbf{n}| = 1$, $d\mathbf{n}$ 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

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

We shall assume that 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 $u > 0$, $\mu = \cos(\theta)$ are the arguments. The quantity $g(u, \boldsymbol{\mu}) > 0$ is the (1.2) is considered as a given function, whose depends on the chosen model of molecules. For the model of molecules under consideration (rigid balls of radius r_0) we have $g(u, \boldsymbol{\mu}) = ur_0^2$. A more involved expression appears for the model of molecules, in which they are considered as point particles with power-law interactions: $U(r) = \alpha/r^n$ ($\alpha > 0, n \geq 2$) $g(u, \boldsymbol{\mu}) = u^{1-4/n}g_n(\boldsymbol{\mu})$, where $g_n(\boldsymbol{\mu})(1 - \boldsymbol{\mu})^{3/2}$ is a bounded function.

The principal mathematical difficulties in solving the Boltzmann equation are related with the nonlinearity and involved structure of the collision integral (1.2). The very first had shown that the boundary-value problem for the Boltzmann equation is much more challenging than the initial-value problem. The problem of relaxation (approximation to the equilibrium) can be stated in the most simple way as follows

$$\frac{\partial f}{\partial t} = I[f, f], \quad f|_{t=0} = f_0(\mathbf{v}) \quad (1.4)$$

Equation (1.4) describes the space-homogeneous Cauchy problem of independent interest. Problems of existence and unique solvability of the Boltzmann equation (both for the Cauchy, and for boundary-value problems) were studied extensively.