Mathematical Engineering

Yuri B. Zudin

Non-equilibrium Evaporation and Condensation Processes

Analytical Solutions

Second Edition

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Mathematical Engineering

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For Tatiana, my beloved wife

Preface

The present second edition substantially augments the first edition of the book (*Non-equilibrium Evaporation and Condensation Processes. Analytical Solutions*, Springer, 2018) 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 processing of materials, it is important to know the laws of both evaporation (for thermal laser ablation from the target surface) and condensation (for interaction with the target of an expanding vapor cloud). Some accident situations in 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 modeling of 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 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 consistent consideration of molecular-kinetic effects on the phase boundary, one can get important non-trivial 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 explosive boiling of superheated liquid resulting in 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 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 nucleate 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 inertia forces, and molecular-kinetic laws on the phase boundary.

Modern progress in microelectronics and nanotechnologies calls for a 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.

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 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 rigid surface.

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 quasiparticles.

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.

The present book is solely concerned with analytical approaches to statement and solution of problems of the above sort. 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 discovery of new methods of solutions of a given mathematical model of a real process, as 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 on the first stage of mathematical modeling. Analytical solutions are also used as test models for 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 the kinetic analysis of the evaporation and condensation processes are 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. 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 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.

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.

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: the inversion of the solution, bifurcation of the solution, transition to two-valued solutions, 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 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 considered 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 "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 homogeneous bubble nucleation is studied. We arrive at the "asymmetry paradox" of the processes of evaporation and condensation.

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. 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 used the scaling law of change in the isobar heat capacity. The problem for the conditions of the experiment on the effervescence of the butane drop was 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 solving 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 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 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 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 coefficient is found.

Chapter 11 provides a vapor condensation upon transversal flow around a cylinder. The analytical solutions for the limiting heat-exchange laws, which correspond to the effect of only one factor, were 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 was 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.

Chapter 12 describes the principal constituents of the general problem of boiling phenomenon: conditions for inception of boiling, formation of nucleation sites, 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. A special attention is given to a debating problem on the effect of thermophysical characteristics of a heat-transmitting wall. An approximate model for periodic conjugate heat-exchange problem for boiling is given. 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. 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 first principles is considered. The use of the quantum-mechanical conception quasiparticles enables us to prove the equivalence of the macroscopic and microscopic levels of He-II thermodynamics analysis.

Chapter 14 describes the heat-exchange 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 viscous compressible gas, a permeable wall past by incompressible fluid. The law of heat transfer for the turbulent flow in the channel in the zone of supercritical pressures was calculated.

In Chapter 15, the derivation of the generalized Rayleigh equation that describes the dynamics of a spherical gas bubble in a tube filled with an ideal liquid is given. An exact analytic solution of the problem on vapor bubble collapse in a long tube was obtained. A quantum-mechanical model of homogeneous bubble nucleation is put forward. The problem of the rise of the Taylor bubble in a round tube is considered. The available solutions are shown to be ill-justified due to divergence of some involved infinite series. An analytical solution of the problem is obtained based on the collocation method and asymptotical analysis of the solution to the Laplace equation.

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 distribution of velocities in the vapor film.

Appendix B presents the results of experimental investigation of heat transfer in a pebble bed for flows of single-phase boiling liquid. The experiments involved measurements of the temperature of 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 coefficient of "pseudoturbulent" 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.

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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 Yuri B. Zudin
December 2018

Contents

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 19th 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 19th 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

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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 is 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 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 tree 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. Bogoliubov [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 **x** and velocities **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

$$\frac{\partial f}{\partial t} + \mathbf{v}\frac{\partial f}{\partial \mathbf{x}} = I[f,f] \tag{1.1}$$

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

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

Here, **w** is the volume element, **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

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

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

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

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. Gilbert, Chapman-Enskog and Grad were first to study approximate solutions by their classical methods. Various extensions of such approaches are also available. Maxwell molecules are particles interacting with the repelling potential $U(r) = \alpha/r^4$. For this model, the scattering cross-section $\sigma(u, \boldsymbol{\mu})$ is inversely proportional to the absolute value of the velocity u. Hence, the function $g(u, \boldsymbol{\mu})$ from (1.2) is independent of u, which substantially simplifies the evaluation of the collision integral. This remarkable advantage of the Maxwell molecules, which was known already to Boltzmann, was researchers. Bobylev [9] was first to show that the nonlinear operator (1.2) can be substantially simplified by using the Fourier transform with respect to the velocity. Setting

$$\varphi(\mathbf{x}, \mathbf{k}, t) = \int d\mathbf{v} \exp(-i\mathbf{k}\mathbf{v}) f(\mathbf{x}, \mathbf{v}, t) \tag{1.5}$$

and changing in (1.1) to the Fourier representation, we arrive at the following equation for $\varphi(\mathbf{x}, \mathbf{k}, t)$

$$\frac{\partial \varphi}{\partial t} + i \frac{\partial^2 \varphi}{\partial \mathbf{k} \partial \mathbf{x}} = J[\varphi, \varphi] = \int d\mathbf{v} \exp(-i\mathbf{k}\mathbf{v}) I[f, f] \tag{1.6}$$

For any function $g(u, \boldsymbol{\mu})$ in (1.2) which is independent of u, the operator $J[\varphi, \varphi]$ has a much simpler form versus the operator $I[f, f]$. It is easily shown that this property is satisfied only by Maxwell molecules among all available models of molecules. This leads to a substantial simplification of the transformed equation (1.6). However, the appearance of the mixed derivative on the left of (1.6) does not allow one to efficiently solve the spatial-inhomogeneous problems. This impediment disappears in examining the relaxation problem (1.4), which has the form in the Fourier representation

$$\frac{\partial \varphi}{\partial t} = J[\varphi, \varphi] \tag{1.7}$$

Let us consider the Cauchy problem for the spatial-homogeneous Boltzmann equation

$$f_t = I[f, f] = \int d\mathbf{w} d\mathbf{n} g\left(u, \frac{\mathbf{u}\mathbf{n}}{u}\right) \{f(\mathbf{v}') f(\mathbf{w}') - f(\mathbf{v}) f(\mathbf{w})\} \tag{1.8}$$

as written in the notation (1.3). Here, the subscript means the derivative in t. The initial condition for (1.8) reads as

$$f|_{t=0} = f_0(\mathbf{v}) : \int d\mathbf{v} f_0(\mathbf{v}) = 1, \int d\mathbf{v}\, \mathbf{v} f_0(\mathbf{v}) = 0, \int d\mathbf{v}\, \mathbf{v}^2 f_0(\mathbf{v}) = 3 \tag{1.9}$$

By the laws of conservation of the number of particles, moment and energy, the solution $f(\mathbf{v}, t)$ to problem (1.8) and (1.9) satisfies the same requirements for all $t > 0$.

$$\int d\mathbf{v} f(\mathbf{v}) = 1, \int d\mathbf{v}\, \mathbf{v} f(\mathbf{v}) = 0 \tag{1.10}$$

The corresponding Maxwellian distribution reads as

$$f_M(\mathbf{v}) = (2\pi)^{-1/2} \exp\left(-\vartheta^2\right) \tag{1.11}$$

An approach to the solution of the above problem can be written as the following formal scheme

- Changing to the Fourier representation

$$\varphi(\mathbf{k}, t) = \int d\mathbf{v} f(\mathbf{v}, t) \exp(-i\mathbf{k}\mathbf{v}) \tag{1.12}$$

gives us, instead of (1.8), the following more simple equation

$$\varphi_t = J[\varphi, \varphi] = \int d\mathbf{n} g\left(\frac{\mathbf{kn}}{k}\right)\left\{\varphi\left(\frac{k + \mathbf{kn}}{2}\right)\varphi\left(\frac{k - \mathbf{kn}}{2}\right) - \varphi(0)\varphi(\mathbf{k})\right\} \tag{1.13}$$

- The following initial condition for (1.13) is set

$$\begin{gathered} \varphi|_{t=0} = \varphi_0(\mathbf{k}) = \int d\mathbf{v} f_0(\mathbf{v}) \exp(-i\mathbf{k}\mathbf{v}) \\ \varphi_0|_{\mathbf{k}=0} = 1, \left.\frac{\partial \varphi_0}{\partial \mathbf{k}}\right|_{\mathbf{k}=0} = 0, \left.\frac{\partial^2 \varphi_0}{\partial \mathbf{k}^2}\right|_{\mathbf{k}=0} = -3 \end{gathered} \tag{1.14}$$

- The solution $\varphi(\mathbf{k}, t)$ to the problem (1.13) and (1.14) is studied.
- Using the inversion formula

$$f(\mathbf{v}, t) = (2\pi)^{-3} \int d\mathbf{v} \varphi(\mathbf{k}, t) \exp(i\mathbf{k}\mathbf{v}). \tag{1.15}$$

we formulate the final results for the distribution function $f(\mathbf{v}, t)$. Here, we assume that the integral (1.15) is convergent.

The Fourier analogues of formulas (1.10), (1.11) read as

$$\varphi(0,t) = 1,\ \left.\frac{\partial \varphi(\mathbf{k},t)}{\partial \mathbf{k}}\right|_{\mathbf{k}=0} = 0,\ \left.\frac{\partial^2 \varphi(\mathbf{k},t)}{\partial \mathbf{k}^2}\right|_{\mathbf{k}=0} = -3,\ f_M(\mathbf{k}) = \exp\left(-\frac{k^2}{2}\right) \tag{1.16}$$

From the above it follows that the precise solutions to the Boltzmann equation can be obtained only in very rare special cases.

1.4 Intensive Phase Change

At present, processes of intensive phase change find more and more practical applications. This involves the physics of air-dispersed systems, air dynamics, microelectronics, ecology, etc. The study of intensive phase change is relevant in for the purposes of practical design of heat-exchange equipment, systems of integrated thermal protection of aircrafts, and the vacuum engineering. We indicate some important applications related to the intensive phase change

- simulation of the evaporation of a coolant into the vacuum under theoretical loss of leak integrity of the protective cover of a nuclear reactor of a space vehicle
- organization of materials-laser interaction [10] (intensive evaporation from heated segments and intensive condensation in the cooling area)
- simulation of Space Shuttles airflow during their re-entry [11]

Intensive phase change plays a governing role in engineering processes accompanying laser ablation [10]. Materials-laser interaction involves a number of mutually related physical processes: radiation transfer and absorption in a target from the condensate phase, heat transfer in a target, evaporation and condensation on the target surface, gas dynamics of the surrounding medium. Anisimov [12] seems to be the first to give a theoretical description of laser ablation in vacuum. Studying the nonequilibrium Knudsen layer, the author of [12] found a relation between the target temperature and the parameters of egressing vapor. Extending the approach of [12], Ytrehus [13] proposed the model of intensive evaporation. The heat model of ablation in exterior atmosphere relating the gas parameters with the radiation intensity was considered by Knight [14, 15], who examined the system of gas dynamics equations conjugated with the heat-transfer equation in the target. Under this approach, the boundary conditions were specified from the solution of the kinetic problem of intensive evaporation. The further development in the heat model of laser ablation was related with the numerical study of radiation pulses of arbitrary form and with the study of the phase change (melting/consolidation) in a target [16, 17].

An important application of the intensive phase change is the problem of simulation of comet atmosphere [18–21]. According to modern theory, the comet core is chiefly composed of aquatic ice with admixture of mineral particles [18]. Subject to radiation the ice begins to evaporate, forming the inner gas-dust atmosphere. Depending on the distance from the Sun, the intensity of ice evaporation and the density of the near-core comet atmosphere vary substantially. At large distances from the Sun, in the atmosphere is small, the flow regime being free-molecular. An Earth orbit, the flow regime in dense regions of the atmosphere on the illuminated (day) side is described by the solid medium laws. The gas density decreases away from the comet core, the continual flow regime changing first by the transient regime, and then by the free-molecular regime. The conjugation of the gas-dynamic region with the comet surface leads to a very involved mathematical problem, for which some particular solutions are known [19–21].

However in the general case (relaxing gas, arbitrary surface geometry, time-variable evaporation intensity solution) the above problem has no solution. Various approximate approaches were found to be useful in setting the boundary conditions for gas-dynamic equations. The system of Navier-Stokes equations in a local plane-parallel approximation was considered in [19]. The boundary conditions on the comet core surface were set as on the rarefaction expansion shock. In [20, 21], various integrated calculation schemes were used involving the Navier-Stokes equations in the gas-dynamic region with specification of boundary conditions in the dense flow region.

The new direction of kinetic analysis related with the turbulence modeling [22, 23] seems to be quite intriguing. In this case, the solution to the Boltzmann equation is sought by expanding the distribution function into a series in Knudsen numbers, which play the role of the rarefaction parameter (the Chapman-Enskog expansion). A decrease in the Knudsen number results in a transition from stable to unstable flows, which corresponds to a transition from a laminar to a turbulent flow region. In the subcritical (laminar) regime, the solution to the Boltzmann equation for macroscopic parameters is known to be close to the solution to the Navier-Stokes equations. In the supercritical (turbulent) region, the solution becomes both unstable and nonequilibrium. Besides, the distribution function becomes rapidly changing in time, the viscous stress and heat transfer rates increasing discontinuously. To the increasing values of the dissipating quantities one may correspond some values of the turbulent viscosity and the turbulent heat conduction. This being so, the Boltzmann equation is capable of giving a closed model for the description of turbulence, without requiring closing conjectures (as in the classical Reynolds equations). It is worth noting, however, that this direction of the kinetic is in an early stage of development.

The simulation of an intensive phase change depends primarily on setting the boundary conditions on the interfacial surface between the condensed and gaseous phases. From the kinetic analysis it is known that the distribution functions of the molecules that emit from the interface, and of the molecules approaching it from the vapor are substantially different. This results in a heavy nonequilibrium condition in the Knudsen layer, which is adjacent to the interface surface and whose thickness is of the order of the mean free path of molecules. The one-dimensional problem of evaporation/condensation in a half-space for the Boltzmann equation can be obtained using the Hilbert expansion in the powers of Knudsen numbers [24].