Article

Thermophysical Properties of Liquids in Not Fully Stable States—From the First Steps to the Current Trends

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Abstract: The present article marks the 95th anniversary of the birth of Vladimir P. Skripov, author of the classic study of superheated and supercooled liquids. It presents a discussion based on the early work carried out by Skripov and his research team in Ekaterinburg during the 1950s and 1960s. Due to their pioneering nature, these works laid the foundation for the study of metastable liquid states. For various reasons, although they remain relevant to this day, these groundbreaking works remain unknown to most non-Russian-speaking readers. As well as elucidating the behavior of the heat capacity of a solution in the liquid–liquid critical region, the presented research also concerns the characteristic features of light scattering and free-convective heat transfer in the liquid–vapor critical region of a one-component system, discussing two options for the position of the superheated liquid spinodal on the phase diagram of water, including the area of supercooled states and negative pressures. The issues involved in the discussion are united by the fluctuating nature of such phenomena. Indeed, the very possibility of their experimental study is due to a significant increase in the scale of fluctuations of the corresponding quantities when approaching the critical point or spinodal. The ongoing development of the approaches proposed in these papers for solving contemporary problems in the thermophysics of superheated liquids is discussed.

Keywords: liquids; not fully stable states; heat capacity; light scattering; free-convective heat transfer

1. Introduction

Research aimed at identifying reliable techniques for the removal of high-density heat fluxes becomes relevant due to the constant increase in the requirements involving intensive heat and power processes. Considering the characteristic sizes of heat transfer devices and release parameters, both active and passive methods are used. An important direction here consists in the search for new classes of liquid heat carriers, as well as the expansion of the range of variables for already known samples [1–5].

In this regard, the scope of interests includes the properties of substances in the area of not fully stable states: superheated with respect to the liquid–vapor equilibrium line and nearly supercritical. In the phase diagram, these regions meet at the liquid–vapor critical point. In view of the peculiarity of properties in the vicinity of the critical point, which is due to the structural rearrangement of the particular substance, its state in this vicinity can be characterized as "a very delicate state of matter" [6]. From an experimental point of view, this circumstance means an increase in the requirements both for the method of measuring primary quantities and for matching the experimental conditions with the requirements of an ideal model used to convert primary quantities into the substance's thermal property values [5,7,8]. Unlike critical and supercritical phenomena, while a description of the superheating phenomenon is not included in known textbooks, it has attracted the attention of researchers for many years [9]. Indeed, such states can-and do-arise when the heat transfer process is intensified, and the size of the device is reduced.

The essential approach of the Ural thermophysical school (to the 95th anniversary of whose founder this article is dedicated) is based on a consideration of spontaneous boiling-up as a random, fluctuation-driven event. In this regard, the primary experimental

data (in the general case, the lifetime of the superheated state) should be averaged over a series of measurements under given external conditions. The very concept of attainable superheating (as well as the widespread term "superheat limit") is conditional in the sense that each mean lifetime corresponds to its own temperature value.

Considering the contents of the books, reviews, and major articles published during this time [10–17], the present discussion is focused on the pioneering early works [18–20] which, despite having laid the foundation for the study of liquids' metastable states, remain obscure to non-Russian-speaking readers. The continuing relevance of these works also applies to the somewhat later research [21]. Therefore, the aim of this work is to address this gap by elucidating the behavior of the solution heat capacity in the liquid–liquid critical region, presenting the characteristic features of light scattering and free-convective heat transfer in the liquid–vapor critical region of a one-component system, as well as discussing options for the position of the superheated liquid spinodal, $(\partial p/\partial V)_T = 0$, on the phase diagram of water, which includes the region of supercooled states and negative pressures. Here, p—pressure, V—volume, and T—temperature. The issues involved in the discussion are brought together under the common fluctuating nature of these phenomena. The very possibility of their experimental study is due to the significant increase in the scale of fluctuations of the corresponding quantities when approaching the critical point or spinodal.

Interest in the study of not fully stable liquids—namely, fluids in superheated and nearly supercritical states—is associated with the significant region occupied by such states in the phase diagram of a substance [9–13]. The elegant solutions obtained in the pioneering early works [18–20] served as a practical basis for the gradual advance deeper into this area. New knowledge obtained for the properties of not fully stable liquids and the revealed fact of the confinement of their relaxation to an equilibrium state with respect to time have found application in novel engineering solutions. These solutions are generally connected with developing technologies for supercritical heat transfer in power generation (especially for 4th generation nuclear reactors in which supercritical water is used as a heat carrier [22,23]) and converting phase transition energy into transport fluids at the microscale [24,25]. In this connection, inkjet printers [26], bubble pumps [27], and fuel transmission and fire-extinguisher technologies [28,29] may be mentioned, as well as various bio-medical applications [30,31]. The prospect for using not fully stable liquids in modern technologies is associated with a steady trend towards the miniaturization of heat-generating devices, the intensification of heat transfer processes, and the increasing involvement of computer science approaches in research [32,33].

2. Background

As a special case of supersaturation, the phenomenon of superheating (stretching) of a liquid is observed when crossing the liquid–vapor equilibrium line, $T_s(p)$, without boiling-up (cavitation) [10]. The study of the characteristic features of this phenomenon has gained a "second wind" in connection with the development of technologies carried out on a scale of small times and sizes [4,32–35]. The search for the properties of superheated liquids is complicated by a number of special requirements for the measurement method and procedure [10,15,16]. First, the reduction in the lifetime of a substance with an increase in the degree of superheating should be noted, namely, $T − T_s(p)$ or $p − p_s(T)$. Examples of liquid superheating and its relaxation through spontaneous boiling-up for various processes are shown in Figure 1. In the case of supercritical pressure, the heating of a compressed fluid ($p > p_c$, $T < T_c$) is accompanied by its transition to a supercritical fluid ($p > p_c$, $T > T_c$) through a series of not quite stable states, but without phase separation [10,19,36].
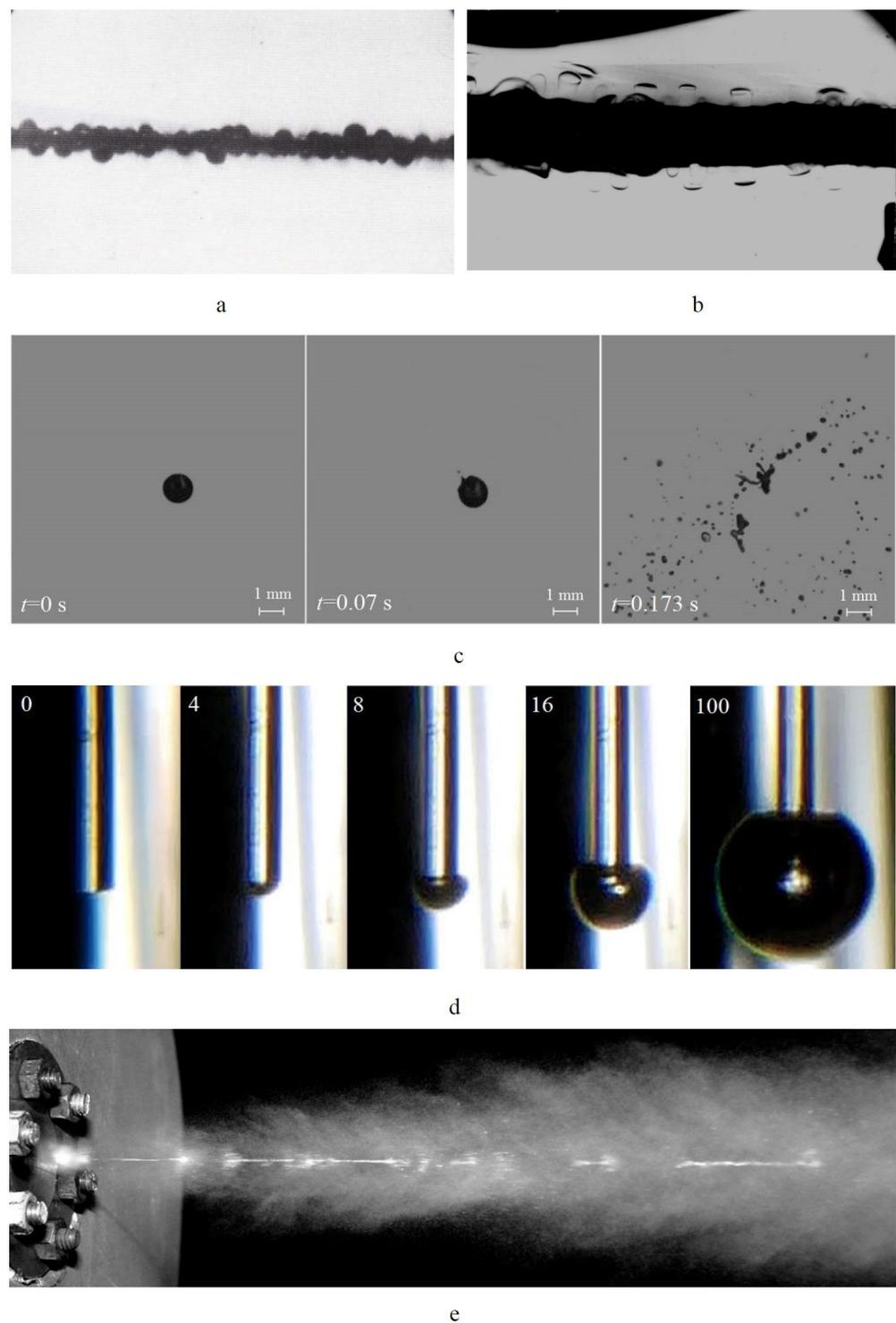
Figure 1. Examples of liquid superheating and its relaxation through spontaneous boiling-up for various processes: boiling-up of methyl methacrylate (**a**) and an aqueous solution of polypropylene glycol (**b**) on the pulsed heated wire probe (20 μm in diameter) at a characteristic time of 200 μs (**a**) and 1 ms (**b**). Boiling-up of a two-liquid (water/rapeseed oil) drop in an ethanol flame (**c**). Activation of a bubble at the end of the light guide (9 μm in diameter) in superheated, by 65 degrees (due to pressure drop), *n*-pentane (**d**). Here, the numbers show the duration of the delay in μs relative to the activation pulse with a length of 0.1 μs. Boiling-up of a jet of superheated water leaving a pressure vessel with a temperature of 160 °C through a short cylindrical channel (**e**).

Another special case of supersaturation relevant to the present discussion is the super-heating of a solution having a lower critical solution temperature (LCST) relative to the liquid–liquid equilibrium line, $T_{ll}(c)$ (and, further, the diffusion spinodal $(\partial \mu / \partial c)_{T,p} = 0$, i.e., the stability limit of a homogeneous solution with respect to concentration fluctuations [9,37,38]), without phase separation of a solution with concentration c. Due to kinetic limitations, the lifetime of solutions superheated relative to $T_{ll}(c)$ is generally longer than in the case of superheating relative to the liquid–vapor equilibrium line. Relaxation of the solution to a stable state is carried out through nucleation or spinodal decomposition [9,39]. A visualization of the spinodal decomposition process can be found elsewhere [25]. As in the case of the liquid–vapor critical state (see Sections 3.2 and 3.3), the properties of solutions in the vicinity of the liquid–liquid critical point undergo anomalous changes (see Section 3.1). In both cases, the presence of anomalous changes in thermal conductivity remains the subject of scientific discussion (see, for example, the discussions presented in [6,40]).

3. Results

3.1. Heat Capacity of Binary Liquid Mixtures in the Liquid–Liquid Critical Region

The task of the study was to elucidate the behavior of the partially soluble binary liquid heat capacity in the critical region of the liquid–liquid phase separation. At that time (1950–1951), there were no data on this issue available in the literature. The work was motivated by the experimental verification of some provisions of the generalized critical phenomena theory by Professor V.K. Semenchenko, who was Skripov's scientific adviser at Moscow State University (1948–1953), on the example of partially soluble binary liquids. Semenchenko predicted the generality of critical phenomena and second-order phase transitions [36].

The object of study was triethylamine/water solution in the vicinity of a lower critical solution temperature (LCST). Critical point parameters at atmospheric pressure were determined to be 19.32 ± 0.02 °C and 34 ± 1 wt.%, respectively. An adiabatic setting of the calorimeter's periodic heating mode was chosen. The key requirements for the design of the setup and the procedure for conducting the experiment were dictated by the specifics of measurements in the vicinity of the phase transition, which is accompanied by a sharp change in the properties of the system. Briefly, the temperature rise was reduced to 0.1 K (on the steep part of the experimental curve—to 0.045 K), while the capacity of the calorimeter was reduced to 20 cm^3 (see Figure 2). However, due to the rejection of mixing in the vicinity of the phase transition, the heat transfer surface from the heater was increased. As a result, the temperature sensitivity of the setup turned out to be $3 \cdot 10^{-4}$ °C, the calorimetric sensitivity for an empty calorimeter turned out to be $9 \cdot 10^{-4}$ cal, and for that filled with water—$5 \cdot 10^{-3}$ cal. Over the course of the experiment, the substance was transferred step-by-step from a single-phase state to a two-phase state. The heat capacity in the experiments was calculated by the formula:

$$C = (Q/\Delta T) - C_0 = (0.239 \cdot I \cdot U \cdot t / \Delta T) - C_0. \tag{1}$$

The variables in (1), which are common for calorimetric measurements, evidently do not require additional explanations. The error in determining the heat capacity at a temperature rise of 0.1 K did not exceed $\pm 2\%$. The design of the calorimeter and the results of its testing on known samples are presented in detail elsewhere [41].

The results of two series of measurements carried out on different days according to [18] are combined in Figure 3. The TEA content was 34.11 wt.%, while the mass of the studied mixture was 12 g. The main result of the work is the discovery of the maximum heat capacity of a partially soluble binary liquid in the critical region of phase separation. The heat capacity maximum has a λ-shaped form, which is characteristic of second-order phase transitions. These results have been repeatedly confirmed [41,42]. Similar results obtained for systems with an upper critical solution temperature (UCST) formed the

basis of Skripov's dissertation [30]. On 1 November 1953, he moved to Sverdlovsk (now Yekaterinburg), where the work described below was carried out.
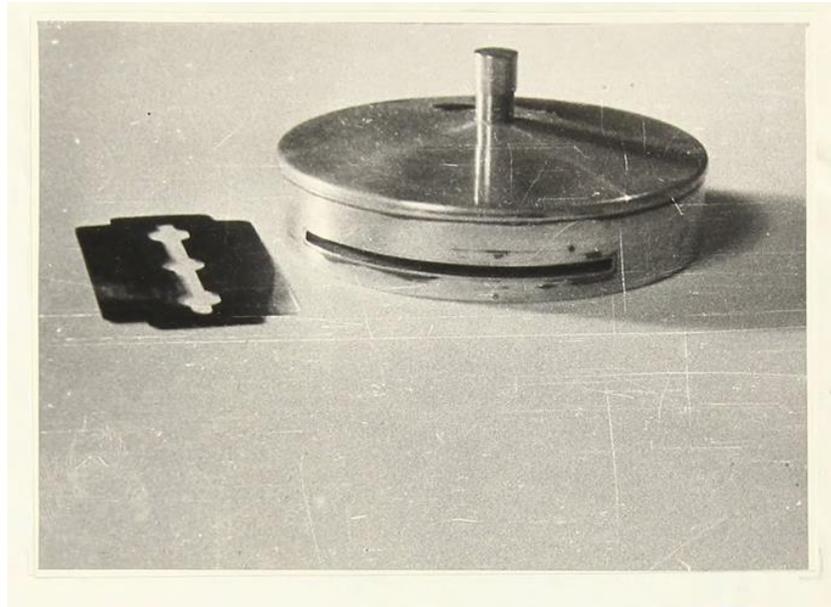

Figure 2. Photo of the body of the calorimeter designed for the measurements in the vicinity of a phase transition.
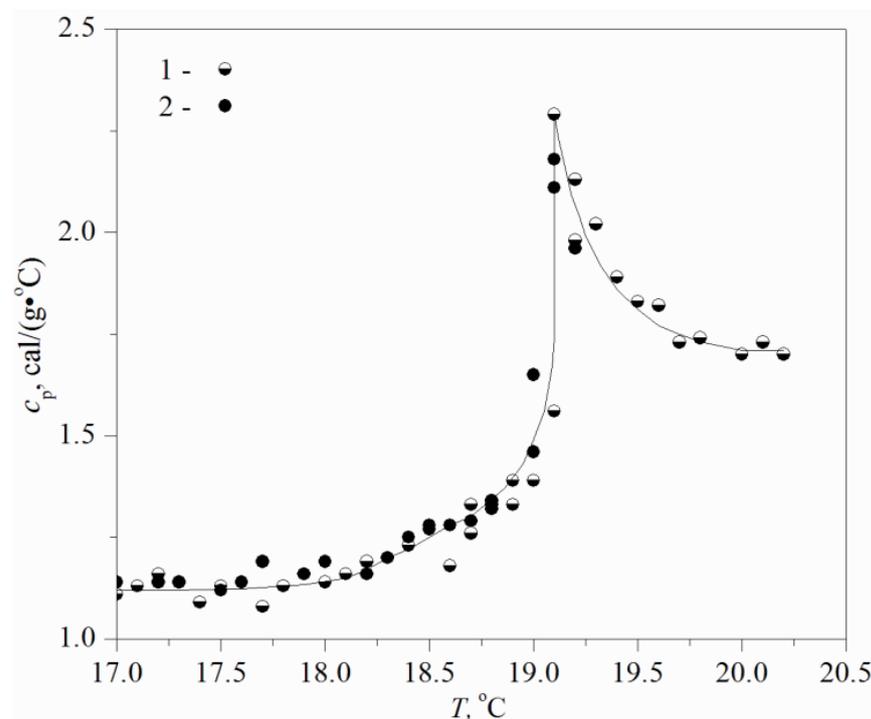

Figure 3. Heat capacity of triethylamine-water system. Experiments on 3 April (point 1) and 4 April (point 2) 1950 are presented.

In general, these results confirmed Semenchenko's point of view on the generality of critical phenomena and second-order phase transitions. An increase in the heat capacity near the critical point is associated with an intensification in the energy fluctuations of the system, which, according to the theory under discussion, is a fundamental feature of any of the generalized critical phenomena. Nevertheless, it was not until the mid-1960s

that the results were generally recognized [43]. Skripov noted that postulates of the theory met "...obvious or covert resistance from physico-chemists. Seeds fell on unprepared soil". This is not the only case in the history of critical phenomena. A similar fate met the results obtained by the experimental work carried out by Jules-Émile Verschaffelt in the Netherlands at around the end of the 19th century [44].

3.2. Characteristic Features of Light Scattering in the Critical Liquid–Vapor Region of a Single-Component System

To verify Semenchenko's hypothesis on supercritical transitions as continuous transitions, a systematic study of the light scattering along sub- and super-critical isotherms was carried out. Simultaneously with the intensity of the scattered light, the intensity of the light passing through the cell containing the substance was measured. The design of the installation developed practically from scratch due to the lack of reliable schemes for solving such problems set a certain standard for subsequent studies in the pre-laser era. A photograph of the working chamber, and a detailed description of the installation, temperature control, and pressure control techniques are provided in [19,45–47]. Briefly, the light source was a mercury lamp. The measurements were carried out for three lines of the mercury spectrum at wavelengths (λ_i) of 5461, 4358, and 4046 Å. Scattered light was recorded by a photomultiplier, whose load circuit included a null galvanometer.

Painstaking methodological work was carried out over a long period of time. To minimize the error associated with the density gradient, the optical cell was positioned vertically. The excitatory light, which traveled parallel to the density gradient, did not change its direction. The curvature of the scattered light traveling perpendicular to the density gradient was considered. As the critical point is approached, the absorption and multiple scattering of light begin to play an important role. For example, for a short wavelength of 4046 Å, the obtained correction for multiple scattering reached 28% at $T - T_c = 0.05$ K. As a result, the main factors in the study of critical opalescence in the liquid–vapor system were revealed: attenuation of the excitatory and scattered light, multiple scattering, as well as the influence of the gravitational effect. The role of these factors grows as the critical point is approached. The demonstrated expediency of using small optical cells is relevant to contemporary methods using a fiber optic light guide.

In view of the convenient position of their critical points on the temperature–pressure state diagram, the objects of study were carbon dioxide (T_c = 304.2 K, p_c = 7.38 MPa) and sulfur hexafluoride (T_c = 318.7 K, p_c = 3.76 MPa).

The first results were presented in January 1960 at a meeting on critical phenomena and fluctuations in solutions in Moscow [19]. Data were obtained on the scattering of light by carbon dioxide along ten isotherms, i.e., along the "wings" of the critical region. The pressure was varied from 63 to 83 bar. The most striking results were obtained for the nearest supercritical isotherm (see Figure 4). The enhancement of light scattering directly indicates the development of fluctuation micro-inhomogeneities in density. In the supercritical region, these phenomena are more pronounced. Indeed, there is a field of unstable states at $T < T_c$ through which the system jumps during a first-order phase transition. During supercritical transitions, the entire sequence of states with continuously varying density occurs. In the latter case, the region of maximum microscopic inhomogeneity is associated with the passage through the minimum of the phase's thermodynamic stability, which is determined by the value of the coefficient $\gamma = -(\partial p / \partial V)_T$, where the coefficient is positive for $T > T_c$ everywhere else. In particular, in the discussion of the results, their correspondence to the Rayleigh scattering law is shown

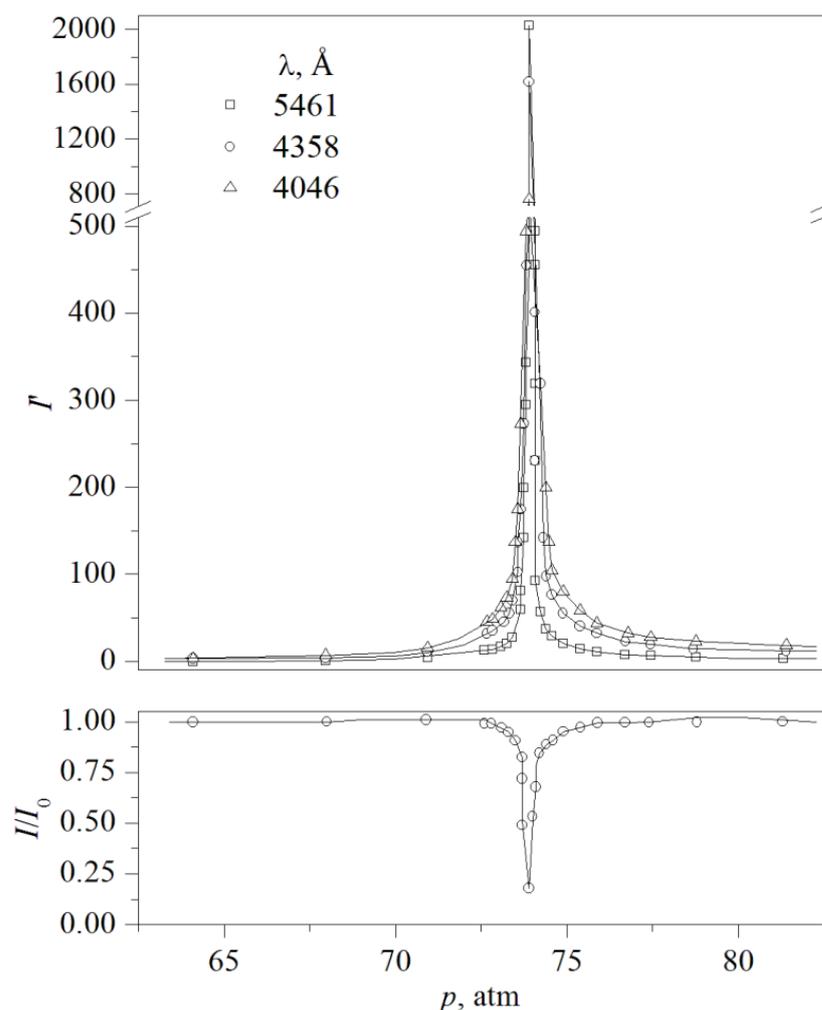$$I_i = (\lambda_i^4)^{-1}. \tag{2}$$

Figure 4. Scattering of light by carbon dioxide along the supercritical isotherm, expressed in mm of the galvanometer scale, at three wavelengths in Å: 5461, 4358, and 4046. The bottom graph shows the intensity of the light passing through the cell I, reduced to that of the excitatory light I_0. Here, $T = 31.2\,°C$, $T - T_c \approx 0.2\,°C$.

As shown in Figure 5, using the example of the 31.91 °C isotherm, the data for (λ_1) and (λ_3) were reduced to the blue line (λ_2) by multiplying I'_1 and I'_3 by $(\lambda_1/\lambda_2)^4$ and $(\lambda_3/\lambda_2)^4$, respectively. A change in the nature of scattering was found only for the nearest supercritical isotherm, at 31.20 °C, for which the value of the exponent in (2) turned out to be close to 3.2. Similar data were also obtained later for sulfur hexafluoride [47].

Generally, in the first work [19], the extremal course of light scattering had been already confirmed for a fairly wide vicinity of the critical temperature. This type of behavior was consistent with the known data for the heat capacity, viscosity, thermal conductivity, velocity, and absorption coefficient of ultrasound [5–7,48,49]. At the same meeting (1960), a report was presented, including a discussion of the solution with LCST (TEA/water) in the spirit of the ideas of V.K. Semenchenko. Nevertheless, in the Decision of the Meeting, it was noted that "... there are neither experimental nor theoretical grounds for rejecting the classical thermodynamic theory of critical phenomena" [50]. As a result, the transition from the classical era in the history of critical phenomena to the period of the fluctuation approach to their description took place, following [43], at the Washington Conference in 1965 [51]. Later, in a short-term experiment, conditions were identified under which anomalies in thermophysical properties do not manifest themselves [52].
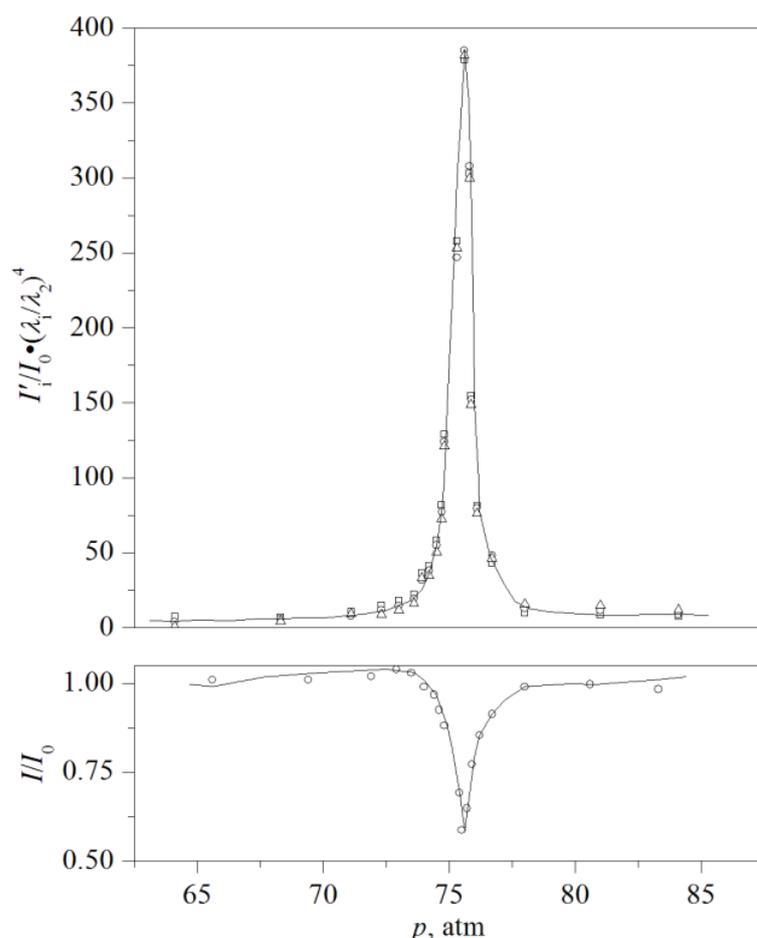
Figure 5. Correspondence of experimental data with Rayleigh's law (2) on the example of the supercritical isotherm of carbon dioxide. Here, $T = 31.91\,°C$, $T - T_c \approx 0.9\,°C$.

3.3. Characteristic Features of Free-Convective Heat Transfer in the Critical Region of Liquid–Vapor of a One-Component System

Liquids at supercritical pressures have attracted and continue to attract the attention of researchers as potential coolants in processes requiring reliable heat removal [1,5,22,23]. The research is aimed at elucidating the possibility of practical application of the above-mentioned anomalies in thermophysical properties. Significant work on the study of heat transfer along isotherms and isobars in the region of a continuous supercritical transition was carried out under Skripov's direction in the early 1960s [20] (see also [53,54]). As a first step, free-convective heat transfer was chosen as a more physically defined case. The main attention was paid to explaining the nature of changes in the heat transfer coefficient in the near supercritical region and the influence of the temperature difference on this character. A variant of the thin-filament method heated by direct current was applied. Compared with the method used in the apparently historically first paper [55], the method turned out to be quite convenient and pertinently informative.

Experiments [20] were carried out under the following conditions. The wire probe, which was 72.5 mm-long and 29 μm in diameter (in subsequent works [53,54], probes of five diameters were used, ranging from 20 to 200 μm), was stretched along the axis of a cylindrical channel 18 mm in diameter ranged in a vertical position. The setup scheme included an electrical power supply circuit for the probe as a heat source and a potentiometric circuit for the probe as a resistance thermometer. The heating power was selected in such a way that the probe temperature increase upon the onset of the stationary regime was $\Delta T \approx 0.5\,°C$. In this case, it is convenient to refer the results to the temperature of the chamber walls and the adjacent liquid. The primary data (including

voltage drop on the probe and on the standard resistors) were used to calculate the values of the temperature of the probe, the heat flux density, and the height-averaged heat transfer coefficient $\kappa = q/\Delta T$. The parameter was the value of pressure in a thermostated chamber with a temperature $T > T_c$. The samples were carbon dioxide and sulfur hexafluoride.

It was found that the values of $\kappa(p)$ pass through a maximum. This is due to the extreme nature of the change in thermophysical properties—primarily heat capacity and volume expansion coefficient, β—in the supercritical region. The developed fine-structured convection in the entire examined volume corresponded to the maximum values (see Figure 6). As in the case of heat capacity, the maximum value decreased with the distance from the critical temperature, while its peak shifted to the region of higher pressures (see Figure 7).
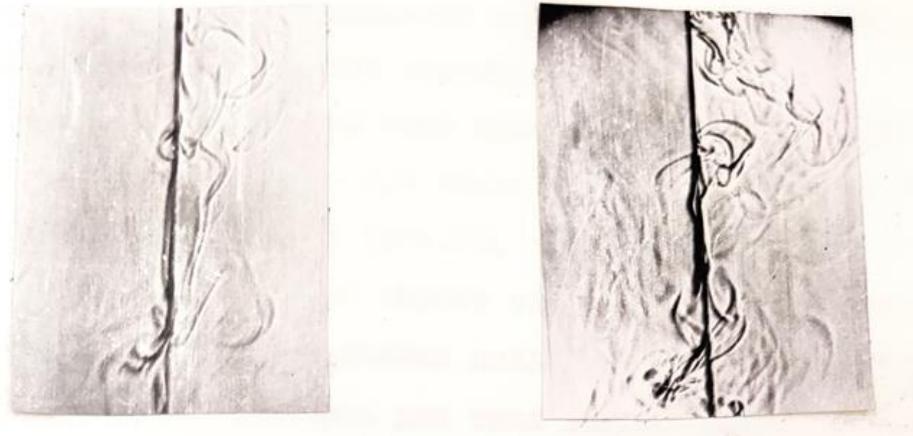

Figure 6. Photo of free convection of supercritical carbon dioxide on a wire probe at two values of the probe temperature increase: $\Delta T \approx 1.2\ °C$ (**left**) and 2.7 °C (**right**). Here, $T = 34\ °C$, $p = 8.17$ MPa.
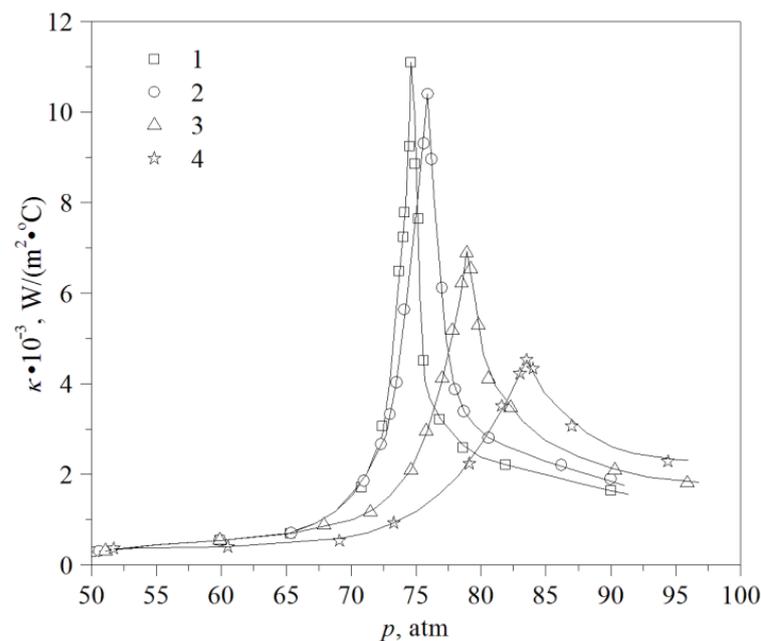

Figure 7. Dependence of the heat transfer coefficient to carbon dioxide on pressure along supercritical isotherms: 1—31.5 °C, 2—32.0 °C, 3—34.0 °C, 4—37.0 °C.

It would appear that the discovery of characteristic peaks of thermophysical properties will serve as a practical guide to the development of new areas for applying supercritical phenomena. At the same time, the specificity of supercritical heat transfer had already

been revealed in the first work [20]. This manifested itself in the fact that an increase in the temperature increase, ΔT, at a constant temperature in the chamber was accompanied by a decrease in the heat transfer peak (see Figure 8) up to its complete "disappearance" [56].
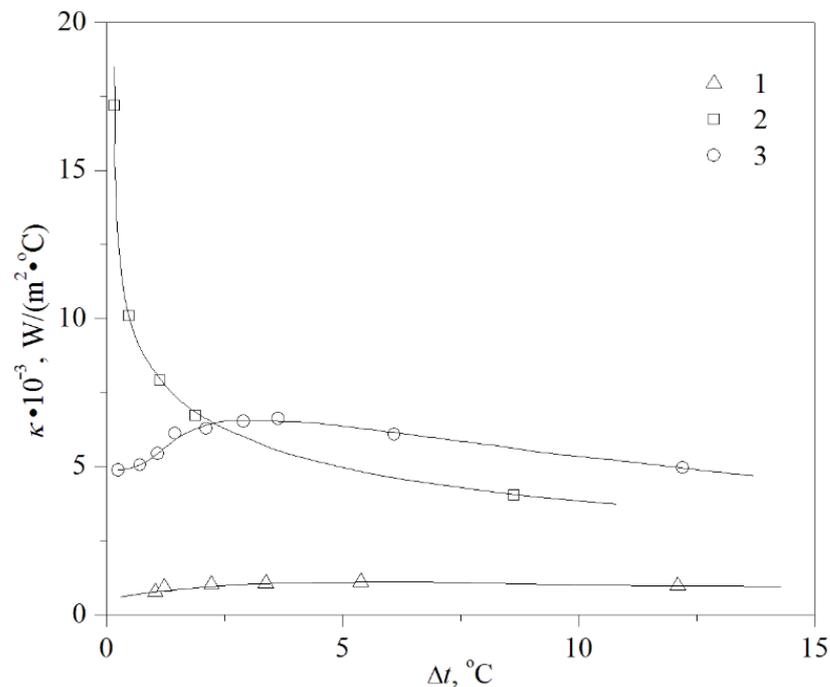

Figure 8. Dependence of the heat transfer coefficient on temperature difference along subcritical isobar (1) and supercritical isobars (2, 3) for carbon dioxide: 1—60 bar, 2—80 bar, and 3—93 bar. Here, $T = 34.0\ °C$, orientation of the probe in space was horizontal.

This effect was observed for all values of the diameter and orientations of the probe in space. Within the framework of the phenomenological approach, this result was explained based on the structure of the criterion equation for free-convective heat transfer:

$$\text{Nu} = c(\text{Pr}\cdot\text{Gr})^n, 0 < n < 1/3. \tag{3}$$

It turned out that the dependence, $\kappa(p)$, is determined, first of all, by the factor $(\beta\cdot c_p\cdot\Delta T)^n$. Obviously, with an increase in ΔT, the basic temperature to which the values of β and c_p must be reduced also increases. However, the condition $T' > T_0$ (where T'—basic temperature, T_0—temperature of the chamber) corresponds to the descending branch of the product $\beta\cdot c_p$. Therefore, the value $(\beta\cdot c_p\cdot\Delta T)$ will decrease with an increase in ΔT. As a result, the following contradiction was formed. While it is relatively easy to remove small heat fluxes, at which the heat transfer peak is relevant, the real problem lies in guaranteeing the removal of high-density heat fluxes.

3.4. Discussion of Variants of a Superheated Liquid Spinodal Position on the Phase Diagram of Water

The article [21] considers two variants of the water spinodal behavior on the p, T phase diagram with decreasing temperature. While the traditional version involves the spinodal comprising a monotonic curve with a positive value $(dp/dT)_{sp}$ in the entire region of existence, the new version assumes the presence of a minimum in pressure at $p < 0$ and a return to the region $p > 0$, with a further decrease in temperature (see Figure 9). By now, this latter view has become generally accepted.
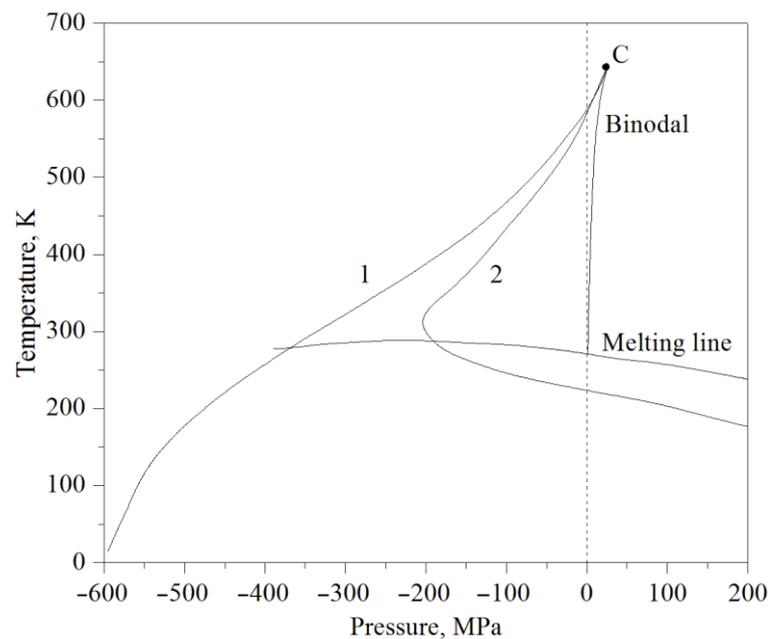
Figure 9. Phase diagram of water. Two suggested shapes of liquid–vapor spinodal (1 and 2) are shown. Here, C is the critical point.

In [21], an analysis was carried out of the input experimental data (1–3), which served as the basis for a new version [57,58]. Here, in comparison with theoretical estimates, smaller attainable values of tensile stress are observed (consideration 1), the rotation of the spinodal as an envelope of isochores in the case of its meeting with the line of water density maxima on the isobars $\alpha_p = (1/v)(\partial v/\partial T)_p = 0$, extended into the region $p < 0$, see Figure 9 (2), and the increase in the heat capacity of water with p as the temperature decreases from 290 to 266 K, which is considered as a trace of the spinodal singularity (3).

The analysis concludes with the idea that the rational selection of an option implies an additional discussion of the problem. The discussion began by using thermodynamic relations to elucidate the properties of characteristic curves—in particular, the derivative $(\partial v/\partial T)_p$—when approaching the spinodal, Equations (4) and (5). Some ratios are reproduced below:

$$(\partial v/\partial T)_p = (\partial p/\partial T)_v/[-(\partial p/\partial v)_T] \tag{4}$$

$$(\partial v/\partial T)_p \to \infty \tag{5}$$

$$dp/dT_{sp} = (\partial p/\partial T)_v \tag{6}$$

The line $\alpha_p = 0$, due to the condition (7),

$$(\partial v/\partial T)_p = 0 \tag{7}$$

serves as the envelope of the families of isotherms on the p, v plane. With the exception of the critical point, the entire spinodal belongs to the limiting metastable states. The thermodynamic description of such states acquires a conditionally asymptotic character. As discussed above, the main emphasis is on the analysis of assumption (2).

Based on ratios (4–7), the type of isobar near the line $\alpha_p = 0$ for the usual ($v_1 > v_2 > v_3$) behavior is qualitatively depicted in Figure 10a. As shown in Figure 9, if the convergence of the line $\alpha_p = 0$ and the spinodal leads to the appearance of a common point, then the spinodal must change direction after their supposed intersection to fulfill condition (6). However, a contradictory requirement then arises when explaining the behavior of the derivative $(\partial v/\partial T)_p$ when approaching a common point. Indeed, on the line $\alpha_p = 0$, we have $(\partial v/\partial T)_p = 0$, while on the spinodal we have $(\partial v/\partial T)_p \to \infty$. It is concluded that a normal conjugation of the line $\alpha_p = 0$ and the spinodal is impossible. Here, it is assumed

that the reaction of the system to the approach to the spinodal, which can be considered as the strongest, suppresses the structural changes in water, leading to the appearance of a minimum of the specific volume on the isobars. For example, an inflection point appearing instead of a minimum on an isobar serves as a termination point for the line $\alpha_p = 0$, even before it meets the spinodal. Such a case is presented schematically in Figure 10b. On the p_3 isobar, the line $\alpha_p = 0$ has a termination point. The branching of isobars in Figure 10b corresponds to two scenarios of spinodal behavior. Spinodal rotation (see Figure 9) corresponds to the isobar branches marked with dots. The continuation of the isobars by a solid line is consistent with the monotonic continuation of the spinodal into the region of low temperatures and negative pressures. From the analysis of the possibility of a temperature maximum on the line $\alpha_p = 0$, it was concluded that this line cannot avoid meeting the spinodal if it does not have a termination point. A similar discussion carried out for other considerations (1, 3) inclines in favor of the non-Van der Waals behavior of the water spinodal. As a result of the discussion, it is emphasized that current knowledge about supercooled (stretched) water properties does not allow us to confidently choose one of the scenarios for the behavior of the spinodal. Nevertheless, the author of [21] prefers the monotonic version presented in Figure 9, which was built according to previously published data (range from T_c to 280 °C), using the Furth equation [59] (range from 280 to 0 °C) and arbitrary extrapolation to lower temperatures. For $T \rightarrow 0$, a Van der Waals limit of $p_{sp} = -27\, p_c$ was adopted.
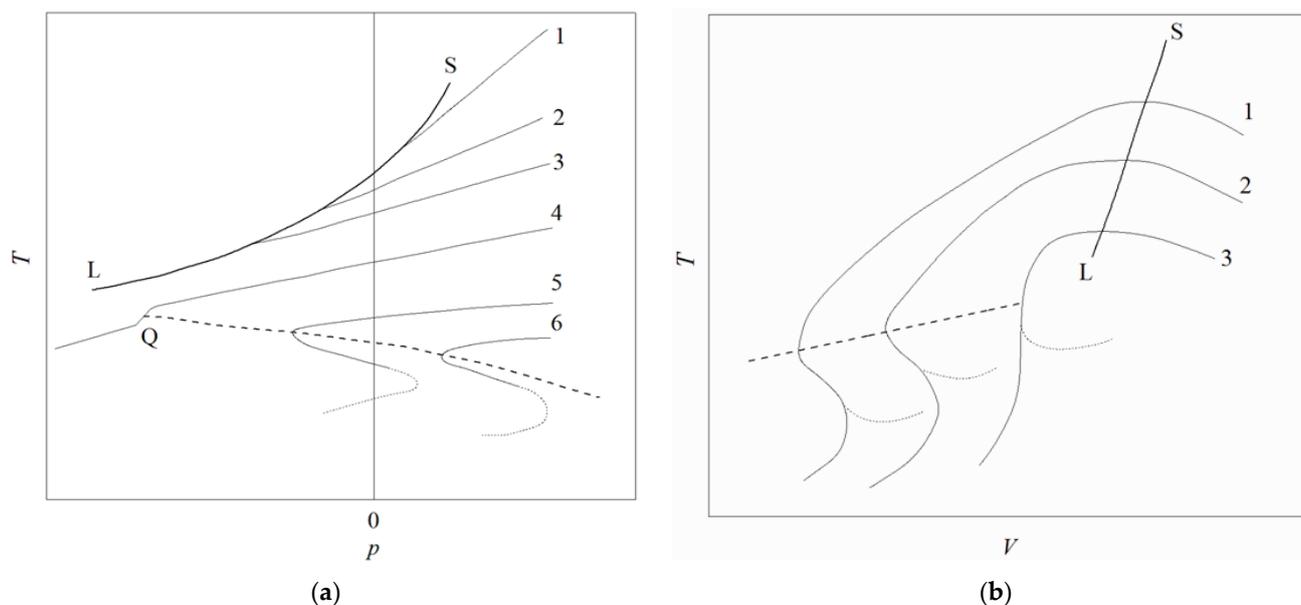

(a) (b)

Figure 10. Fragment of the phase diagram of water. Isochores (1–6) near the spinodal SL, the line $\alpha_p = 0$ (dashed line), and the termination point of this line (Q) before it meets the spinodal are shown (**a**). Isobars (1–3), spinodal SL, and line $\alpha_p = 0$ (dashed line) with a termination point on isobar 3 are also shown (**b**).

4. Conclusions

Based on the primary experimental data, a review of the early works of Vladimir P. Skripov was presented. Due to lying outside the "metastable field", comprising the main object of Skripov's research, these works remained obscure to the scientific community. Due to the significant reserve of capabilities of the devices and methods proposed in these works, they were lately developed at the Ural Thermophysical School. In particular, a variant of the light scattering method was applied to the systematic study of liquid–liquid phase diagrams. The objects were solutions with both UCST and LCST in a wide range of pressure changes [13]. The quasi-static study of solutions with LCST was supplemented by experiments carried out under conditions of powerful local heat release. As a result, the

phenomenon of superheating of solutions with respect to the liquid–liquid equilibrium line and the liquid–liquid spinodal was involved in the study [60]. A significant heat transfer enhancement accompanying the spinodal decomposition of an unstable solution was demonstrated [61]. This effect can be used in problems of removal of high-density heat fluxes. The elaborate choice of the heating power variation as a function of time has enabled us to develop the technique for searching for the upper branch of the diffusion spinodal of solutions with LCST and to test this technique for the above-mentioned TEA-water system.

Miniaturization of the optical cell and radiation source (optical fiber with a core diameter of 9 μm, introduced into the capillary of the bubble chamber with a diameter of 1 mm) allowed the initial stage of the liquid–vapor phase transition to be studied. The revealed propagating jump in the density of a superheated liquid that accompanies the onset of boiling-up [62] manifested itself in both spontaneous and activated phase transitions [63]. Presumably, for the first time in the practice of thermophysical experiments, the growth rate of a vapor bubble at the end face of a quartz fiber was traced through the very first microseconds of vapor phase nucleation in a uniformly superheated liquid (Figure 1d).

Pulsed modifications of the developed method for heating a thin wire probe have found application in problems of attainable superheating and stretching of liquids [64,65], as well as in determining the critical parameters of thermally unstable liquids [66,67]. The most advanced version [68] performs the function of electronic control of the heat release power in the wire probe directly during the pulse. This has been applied to study supercritical heat transfer [69] and heat transfer to superheated binary fluids [70] on the scale of small characteristic times and sizes.

Notations

C	heat capacity
c_P	specific isobaric heat capacity
c	concentration
Gr	Grashof number
I	current
I'	intensity of the scattered light
Nu	Nusselt number
p	pressure
Pr	Prandtl number
t	time
T	temperature
ΔT	temperature rise
U	voltage drop
V	volume
v	specific volume
β	volume expansion coefficient
κ	heat transfer coefficient
λ	wavelength
μ	chemical potential

Symbols

c	critical point
ll	liquid–liquid equilibrium
s	liquid–vapor equilibrium
sp	spinodal

Abbreviations

LCST	lower critical solution temperature
TEA	triethylamine
UCST	upper critical solution temperature

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