1 Introduction

When dealing with the thermodynamic properties of matter, the systems under consideration are usually investigated in thermodynamic equilibrium states. However, in a variety of cases configurations are realized which do not correspond to global but local maxima of the entropy or minima of the internal energy or other relevant thermodynamic functions. These states are metastable and have a finite lifetime. Metastability is a common property of first-order phase transformations and manifests itself in systems of quite different nature such as nuclear matter and quark–gluon plasmas, electron–hole fluids, biological systems near the self-organization threshold, as well as in more conventional evaporation, condensation, segregation, crystallization, and melting processes.

Phase transformations represent a macroscopic manifestation of the action of the intermolecular forces in systems consisting of a large number of particles. The similarity of the interaction forces results in an essentially universal picture of phases and phase transitions, at least, in simple systems. Properties of substances may behave differently in the course of phase transformations. Phase transitions can roughly be separated into first and second orders. Correlations of anomalously growing fluctuations in the vicinity of points of second-order phase transformations result in the scale invariance of the properties of systems, which differ profoundly with respect to the structure and character of the interactions between the particles of the system. In contrast, such fluctuations may be disregarded at first-order phase transformations, and the properties of the substances under consideration are characterized by a lower order universality at this point, i.e., by the thermodynamic similarity, which is a reflection of the similarity of intermolecular forces. Therefore, the microscopic theory of phase transformations of first order and phase metastability encounters the same difficulties as the physics of the condensed state.

Since the law of particle interactions dominates first-order phase transformations, for the study of principal problems of phase metastability and phase transitions, those systems are of particular interest whose molecules have a spherically symmetric or an almost spherically symmetric shape and a simple dispersion type dependence of the intermolecular forces. Such (simple)
substances serve as a “touchstone” in the theoretical analyses of problems directed to condensed media. Since the interparticle bonding forces are weaker than those in complex molecular compounds, simple substances exist in the liquid state at temperatures lower than normal temperatures on the Earth, i.e., they represent liquefied gases.

Liquefied gases with a normal boiling temperature of below 120 K are classified as cryogenic fluids. Local heat supply and pressure pulses in storage and transport systems of cryogenic fluids can cause considerable superheats of the fluids. The establishment of such high local degrees of superheating is facilitated by good wettability of most of the solids with cryogenic fluids and a small content of dissolved gases contained in them.

A superheated fluid represents a particular case of a system in a metastable state and a very convenient object of study. A low viscosity of superheated fluids ensures quick relaxation of the structure. This is not always the case in supercooled fluids. Unlike the liquid–crystal phase transformation, where the interfacial energy is unknown in most cases of interest, the surface tension in the liquid–vapor system can be measured directly. If the condensation of a supersaturated vapor is studied, it is much more difficult to remove the initiating effect of walls, which represent ready and/or easily activated centers of condensation, than active centers during boiling.

The observation of a fluid in the state of a metastable equilibrium was first mentioned in the second half of the 17th century when experiments, which were performed by Huygens and Boyle, revealed the existence of water and mercury at negative pressures. An interpretation of this phenomenon in physical terms became possible only after van der Waals derived his famous equation of state (1873). The terms “metastable” and “unstable” were introduced by Ostwald in order to distinguish sections of different degree of stability in the van der Waals isotherms. Pioneering reproducible quantitative data concerning the accessible temperature of superheating of some fluids were obtained by Wismer et al. (1922–1927). Still earlier, in 1878, Gibbs [1] explained phase transformations with the appearance of nuclei of a new phase. The ideas expressed by Gibbs laid the foundation of the classical theory of thermally induced fluctuation nucleation. It was formulated by Volmer and Weber [2], Farkas [3], Becker and Döring [4], Zeldovich [5], and Frenkel [6]. This theory is universal in its thermodynamic principles and is applicable to various types of phase metastability.

The study of phase metastability includes a wide range of tasks. The present monograph is dedicated mainly to the analysis of the nucleation kinetics in metastable liquefied gases and their solutions. Nuclei may be formed spontaneously in systems which are free of inclusions which may initiate a phase transformation. Such a mechanism of initiating a phase transformation is denoted as homogeneous nucleation. The knowledge of the mechanisms of ho-
homogeneous nucleation is highly significant since it determines the upper limits of stability of a metastable phase with respect to discontinuous changes of the state parameters. In the theoretical description of thermodynamic and kinetic aspects of these processes, we employ both Gibbs’ thermodynamic method and the continuum’s approach, which goes back to van der Waals’ works on the theory of capillarity [7] (Chapter 2).

The fluctuation-induced boiling-up of a superheated fluid is preceded by the formation of nuclei having a characteristic size of 5 to 10 nm. Properties of such small objects can be expected to depend considerably on the character of interparticle interactions and should differ from the properties of the respective bulk phases. By comparing experimental results with the theory of homogeneous nucleation it is possible to develop estimates of the lower bound of the validity of the thermodynamic description of such small molecular systems.

In a variety of cases, the theoretical limits of accessible supersaturation determined by the homogeneous nucleation theory may not be reached in real systems due to the presence of foreign nucleation centers in the system under consideration, which favor the formation of nuclei of the new phase. Beyond them, specific nucleation centers, which are not found in ordinary fluids, may be present in liquefied gases at low temperatures. Such specific nucleation centers include electron bubbles in liquid He, H$_2$ and Ne, vortex lines, and rings in superfluid helium, thermal spikes resulting from the ortho–para conversion in normal hydrogen. These and other topics of nucleation in one-component liquefied gases are discussed in Chapter 3.

Chapter 4 deals with the fluctuation-induced boiling-up kinetics in superheated solutions. Two types of solutions are considered: solutions with a complete solubility of the different components, and gas-saturated systems with partial solubility. In contrast to one-component fluids, the problem of the theoretical description of the spontaneous boiling-up kinetics in liquid solutions is so far not completely solved. In addition to size effects, both adsorption and the time scale of establishment of the absorption equilibrium may considerably affect nucleation in solutions.

The critical point of one-component fluids or solutions is the only point where the boundaries of the regions of essential instability of a metastable phase are adjacent to the region of stable states of the substances under consideration. As this point is approached, the width of the metastable region tends to zero, and the radius of correlations and the relaxation time of hydrodynamic modes increase unlimitedly. These factors have a specific effect on the character of the phase transformations in the vicinity of the critical point. In this range of initial states, not only the metastable region becomes more or less easily accessible to experimental studies, but also the region of unstable states. The theoretical description of nucleation in intensively fluctuating sys-
tems near critical and tricritical points is discussed in Chapter 5. This chapter also deals with relaxation near the spinodal and the theoretical description of spinodal decomposition.

The occurrence of nucleation induced by thermal fluctuations is impossible near the absolute zero temperature, and the decay of a homogeneous metastable phase can proceed here only via quantum tunneling of a heterophase fluctuation through the respective thermodynamic potential barrier. In its basic premises, the theory of quantum nucleation was developed by Lifshitz and Kagan [8]. In the recent years, considerable attention was devoted to the experimental detection of processes of quantum nucleation in liquefied gases and solutions as well as in other systems. The achievements and problems encountered in this field of research constitute the contents of Chapter 6.

The design and creation of large cryogenic systems for transportation and storage of cryogenic fluids, bubble chambers, ultrahigh frequency cooling systems and molecular quantum generators have set up some fundamentally new scientific problems including the problem of fast phase transformations, which are accompanied by deviations from phase equilibrium. The cessation of superheating may in some cases lead to considerable hydraulic shocks. The prevention of any superheating of the fluids is one of the possible methods for making the cryogenic equipment more reliable. At the same time, it is desirable to maintain phase metastability of fluids for a long time in order to ensure the cavitation-free operation of cryogenic pumps. A strong metastability is required for the operation of bubble chambers, too. Superheated fluids represent an interesting object not only for theoretical studies but also for new technological applications. Problems regarding the dynamics of boiling-up of cryogenic fluids are discussed in Chapter 7.

Since 1961, systematic studies of the phenomenon of superheating of fluids and boiling have been performed by Skripov and his co-workers first at the Ural Polytechnical Institute and then at the Institute of Thermal Physics of the Ural Branch of the Russian Academy of Sciences. Results of those studies were summarized in the monographs [9–13]. After the publication of Skripov’s monograph “Metastable Liquids” [9], published in its English translation by Wiley in 1974, a large number of investigators joined the study of these types of problems, resulting in an increase in the number of publications. The results of the research performed in the last few years are generalized in reviews and monographs [14–16]. They are extended and systematized in the present monograph.

The demand for such a systematic presentation of the state-of-the-art problems and prospects of experimental investigations of phase metastability is felt not only by experimental physicists but also by theorists who, in the course of their analyses, come across with a variety of problems regarding the interpretation of experimental results concerning the properties of different systems in
the metastable state, and also by engineers who have to deal with processes of
intensification of heat and mass exchange, and fast phase transitions. One can
confidently say that the requirements concerning the level of knowledge of
the properties of matter in metastable states and the processes taking place in
them will increase in the course of further progress in science and technology.

This book is primarily meant for readers who are interested in the liquid
state of substances, liquid–vapor phase transitions, and boiling. It is based on
studies performed at the Institute of Thermal Physics of the Ural Branch of the
Russian Academy of Sciences. A considerable part of the experimental data
was obtained jointly with Kaverin, Rubshtein, and Sulla. I would also like to
express my sincere thanks to Professor Vladimir P. Skripov, who acquainted
me with the “world of phase metastability,” for his advice and support.