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Statics of Critical Phenomena in the Nearest Vicinity of the Critical Point: Experimental Manifestation

1.1

Short History of Critical Phenomena Research

The problem of the analysis of second-order phase transitions and the critical phenomena related to them, despite of nearly two century long history of their existence and thousands of articles already devoted to them, remains actual till now and is one of the key problems of condensed state physics and physics as a whole [1].

G. E. Uhlenbeck (1900–1988),[1] opening the famous Washington conference of 1965 on critical phenomena [5], started his review [6] with the description of the historical experiments (1861–1869) of Thomas Andrews (1813–1885), who carried out the classical works on the continuity of gaseous and liquid states on CO_2 [7–9]. Later, Andrews not only developed the theory of this phenomenon, but he also developed the very important assumption concerning the universality of matter behavior discovered by him, using CO_2 as an example. He also introduced (in 1861) the concepts of the critical point, critical temperature, and critical pressure. In a parallel development, as early as in 1860, Mendeleev [10] anticipated Andrews's conception of the critical temperature of gases by defining the absolute boiling point of a substance as the temperature at which cohesion and heat of vaporization become zero and the liquid changes to vapor, irrespective of pressure and volume. Later, Mendeleev pointed out that the critical temperature of Andrews is the same as the absolute boiling point introduced earlier by him in 1860 [11].

However, long before Andrews and Mendeleev, in 1822, Ch. Cagniard de La Tour [12] described experiments, which he had carried out in order to prove the existence of a certain maximum expansion limit for liquid, *which after this point will turn completely into steam regardless of applied pressure*. Faraday [13] also came to similar conclusions in 1822–1823 based on his experiments on gas liquefaction. It is these first experiments that should be considered as the beginning of the history of critical phenomena.

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[1] G. Uhlenbeck (1900–1988) together with S. Goudsmith (1902–1979) introduced into physics the spin concept of the electron (1925).

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Van der Waals's thesis (1873), which was also devoted to the problem of the continuity of gaseous and liquid states [14, 15] and for which the author was later awarded the Nobel prize in physics (1910), became an outstanding historical milestone. We can agree with Uhlenbeck [6], and say that this work proposes one of the most remarkable equations, which together with Maxwell's (1874) equal areas rule, describes surprisingly qualitatively truly for such a simple equation the whole liquid–gas area in the phase diagram including both stable and metastable states and the critical point. After that it was clear that there do not exist so-called permanent gases (in the sense that they remain always gases and cannot be liquefied), and that the presence of a critical point, as Andrews suggested, is a universal property of matter.

Van der Waals demonstrated his profound understanding of the real role and meaning of the critical point several years later (1880), when he formulated the principle of corresponding states. The essence of this idea consists in using the critical parameters themselves as units of measurement. Employing them, then the resulting equation of state, in such a reduced form, becomes universal. Apart from everything else, this law played an especially important role in the liquefaction of gases, particularly, of helium (H. Kamerlingh Onnes, 1908).

Over the next few years, other phase transitions, which had amazing similarity with critical point liquid–gas behavior, were discovered. So, in 1885–1889, John Hopkinson found that iron, when heated higher than a certain temperature, loses its magnetic properties and just before this transition its susceptibility has a sharp maximum (Hopkinson effect [16]). This phenomenon was thoroughly examined and described in the classical article by Pierre Curie[2] (1895). The temperature of this transition now bears his name. In 1907, Pierre Weiss introduced the concept of an internal field and explained both the existence of the Curie temperature and the spontaneous magnetization occurrence below it [17].

One more phenomenon which demonstrates the existence of a critical temperature is the order–disorder phase transition in binary alloys, which was first suggested (1919) for crystals by Gustav Tammann on the basis of the increase of electrical resistance in Cu_3Au with rising temperature [18]. Later this type of phase transition was confirmed (1925) for Au–Cu and Pd–Cu alloys via X-ray analysis by Johannson and Linde [19]. W. L. Bragg[3] and E. J. Williams in 1934–1935, using an analogy with Weiss's theory, explained it theoretically [20, 21]. Even earlier, in 1928, a similar result was published by Gorsky [23]. So, this theory should be more correctly called the Gorsky–Bragg–Williams theory even more taking into account that, to Bragg and Williams, Gorsky's work was known.

All three classical theories (the van der Waals, Weiss, and Bragg–Williams theories), despite their formal differences, have, as became clear, the same important unique feature: the attracting forces between molecules, which guaranty the

[2] Pierre Curie (1859–1906): Nobel-Prize laureate for physics (1903) for his research on radiation phenomena (together with M. Sklodowska-Curie (1867–1934)).

[3] W. L. Bragg (1890–1971) together with his father W. H. Bragg (1862–1942) are Nobel-Prize laureates in physics (1915) "for their services in the analysis of crystal structure by means of X-rays."

cooperative effect, are assumed to be long range. As a result, these types of theories turned out to be equivalent to the model of interacting particles with an infinite interaction radius (see, e.g., [24]). They bear the general name *mean-field theory*, which was adopted from Weiss's theory, and predict exactly the same singularities for the transition point [25]. As these theories do not predict unstable regions (see, e.g., pp. 127–130 in [26]), the need of the van der Waals isotherms in Maxwell's rule disappears.

Lev D. Landau first pointed out the general connection between these kinds of phase transitions (second-order phase transitions) and the change in the system's symmetry. He developed (1937) a quantitative theory of such transitions,[4] based on the expansion of the thermodynamic potential into a power series of the so-called order parameter, representing the deviation of some thermodynamic quantities in the unsymmetric from those in the symmetric state. The possibility of such an expansion was suggested a priori [25, 27]. The Landau theory, which is the most general formulation of the classical ideas, continues up to now to maintain its role as a universal zeroth-order approximation in the physics of phase transitions and condensed states.

As for experimental researches of critical phenomena, the works of R. Gouy (1892–1893) [28, 29] should be mentioned first. Carried out long ago, these works have much outstriped the experimental level of that time. Gouy was the first to describe, with surprising perspicacity, the influence of the gravitational field on matter close to the critical point (see below for more). A great contribution to the understanding of the critical state was made by A. Stoletov at the end of the 19th century. His critical articles on this problem [30, 31] contain a huge amount of precise observations, remarks, and judgments and are still relevant up to now. A valuable continuation of Gouy's experiments was the extensive series of papers by a group of Canadian researchers (see, in particular, [32–34]). In the mid-1950s, by increasing the level of experimental precision, they methodically studied the thermodynamics of the critical point, carried out spectacular research on the influence of gravity on the coexistence curve in vessels of large and small height [32, 33] (see below for more).

When talking about the nature of critical phenomena we must not forget to discuss the behavior of correlation functions. Correlation function properties take on a particular importance due to three phenomena observed near the critical point, which initially seem disparate, but are in reality closely connected. They are (i) amplification of density fluctuations, which von Smoluchowski proposed (1908) as the reason for critical opalescence [35], (ii) increase of compressibility [14, 15], and (iii) increase of the radius of action of density–density correlation functions (L. S. Ornstein, F. Zernike[5] (1914) [36]). The Ornstein–Zernike (O–Z) theory [36] was the first which could explain the anomalous growth of forward scattering when

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[4] Lev D. Landau (1908–1968): Nobel-Prize laureate in physics in 1962 "for his pioneering theories for condensed matter, especially liquid helium."

[5] F. Zernike (1888–1966): Nobel-Prize laureate in physics (1953) for his demonstration of the phase contrast method and invention of the phase contrast microscope.

investigating critical opalescence (see Chapters 4–6 for more) and paid attention to the presence of a significant long-range part in the correlation function. However, it is this circumstance which makes the O–Z theory classical, in the above-mentioned sense, as it is also based on the suggestion concerning long-range forces, and fluctuations are only considered as small corrections.

The first nonclassical result, which was practically the only one at the time of the Washington conference, was obtained by Lars Onsager[6] (1944) [37] in the analysis of the two-dimensional Lenz–Ising model, the so-called nearest-neighbor model with clearly short range forces (the history of the Lenz–Ising model can be found in the article [38]). Despite the fact that Onsager's most impressive result was the prediction of the logarithmic singularity of isochoric heat capacity in the neighborhood of the phase transition point instead of a classical "jump," this result was considered in the 1940s–1950s to be a mathematical curiosity rather than a physical reality. Such an approach to it continued until, in the 1960s, such type of behavior was discovered for the heat capacity of helium, argon, and oxygen (see, e.g., [39, 40]). So, in the early 1960s the appearance of additional experimental proofs of the inadequacy of the critical phenomena description by classical theories not only stimulated a renewal in interest and further rapid growth in their development (this explosive growth was noticeable, despite that even thousands of investigations into critical phenomena in liquids carried out between 1950 and 1967 (see, e.g., [39])) but also marked the beginning of the new modern stage in the research of phase transitions.

In general, as correctly mentioned by many authors (see, e.g., [26,41]), it is difficult to fix any certain date by which the modern period in studying critical phenomena has begun. Such a point could possibly be either the Onsager's exceptionally important work [37], if we agree with E. Stanley [26], or E. Guggenheim's famous analysis [37] which demonstrated a cubic rather than a square shape of the coexistence curve for eight simple liquids. Or maybe, as M. Fisher said [41], it was slightly earlier when the same result was obtained in another well-known research for CO_2 [43].

Undoubtedly, this would all be true if it was not for one extremely important circumstance. In fact, in the 1890s van der Waals found that experimental data on the critical behavior of surface tension showed an unusual (what we would now call "nonclassical") value of the critical index. Actually, the very idea of critical indices was also not new, but was introduced by van der Waals himself (1893) for describing just the critical behavior of surface tension. Van der Waals was not the only one in detecting deviations from his own theory. We must not forget the Belgian researcher J. E. Verschaffelt who, as a young man, came to the Netherlands on a 2-year apprenticeship in 1893, began working with J. van't Hoff, the first Nobel-Prize laureate for chemistry (1901). He then continued working with van der Waals

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[6] L. Onsager (1903–1976): Nobel-Prize laureate in chemistry (1968) for the discovery of the reciprocity relations bearing his name.

and, finally, ended up at the laboratory of H. Kamerlingh Onnes,7) which was one of the best laboratories of the time. He stayed there for many years. As a result of applying an analysis technique, the logarithmic differentiation method, developed by him [45] on his own data as well as on already published experimental data, Verschaffelt in 1900 (!) as obtained practically modern critical index values for pure liquids. (It is interesting that the logarithmic differentiation method was again rediscovered in the 1960s and it is called now the Kouvel–Fisher method [44]). Critical index values obtained by Verschaffelt: $\beta \sim 0.34$ for the coexistence curve, $\delta \sim 4.26$ for the critical isotherm, and $\overline{\mu} \sim 1.32$ for the surface tension coefficient, instead of their classical values 0.5, 3.0, and 1.5, respectively. Besides, Verschaffelt managed to develop an equation of state similar to modern equations of state close to the critical point. But, as J. M. H. Levelt Sengers wrote in [46], from where all this information about Verschaffelt's work is taken, all this, unfortunately, fell "on deaf ears." Looking at the reasons why Verschaffelt's work was largely ignored Levelt Sengers comes to the seemingly correct conclusion that this was "the seed on the rock." Every idea needs to be mature and in demand. It is also suggested that the fact that practically all of Verschaffelt's works were written in Dutch played a negative role. Levelt Sengers, who did a great work for the physics of critical phenomena, took over the task of translating and commenting on these works. This was a difficult but useful task [46] which typically also passed almost unnoticed.

So, we can see that the reasons for looking again at the classical theory of critical phenomena arose almost at the same time as its creation, but fate disposed differently. It was necessary to wait for a really not ordinary event, the appearance of L. Onsager's work [37], for the reasons of inadequacy of all classical theories of phase transitions to became clear. This created the certainty that it was possible to understand them deeper and pointed to the directions which should be followed. As C. Domb and M. S. Green, the first editors of the famous multivolume collection "Phase Transitions and Critical Phenomena" wrote in the preface: 'The problems to be faced in extending Onsager's work were formidable, and at first progress was slow. However, there were many different aspects to be investigated and a number of alternative lines of theoretical approach to be pursued. The field began to attract new experimentalists and theoreticians of ability' [47].

Finally, it was this last circumstance that was the deciding factor. A new modern stage in the development of views on the nature of phase transitions and critical phenomena, in which not the classical but the fluctuating approach to describing them dominates, began to develop and still continues today. The essence and details of this approach are presented in depth and fully in the reviews [39, 48, 49], in the books [26, 40, 41, 50–56], and also in the above-mentioned encyclopedic series [47]. Therefore, below, within the limits of our brief historical review, only main ideas underlying modern representations concerning the nature of phase transitions and the critical phenomena will be noted. These ideas [57–64] were formulated almost

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7) Heike Kamerlingh Onnes (1853–1926): Nobel-Prize laureate in physics (1913) "for his investigations on the properties of matter at low temperatures which led, inter alia, to the production of liquid helium."

immediately after the 1965 Washington conference [5], where their appearance was so wisely predicted by Uhlenbeck (see below). Moreover, it was in those years that significant experimental material [26, 39–41, 48, 49, 65, 66] was obtained, which did not play a small role in the establishment, development, and enrichment of the theory.

By ''fundamental ideas'' we are first of all thinking of the scaling hypothesis (or *scaling*), which makes it possible, in particular, to understand the fact of the universality of second-order phase transitions and critical phenomena. This idea was formulated almost simultaneously and independently by B. Widom (1965) [58] for liquid–vapor systems, by C. Domb and D. Hunter (1966) [59] for the Ising model, by A. Patashinsky and V. Pokrovsky (1966) [60] for ferromagnetic and in an apparently clearer physical form leading to an understanding of the universality of critical phenomena (see, e.g., [51, 67]) by L. Kadanoff (1966) [61] for correlation functions.

Once more, all this would correspond to reality if it were not for one fact. Today, when the idea of the universality and generality of second-order phase transitions and critical phenomena has become generally accepted and is beyond any doubt, we must remember V. Semenchenko whose fundamental ideas were always based on the general fluctuating nature of these phenomena. As a result, he was the first, in 1947, to formulate the idea of their thermodynamic generality [68]. However, as one of his brightest pupils and followers, V. P. Skripov, wrote: '. . . at the end of the 40's and 50's the idea came up against clear or hidden opposition by physical chemists. The seed fell on stony ground' [69]. So, unfortunately, the author of the idea to unite critical phenomena and second-order phase transitions based on fluctuation theory concepts suffered almost the same fate as Verschaffelt.

The idea of the universality of these phenomena is inherent in V. Ginzburg's[8] already classical work [70], where different second-order phase transitions which have a clear heat capacity anomaly (liquid helium, alloys, etc.) and those which have not (superconductors, ferroelectrics, etc.) are considered as the same-type transitions, transitions of the same physical nature whose difference is of an exclusively quantitative character. Ginzburg succeeded in taking this idea to its logical final and proposed the criterion which now bears his name and which, in principle, makes it possible to predict when the ''normal'' character of the transition is switched to fluctuation determined [70].

At the beginning of the 1970s, Kenneth Wilson made the next step. Starting his analysis with Kadanoff's ''blocking picture'' [61] and using then the ideas of the renormalization group method (RG) developed in the relativistic field theory in the 1950s, Wilson managed to transform the semiphenomenological ideas of scaling and universality into a real calculation scheme close to the critical point [71]. Then F. J. Wegner showed [63] how universality and scaling naturally followed from Wilson's method [72]. A year later, Wilson and M. E. Fisher succeeded in completing a self-consistent calculation method within the limits of RG by

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[8] V. L. Ginzburg (1916): Nobel-Prize laureate in physics in 2003 ''for pioneering contributions to the theory of superconductors and superfluids'' together with Alexey A. Abrikosov and Anthony J. Leggett.

introducing the so-called ε-expansion [73]. They showed that if one introduces variable space dimensions $d = 4 - \varepsilon$, then it becomes possible to calculate indices in the form of a series of ε. Therefore, in order to describe critical behavior there was created ''a new language no less universal than Landau's old theory, but more flexible and possessing a great 'predictive power' '' [51]. In 1982, Kenneth G. Wilson was awarded the Nobel Prize ''for his theory for critical phenomena in connection with phase transitions.''

In no way negating K. Wilson's merits, L. Kadanoff should, unarguably, also be recognized for completing a possibly more important, though intuitive, advance in the route to working out critical phenomena theory. He postulated universality classes and scaling hypothesis, based mainly on the fact that the only defining length in the critical region is the correlation length and also on the idea that the symmetry of interactions, but not their details, determines the critical behavior. The RG-theory successfully used these ideas, thereby confirming the validity of Kadanoff's foresight. Later the RG-theory was developed thanks to the works of many people and it is now an extremely powerful instrument which makes it possible to calculate many different properties: critical indices, critical amplitude ratios, universal correlation functions, equations of state, etc. (see, e.g., [50–55, 67, 74–78]).

These theoretical successes were closely related, as already mentioned above, to the progress made in experimental researches close to the critical point: the pioneering works of Skripov and Semenchenko [79], Voronel and Amirkhanov with their colleagues on heat capacity [80, 81], Skripov with his colleagues on the use and study of light scattering (in the prelaser era) [82], Shimansky and his colleagues on the wide research of the static properties of matter [83], Makarevich from the Krichevsky laboratory who brought a technique of (pVT)-experiments to perfection [84], Krichevsky's thermodynamic works on critical phenomena in dilute solutions [85], which have outstripped time much more (see, e.g., [86]). Ivanov et al.'s precision experiments [87, 88] could also be added to this list, where for the first time coexistence curve asymmetry and change in the static critical indices in the nearest vicinity of the critical point to the direction of their classical values were attributed to gravitation [89–92].

Daniel Beysens and his colleagues in Saclay (France) carried out the encyclopedic work on investigating the features of static critical phenomena using the example of binary mixtures (see, e.g., [93, 94]). Beysens also initiated and carried out the first experiments on research on the critical behavior of binary mixtures in flow [95], which gave, in principle, the same result as the experiment on pure liquids with gravitation [87, 89], transformation of critical indices to their mean-field values (see also [96, 97]). At the same time the fundamental theoretical Onuki–Kawasaki paper [78] appeared. In this work, within the framework of the RG-approach, the authors showed that a system influenced by shear flow crossed over to mean-field behavior on approaching the critical point due to deformation, up to suppression, of the long-wave critical fluctuations. As a consequence, critical indices get classical values.

Finally, we should mention the research of Wolfgang Wagner's group [98, 99] in which, as it earlier was in our studies [87, 89, 91], during the brilliantly organized, fully automated ($p\rho T$)-experiment on SF_6 [98] in the nearest neighborhood of the critical point the classical values for three (β, γ, δ) static critical indices were obtained. The reason put forward for this behavior was gravitation. Subsequently, by repeating their experiment on CO_2, they not only showed that SF_6 is not an exception but also that the change of indices to their classical values can be directly attributed to gravitation [99].

Referring for the last time to the Washington conference (1965), which can be considered to have concluded one classical, era of critical phenomena, and actually initiated the new era related to the fluctuation theory of phase transitions, we quote again the introductory remarks by G. Uhlenbeck [6]: ''If there is such a universal, but nonclassical behavior (*of heat capacity singularity*, D.I.), then there must be a universal explanation which means that it should be largely independent of the nature of the forces. The only corner where this can come from is I think the fact that the forces are not long-range . . . With regard to the correlation function and the Ornstein–Zernike theory I hope that the new experimental work will show that there is a *critical region*, where already deviation from the classical van der Waals–Ornstein–Zernike theories begin to show up. I think there are indications (as the specific heat anomaly) that such a region exists.'' Let us add another final remark by Uhlenbeck concerning nonequilibrium phenomena: ''There are very surprising experimental results found about various transport coefficients,9) which clearly are worth pursuing. Till now there is no theory, not even a van der Waals like theory'' [6].

It really was another era, although only a few decades ago. It was also different, as today after Uhlenbeck's prediction has come brilliantly verified, this critical area was not only discovered but has also been analyzed in detail. We hope to show that (see Chapters 1 and 2) beyond the critical area, even closer to the critical point, classical behavior returns once more! Maybe, in the grand scheme of things, Krichevsky, who was the most thorough and consistent supporter of the classical views on critical phenomena and kept his faith until his death, was not so wrong. Maybe he was just as wise as Newton with his ''corpuscles.'' Fortunately, the history in both cases developed in their own way without terminating the appearance and development of other ideas. As a result we have a perfect wave theory of light and also the timely appeared quantum theory. Finally, quantum electrodynamics could once more explain ''everything'' using only ''corpuscles'' [100]. The theory of critical phenomena has not yet reached such perfection but we hope that it is close.

This short historical excursion10) is, undoubtedly, necessarily very subjective, but the presence of a great number of excellent reviews and books on this theme [39–41, 46, 48–53, 55, 56, 65, 66] significantly simplified the author's task and gave the opportunity to look at the key moments and little-known facts from the history of the development of ideas concerning the nature of critical phenomena. Anticipating the passage to the description of the basic theme, it should be noted that, unlike most well-known monographs and reviews (theoretical and experimental) whose

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9) For more details on the behavior of the transport coefficients close to the critical point, see Chapters 4 and 7.

10) It should also be noted that Chapter 4 is concentrated on a review of research and ideas related to the dynamics of critical phenomena.

authors did not look at all at the influence of external factors on the behavior of critical phenomena or interpreted them as an obstacle in the way of investigating a "true" critical behavior, the first two chapters, and most of the whole book, are dedicated to the evolution of critical behavior of various nonideal systems as they approach the critical point under an influence of fields of different physical nature.

1.2
Peculiarities of the Experiment in the Nearest Vicinity of the Critical Point

1.2.1
"Experimental" Critical Indices

In the asymptotic vicinity of the critical point, independent of whether a classical or fluctuation type description is chosen, different physical quantities can be represented as simple power-law dependences. These exponents, critical indices introduced already by van der Waals, play a central role in any critical phenomena theory, as one or another set of their concrete values determines one or another type of the critical behavior. An exact critical index determination looks like this [26, 101]:

$$\lim_{x\to 0+} \frac{\ln f(x)}{\ln x} = \lambda \quad \Rightarrow \quad \underset{x\to 0+}{f(x)} \propto x^{\lambda}. \tag{1.1}$$

At the beginning of the 1970s, it became clear on the basis of experiments on liquids and the RG-analysis [63, 102–104] that precise experimental data cannot be described by simple power-law dependences and in general $f(x)$, which represents one or another physical (thermodynamic) quantity in the wide vicinity of the critical point, should be represented in a more complex form as

$$f_i(x) = \Lambda_{0i} x^{-\lambda_i} \left[1 + a_1 x^{\Delta} + O\left(x^{2\Delta}\right) + \cdots\right] \; s, \tag{1.2}$$

where x is the relative distance from the critical point in the thermodynamic variables, λ and Λ_0 are critical index and amplitude, while Δ and a_1 are the exponent and coefficient for the correction term, respectively.

Critical indices, unlike the full functions like Eq. (1.2), are experimentally measurable, which is one additional reason why they are playing such an important role. Really, as the polynomial behavior (Eq. (1.2)) close to the critical point is mainly determined by its leading term, so in accordance with definition (1.1), by the slope in the log–log scale graph of the dependence $f(x)$ on x, the critical index λ can be determined. Thus, the obtained critical index can generally be considered as an *effective*. Two circumstances should be mentioned in this connection. First of all, it can be easily shown (see, e.g., [104]) that the real (λ) and effective (λ_{eff}) critical indices are connected by a rather simple relation (see the very interesting papers [105–107] devoted to this subject):

$$\lambda_{\text{eff}} \cong -\frac{\partial \ln f}{\partial \ln |x|} \cong \lambda - a_1 \Delta \, |\overline{x}|^{\Delta} + O\left(|\overline{x}|\right)^{2\Delta}. \tag{1.3}$$

Here $x = \tau$, $\tau \equiv (T/T_c) - 1$, where T_c is the critical temperature, and $\overline{x}$ is some average temperature of experiment. Taking into account the fact that $\Delta \approx 0.5$ [102, 103] and $a_1 \leq 1$, then for the mean value $\tau \sim 10^{-4}$ the difference between effective and "true" critical indices does not exceed 0.005, which is well beyond the measurement error. Secondly, as was shown in [108], effective critical indices in leading order in ε obey all scaling relations (apart from hyperscaling one, which includes a space dimension). Below, we shall show, in the course of discussion of the precision of (pVT)-experiments on pure sulfur hexafluoride, that this point of view, which is only justified for ideal experimental conditions, should be corrected for real systems. Another no less important reason why critical indices receive such attention is related to the fact that thermodynamic and statistical fundamentals lead to the existence of a defined set of relations between them, usually inequalities (see, e.g., [26, 40, 41]).

Although thermodynamic conclusions are always categorical, that is why these dependences have a universal and valid character for any particular system, the nonstringency[11] of these inequalities, however, permits them, within the limits of scaling, to pass to equalities without violating any thermodynamic limitations.

Finally, as every model which can be used for describing critical behavior has its own set of critical indices [26, 40, 41, 52], so their experimentally determined values can make it possible to decide which model is preferable. In addition, the theoretical values of critical indices for systems with different values of space dimension (d) and number of components of order parameter (n) are known only as a result calculated for concrete idealized models (like the Ising model, Heisenberg model and their modifications) [26, 40, 41, 48, 52–55, 71–74, 102, 103]. At the same time, the conditions for a real experiment automatically include significant additional factors, especially in the nearest vicinity of the critical point, such as the existence of gravitation, dipole magnetic and Coulomb forces, surface tension forces, etc., which are commonly not considered when calculating critical indices. This is the reason why the comparison of experimental and theoretical values, where the influence of these factors can be very strong and often lead to unexpected consequences, should be made very carefully. It is also important to take into account the experiment's precision, as well as the way of approach to the critical point.

The fluctuation theory of phase transitions, in particular, leads to the conclusion that critical indices only depend on space dimension and the number of components of the order parameter. Transitions with the same number of order parameters form the same universality class [40, 62]. Liquids, solutions, binary alloys, and anisotropic ferro- and antiferromagnets together with the Ising model ($n = 1$) form the same universality class. This is the type of objects that we are examining in this book and in particular we shall discuss their behavior using the example of the liquid–gas critical point.

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[11] So as to avoid terminological confusion, it should be said that by "nonrigorous" we are referring to the sign "$\geq$." This is often (see, e.g., [26, 40]) called "rigorous" keeping in mind the thermodynamic rigor of their proof.

1.2.2
Determination of Critical Parameters

To process the results of any experiment in the vicinity of the critical point by equations like Eqs. (1.1) and (1.2) it is necessary to know the critical parameters of the substance being used for the experiment. To our opinion, it is not only desirable but absolutely necessary to determine these parameters using the same experimental setup which is being used for the main experiment.

It is sufficient to say that, within the framework of the International Practical Temperature Scale (see, e.g., p. 81 in [109]) it is not possible to determine either the temperature of absolute zero or temperature of reference points better than one hundredth of a kelvin, whereas in the best experiments thermostatting temperature fluctuates only within the range 10 to 200 μK. Therefore, near the critical point it is necessary to use the thermometer's (usually a platinum resistance thermometer) own scale.[12] Moreover, one must determine the distance from the critical point on temperature with one's own thermometer. However, this cannot be accomplished unless the critical temperature is determined during the experiment itself. It is actually quite usual to leave the critical temperature as a free parameter when approximating experimental data by Eqs. (1.1) and (1.2). However, it seems that such a method is forced upon but not effective, and therefore does not always help to obtain an objective picture.

Another peculiarity of experiments in the nearest vicinity of the critical point is that they are carried out against the background of ever increasing system susceptibility to different external factors. That is why there are such high requirements for purity of the investigated substance, for the absence of gradients etc. (see, e.g., [40]). Moreover, it is necessary to have criteria for reaching the critical state, and in order to determine the critical indices needed for comparing the obtained results with theoretical ones it is necessary to obtain values of no less than three critical indices on the same experimental setup. This latter requirement is due to the fact that, although relations existing between critical indices make it possible to consider any two of them as independent, however, the test of these relations themselves demands independent determination of, at least, three indices. To obtain a self-consistent set of indices it is absolutely essential that this requirement is fulfilled.

Further we shall discuss all of these questions and, despite the abundance of works on this problem, the number of research papers which satisfy all the above criteria are not that great. Therefore, we have to use our own experiments carried out on pure SF_6 [87–92] and use other authors' papers when possible. As some additional justification of this approach we can say that these researches,

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12) It should be noted that when investigating critical phenomena where all these values are referred to the critical point, this condition plays no role. However, it seems that if the investigated samples are properly cleaned, then their absolute value T_c corresponds to each other properly (see, e.g., [98], where the found T_c differs from that determined in [87] by only 1.5 mK, which lies within the margins of error even for absolute temperature measurements).

which began in 1974, were for many years the only ones in the world scientific literature where in the same experiment the changes of three static critical indices toward their classical values in the nearest vicinity of the critical point were found. Moreover, these changes were, for the first time, interpreted as the consequence of the gravitational effect.

For many years this hypothesis was considered, at best, as an overbold one. Many people, including such a great authority on critical phenomena as I. R. Krichevsky, in whose laboratory this experiment was carried out, tended to consider such behavior as a natural consequence of the validity of the classical critical phenomena theory. It was not that long ago that papers appeared where analogous results were once more obtained on SF_6 [98] and CO_2 [99]. In these papers, the authors also treated the transition of the indices to classical values as a consequence of gravitation. The results of these works will be discussed in detail further, but we should start with a brief look at the peculiarities of critical parameter measurement methods and methods of assessing purity of matter.

1.2.3
Purity of Matter

Already in the 1870s, Andrews [7–9] noted that the critical temperature of CO_2 mixed with air can go right down to 0 °C depending on the degree of impurity. In fact, this is so obvious that the only surprise is the reaction against Andrews by such famous scientists as J. Jamin and L. Cailletet who supposed that "the addition of a gas harder to liquefy (air) should not effect the critical temperature of a gas easier to liquefy like carbon dioxide (CO_2)" (see [31], pp. 290–297).

The effect of impurities on critical parameters can be observed by studying diluted solutions. In his thesis, Makarevich [110] determined the critical parameters of diluted solutions of carbon dioxide in sulfur hexafluoride. By analyzing his results we managed [141] to ascertain that a good test on matter purity can be the so-called *critical coefficient*, $K = (RT_c/p_c V_c)$, where the subscript "c" denotes "critical," R the universal gas constant, $R = 8.3145\ \mathrm{J\ mol^{-1}}\ K^{-1}$ (Fig. 1.1). The figure clearly shows that as the amount of CO_2 decreases this coefficient increases. As this coefficient continues to grow as other impurities are removed, it can be supposed that this feature relates not only to SF_6 and its impurities, but has a more general character. Unfortunately, we are not aware of such tests carried out on other substances.

As for the two purest of the tested samples (matter purity 99.9994% [98] and 99.9995% [87–92]), although only semiquantitative evaluations were made, the dependence found in [141] turned out to be very good (Fig. 1.1). Clearly, these conclusions are valid only if the proposed criterion continues to operate even at such a low degree of impurity and if there were no systematic errors in determining the critical parameters in the quoted papers. It is in any case clear that in [91, 98] we are dealing with the purest ever investigated samples of sulfur hexafluoride (and not only of this).

In addition, the evaluation of the degree of purity performed in [87, 91], as for [110] in its time, was carried out using one of the typical features of pure matter,

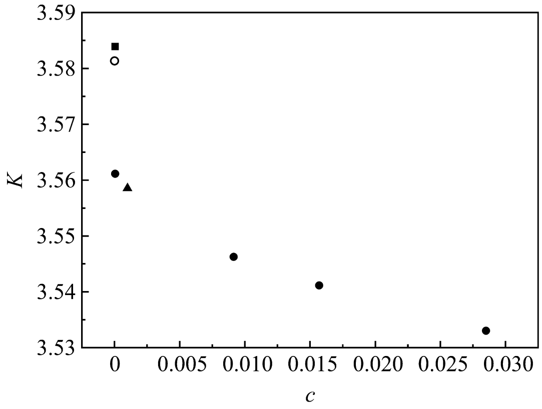

Figure 1.1 Dependence of the critical coefficient of SF_6 on impurity concentration [141]. Plots are made using experimental data from different sources: (•) SF_6 and CO_2 [110]; (▲) data from [113] (quoted from [114]); (■) [87, 91]; (○) [98].

the horizontality of its isotherms in the coordinates ($p-\rho$) in the two-phase region. After a double purification by the first rectification column the pressure difference at the ends of the isotherm with a four times change in volume did not exceed ±0.5 kPa. The purification by the second column stopped only when the pressure difference, under the same conditions, was not noticeable within the limits of the sensitivity of the pressure gauge (±2 Pa). To do this it was enough, as a rule, to carry out two to three distillation cycles on the rectification column for a final purification [91].

With precision thermostatting and a sensitively stable pressure gauge this test, although not providing a quantitative or qualitative estimate of the composition of the impurities, has, in our opinion, an incontestable advantage over other methods (chromatography, mass spectrometry, etc.). Most importantly this check is carried out on the same experimental setup which is then used for the main experiment. This makes it possible to carry out a closed cycle, which guarantees that impurities will not enter the checking process itself and also its efficiency. Finally, this method is universal, while quantitative analysis methods are to different degrees developed for different substances. In a recently published work [111], one of the authors of which is the renowned researcher in the field of critical phenomena, L. Weber (see for example one of his early works [112]), not only such method of definition of substance purity is proposed, but also detailed recommendations for its calculation are given.

1.2.4
Determination of Critical Density

One of the most difficult problems of determining critical parameters is critical density, (ρ_c). This is due to the natural peculiarities of the critical point. The small curvature of the coexistence curve close to the critical point leads to low pressure sensitivity to density changes. It is also due to terrestrial observation conditions when the gravitational effect [28] causes additional flattening of the peak of this curve [32–34, 88, 89, 91, 115]. All this leads to the fact that, even in the best works, the precision of critical density determination is, as a rule, two to three times lower than the determination of other critical parameters and does not exceed ±(0.1–0.2)%. In our research the precision of critical density determination was of an order higher, ±0.02% (see below for more).

The most common method of determining critical density is the disappearance of the meniscus method [28, 31–34, 84, 116, 117] or the so-called Cailletet and Mathias "rectilinear diameter" rule (1886) [118]. In recent years, however, the validity of this rule for the nearest vicinity of the critical point has raised such serious doubts that the diameter of the coexistence curve was even given its own name "singular" (see, e.g., [119–124] and also [125] and references therein). Therefore, it was necessary to have a method for independently determining the critical density. Such a method, in view of all previous experience (see, in particular, [31]), was suggested by Makarevich and Sokolova [84] and then used in [87–92]. In view of this problem's great importance it is necessary, albeit briefly, to look at the principal peculiarities of this method of determining critical density.

The method is based on using visual observation of meniscus movement in a constant-variable volume piezometer. The high precision of critical density determination (±0.02%) in this case is due to both the high sensitivity of such a method of observation, as Gouy [28] and Stoletov [31] still noted, and the improved sensitivity of the volume measurements as a whole [84]. The sharp increase in sensitivity and precision of the volume measurements in its turn was possible only thanks to the making and application of the micropress, an original refinement of the (pVT)-setup. The micropress is a successful technical realization of I. R. Krichevsky's fruitful idea which makes it possible to unite the advantages of constant and variable volume piezometers in one apparatus [84].

Let us assume that the critical parameter values of the substance being investigated have been roughly determined (this is not usually very difficult). Then, an appropriate amount of the substance is placed into the piezometer and the temperature of the thermostat is raised by $(3-5)\times10^{-3}$ K and is further kept at this level with extreme precision (in this case $\pm2\times10^{-4}$ K). Next, using the micropress the volume of the piezometer is quickly (quasiadiabatically) increased by (0.3–0.5)% (AB, see Fig. 1.2) from the whole volume which leads to cooling of the substance (BC), appearance of the second phase, and the meniscus.

Then, the volume is slowly decreased down to the initial one (CD), at the same time generating an undulatory motion of the meniscus by light shocks of the stirrer. The less intensive this motion, the greater is the time for transition to equilibrium. In particular, the motionless meniscus is dissipated in at least 2 h, while with intensive stirring it disappears within several seconds against the background of very strong opalescence. The speed of the meniscus undulation

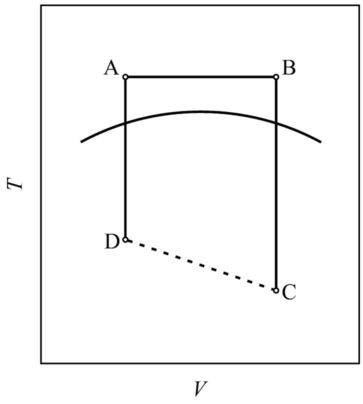

Figure 1.2 Schema of determination of the critical density by the disappearance of the meniscus method.

increase was experimentally chosen in such a way that in 1–2 min the meniscus begins to darken, finally turning into a 1-mm-thick dark brown stripe with very weak opalescence in the rest of the vessel. These observations demonstrate that without stirring the critical phase inside a piezometer can, apparently, exist only in a thin layer of the substance.

The transition from a nonequilibrium state (*D*) to an equilibrium one (*A*) is accompanied by the meniscus moving up or down the vessel's height depending on the value of the mean density of the substance therein. When $\overline{\rho} > \rho_c$ holds, the meniscus moves up and when $\overline{\rho} < \rho_c$ is fulfilled, it moves down. Thus, the task is reduced to find the position at which the meniscus movement changes to the opposite at the minimal change of average density (volume). The sensitivity of such a method is limited only by the micropress's sensitivity which in [84] and then in [87–92] was not worse than 0.002%. If we take into account the limits of error of the micropress's and piezometer's calibrations, then the error in determining the critical density did not exceed ±0.02%. It should be mentioned that the possible systematic influence of gravitation on the result of the measurements, naturally, is not included in this estimation.

1.2.5
Determination of Critical Temperature and Pressure

The precision in determining the critical temperature (T_c), using the same visual observation method for the appearance–disappearance of the substance's two-phase state in the piezometer when the average density being equal to the critical one, was not worse than $\pm 2 \times 10^{-4}$ K with thermometer sensitivity no less than 2×10^{-5} K [87, 91]. The adjusted values are, of course, not related to the absolute scale but only to the own one of a secondary reference platinum resistance (100 Ω) thermometer. Wagner and his colleagues did not carry out visual observations, but temperature instability was reduced to 10–25 μK [98, 99]. The measuring system of pressure, including critical one (p_c) used in our experiment [87–91], consisted of a piston gauge, belonging to the group of the national standards, a mercury null indicator, and a reference control mercury barometer (for measuring changes in atmospheric pressure during the experiment). This guaranteed an overall error not exceeding ±40 Pa (∼0.001%) in the own setup scale with a sensitivity of ±2 Pa and reproducibility of the measurements no worse than ±5 Pa. The experimental setup in [98, 99] used almost the same parameters.

Such setups are extremely rare in the world and the quality of the data obtained is usually well known. The (pVT)-setup with visual observation discussed here is not an exception (see, e.g., [40], p. 112). In addition to subjective judgements on this theme, one can obtain an objective idea about the accuracy, sensitivity and reproducibility of the data in this experiment from Figs. 1.6, 1.12, and 1.21, where (partly or in full) the coexistence curve, critical isotherm, and critical isochore of pure SF_6, obtained with the help of this setup, are shown [87–91, 128]. Figure 1.6, for example, clearly shows that the scattering of experimental points lies within the margin of error for temperature. In Fig. 1.12, where only a part of the isotherm, immediately adjacent to the critical point is shown, apart from the horizontal part the precision of the pressure measurement and stability of thermostatting are distinctly visible. It should be noted that the ‘‘height’’ of the rectangle in the graph is twice the measurement error of pressure (which indirectly also includes temperature instability, which gives $\sim 1/3$ of the whole of error when $(dp/dT) \sim 8 \times 10^5$ Pa K^{-1} which does not exceed 0.5 g at 38 kg (calculated at 1 cm^2) that is better than ∼0.001%. As for the peculiarities of Wagner and colleagues' (pVT)-setup one can find more details in [98, 99].

1.3
Experiments Near the Critical Point in the Presence of the Gravitational Field

In this section we shall discuss the results of precise (pVT)-experiments, in which the nearest vicinity of the critical point of pure sulfur hexafluoride was studied in detail. The coexistence curve, critical isotherm, isothermal compressibility in the single-phase area, and the (pT)-dependence along the critical isochore were investigated [87–92, 126–128]. All the experimental material was concentrated in narrow temperature ($-0.3\,\mathrm{K} < T - T_c < 1.3\,\mathrm{K}$) and density ($|\Delta\rho^*| \le 0.15$) intervals. The main result of this research, apart from the high accuracy experimental data themselves, was, as we have already said, in obtaining three static critical indices (β, γ, and δ) under conditions of the same experiment on the same experimental setup. It became clear that in the studied vicinity of the critical point there are own ‘‘far’’ and ‘‘near’’ regions. In the far region, all the critical indices have values close to Ising, whereas in the ‘‘near’’ one the indices again become typical for mean-field behavior. In the works [87–91] such a behavior was for the first time related to the strong specific influence of gravitation. Such an unusual, for its time, interpretation has still not become generally accepted up to now, which makes it necessary for us, even if briefly, to recall the main facts.

1.3.1
The Gravitational Effect

As for the experiment, the effect of the gravitational field, as has already been mentioned, on critical phenomena was first noted and described surprisingly accurately and comprehensively more than 100 years ago by Gouy [28]. He was the first to describe the density distribution of matter along the height of the vessel in the presence of gravitation under conditions of extremely high compressibility near the critical point. Noting the necessity of having a very high degree of temperature stability, he wrote: "changes by several thousands of a degree per hour completely impede observations which only become satisfactory if the changes do not exceed 0.0001°" ([28], quoted from [31], p. 334). Gouy was actually the first to connect the presence of a flat top of the coexistence curve near the critical point with the gravitational effect and noted the necessity of stirring in order to achieve equilibrium, which otherwise would not happen "even after one week had passed." Despite the brevity of Gouy's remarks it is possible to get quite a good idea of how well his experiment was carried out and the high degree of his own observational skills and intuition even though the experiment was performed in the 19th century.

A brilliant continuation of Gouy's work was carried out in the mid-1950s by a group of Canadian researchers [32–34] who studied the coexistence curve on a (pVT)-setup with visual observation and stirring. This analysis was the first quantitative study of the effect of gravity on the shape of this curve in the vicinity of the critical point. In this paper, they managed to achieve a record, for that time, measurement accuracy; temperature was determined with an accuracy of $\pm 0.001\,^\circ$C, critical density with $\pm 0.2\%$, and pressure with $\pm 0.01\%$. Technically the research was also faultlessly designed. The gravitational effect on the shape of the curve in big (190 mm) and small (12 mm) vessels was studied. This was in fact a test of Mayer's theory [134], which it did not hold up and so ceased to exist. Today the Mayer theory, according to which the coexistence curve has a flat top even without the gravitation effect, has been almost forgotten.

Leaving aside the already familiar discussion about gravitation as the reason for the coexistence curve's flat top let us look at the clear, but up to now, nobody noted asymmetry of the gravity field effect on the different branches of this curve. The effect of the field on the liquid branch stops being noticeable, i.e., both curves close up, when $|\tau| = 1.38 \times 10^{-3}$, while the merging of the gas branches only happens when significantly removed from the critical point by $|\tau| = 4.8 \times 10^{-3}$ (see Fig. 1.3). While looking at the form of the critical isotherm [88, 90, 91] (see Chapter 2) we will see that the behavior of its "gas" and "liquid" branches is analogous to the case considered. We do not know the reason for such peculiarity.

When discussing the gravitational effect we must not forget to mention the influence stirring has on it. Many years after Gouy, D. Cannell from the University of California studied this problem and came to the fundamentally important conclusion [135] that stirring, which removes the density gradients caused by

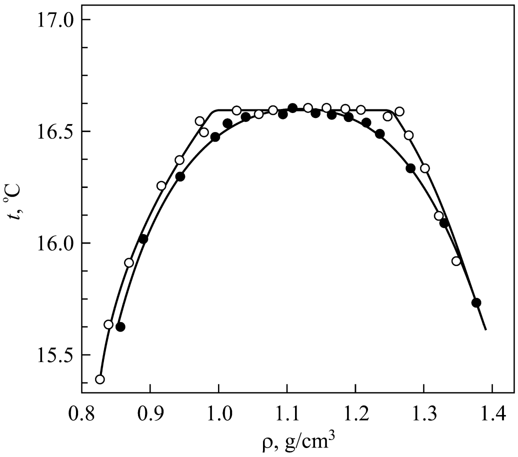

Figure 1.3 The coexistence curve of Xe in vessels of big (19 cm) and small (1.2 cm) height [32].

gravitation, does not affect the critical properties of the studied matter. It should be added that the experiments discussed [98, 99] were carried out without stirring and led to exactly the same results as in the experiments with stirring [84, 87, 88, 91, 92]. The only difference was that it took several hours to achieve equilibrium in the first case while it only took a few minutes when stirring took place. It should also be mentioned that stirring can help to get rid of the consequences of the ''primitive'' gravitational effect only, which consists in the redistribution of density along the vessel height, and apparently does not affect the manifestation of the intrinsic gravitational effect which modifies the nature of the phase transition (for more see the second paragraph in Chapter 2 and [181–183]). We believe that this is the reason why our results coincide with those of Wagner and colleagues independently of the presence or absence of stirring. Therefore, when discussing the gravity influence on a measurement of a property in the nearest vicinity of the critical point, we will mean only the intrinsic gravitational effect.

1.3.2
The Coexistence Curve

The equation for the determination of the coexistence curve, according to extended scaling (see, e.g., [63, 104]), is

$$\Delta\rho^* \equiv \frac{\rho_{\text{liq}} - \rho_{\text{vap}}}{2\rho_c} = B_0(-\tau)^{\beta}\left(1 + B_1\,|\tau|^{\Delta} + \cdots\right). \tag{1.4}$$

Here, ρ_{liq} and ρ_{vap} are the orthobaric densities of the coexisting liquid and vapor, respectively; ρ_c is the critical density; B_0, B_1, and β are the critical amplitudes and critical exponent of the coexistence curve; and Δ is the so-called Wegner exponent, a universal correction of the main asymptotic term [63]. Calculation using the ε-expansion gives $\Delta \approx 0.5$ (more precisely 0.493, see, e.g., [103]). Other possible representations of a coexistence curve look like

$$\left.\begin{aligned} \Delta\rho_{+}^{*} &\equiv \frac{\rho_{\text{liq}}-\rho_c}{\rho_c} = B_{0+}(-\tau)^{\beta_+} \\ \Delta\rho_{-}^{*} &\equiv \frac{\rho_c-\rho_{\text{vap}}}{\rho_c} = B_{0-}(-\tau)^{\beta_-} \end{aligned}\right\}, \tag{1.5}$$

where B_{0+} (β_+) and B_{0-} (β_-) are the critical amplitudes (critical exponents) of the liquid ($\rho > \rho_c$) and vapor ($\rho < \rho_c$) branches of the coexistence curve, respectively. On the coexistence curve, $\tau < 0$ holds.

Note that Eq. (1.4) is of more traditional nature. It implies that the critical behavior of real systems coincides with an idealized model behavior for which the equality $\beta = \beta_+ = \beta_-$ is characteristic. The two other representations given by Eq. (1.5) are useful, because they allow one to reveal the possible asymmetry of the upper part of the coexistence curve, which is manifested in the inequality between the critical exponents β_+ and β_-.

The coexistence curve is fairly simple to study as it is not necessary to measure the most ''labor intensive'' parameter, pressure. Density is measured by optical or dielectric methods using the Lorentz–Lorenz or Clausius–Mossotti formulas. A large number of papers have been dedicated to research on this curve (see, e.g., [39, 40, 49, 65, 66]). However, the results of these studies cannot be easily used for our purposes as they were not carried out very near to the critical point. In the case of optical measurements this restriction is caused by the need to avoid considering multiple scattering when working in the region of developed critical opalescence, where the laser beam deviates from rectilinear propagation and then completely disappears, totally scattering in the cell filled with matter (see Chapters 5 and 6 for more details).

Dielectric experiments have their own difficulties. For example, the authors of the carefully carried out investigation [136] had to ignore all experimental points, located in the region $|\tau| < 4 \times 10^{-4}$, in their analysis because, as they said, of the distorting effect of gravitation. At the same time, as the papers [87, 89, 91] showed, the peculiarities in the coexistence curve's behavior caused by gravitation begin only (!) when $|\tau| \leq 10^{-5}$. The natural desire to reduce the gravitational effect in dielectric experiments makes it necessary to use even thinner condensers where the effect of surface forces can be fully compared to the effect of gravitation (see, e.g., [137]). To our opinion, it is the surface forces, but not gravitational ones, in capacitors with a very small gap (0.076 mm [136]) that are the real reason for the observed effects in this paper in the region $|\tau| < 4 \times 10^{-4}$.

It should also be mentioned that both optical and dielectric methods are indirect and their applicability in such complex conditions is not very obvious. It is well known that to apply the Lorentz–Lorenz formula one must adequately account for local field effects, which is not very simple to do (see Chapter 7 for more). This problem was especially studied in [138, 139] in which Beysens et al. concluded that this formula could not be applied near the critical point. The Clausius–Mossotti approximation suffers from the same inadequacies as the Lorentz–Lorenz formula as they are practically two different formulations of the same idea. Thus, by attempting to apply these dependences in order to study critical phenomena, the researcher finds himself in a kind of closed circle. This is because the main peculiarity of these formulas is that they are very approximate everywhere [140], especially in the vicinity of the critical point. If the critical point is excluded from the study then, as experience shows, both methods lead to very reasonable results [40].

In contrast, precise (pVT)-experiments with visual observation and stirring are free of all the listed shortcomings and, to our opinion, are perfectly suitable for studying static properties near the critical point. However, there is a very widespread opposite view that the (pVT)-method is limited by the gravitational effect (see, e.g., [40]) which disturbs the experiment in the immediate vicinity of the critical point, deforms the shape of the curve, distorts the critical indices etc., and stops them being "true."

Actually, if one accepts an alternative point of view, stating that the critical indices are not distorted by gravitation but obtained in its presence and, consequently, are true for these circumstances, then the situation is cardinally changed. This approach also gives us a way of looking deeper into the nature of critical phenomena [2, 141, 142]. All known experimental material shows that the presence of an additional factor such as the weak influence of the gravitational field (in small vessels) really makes it possible to reveal new features of critical behavior (concerning the effect of the weak magnetic field on phase transitions near the Curie point; see, for example, Chapter 4 in [143]).

In (pVT)-experiments [87,91] more than 60 experimental points on the coexistence curve of pure SF_6 in the range $\Delta T = 0.2$ K below T_c were registered (Figs. 1.4 and 1.5). Moreover, the top of the curve was studied in detail. The points, closest to the critical state, are only 0.0001 K apart from it, while, in the interval $\Delta T = 0.003$ K, 10 values were obtained on the "liquid" branch and 11 on the "gas" branch (Fig. 1.6). In fact, this interval is 15 times larger than the error in temperature measurements.

One can see the considerable asymmetry of the curve's top. It is also found that the critical density value ($\rho_c = 0.73883\,\mathrm{g\,cm^{-3}}$), obtained by visual observation, significantly differs from the value $\rho'_c = 0.7416\,\mathrm{g\,cm^{-3}}$, arrived at using the "rectilinear diameter" rule. All the data and figures presented hereinafter reflect the results of a reanalysis [141] of experimental data [87, 89, 91]. Modern computer analysis techniques made it possible to bring in correspondence calculation accuracy with volume measurements precision. Previously, the determined ρ'_c-value was $\rho'_c = 0.742\,\mathrm{g\,cm^{-3}}$ [91]. The mentioned difference, as already discussed, is 0.4%, which is 20 times higher than the error of volume measurements. In our opinion, there is nothing very surprising about this difference as the critical density determination was practically reduced to the measurement of the coexistence curve part closest to the critical point [87, 91], as was suggested in [84]. Thus, the asymmetry of the whole upper part of the coexistence curve finds its the natural reflection in the critical density shift. The reasons for this asymmetry, as was already noted, can be attributed to gravitation.

The coexistence curve is shown in Fig. 1.7 in a wider temperature range $\Delta T \geq 0.03$ K, together with its diameter which, starting from $\Delta T = 0.01$ K ($\tau \sim 3 \times 10^{-5}$),

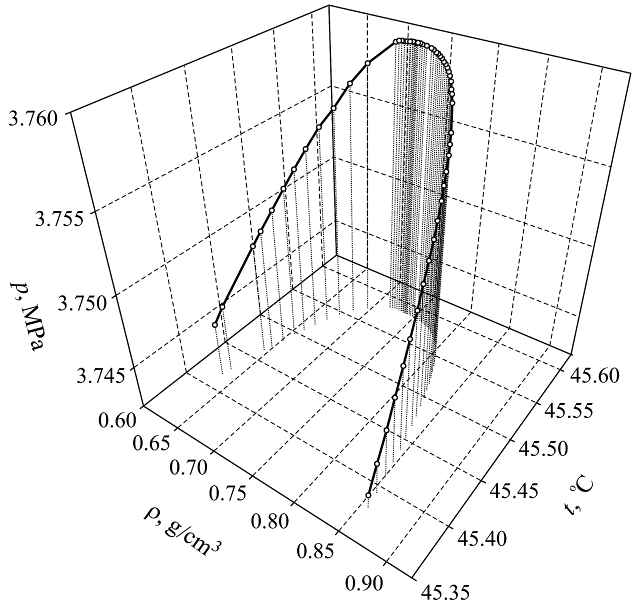

Figure 1.4 Three-dimensional representation of the coexistence curve of SF_6. The domain of variability of state parameters is $(T_c - T) \approx 0.2\,\text{K}$, $p_c - p = 17\,\text{kPa}$, $\Delta\rho^* = \pm 0.15$ [141]. The plots are drawn using data from [87, 91].

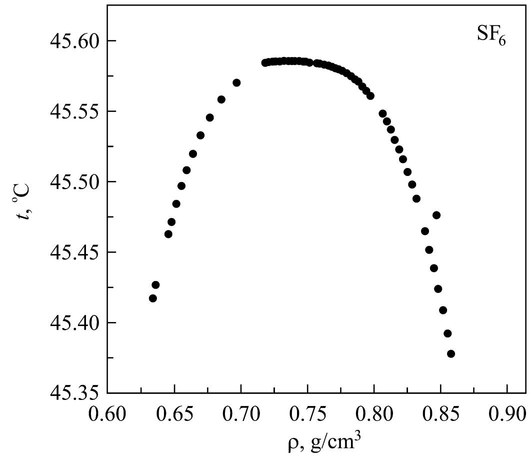

Figure 1.5 The coexistence curve of SF_6 [87, 91].

becomes curvilinear [87, 89, 91]. Such behavior in pure liquids was simultaneously and independently found on SF_6 [87, 144]. In [87], it was observed using direct (pVT)-measurements, and in [144] by analyzing the temperature dependence of the dielectric constant. These results not only aroused a wide discussion at the time, but also led to a great number of additional experiments dedicated to this

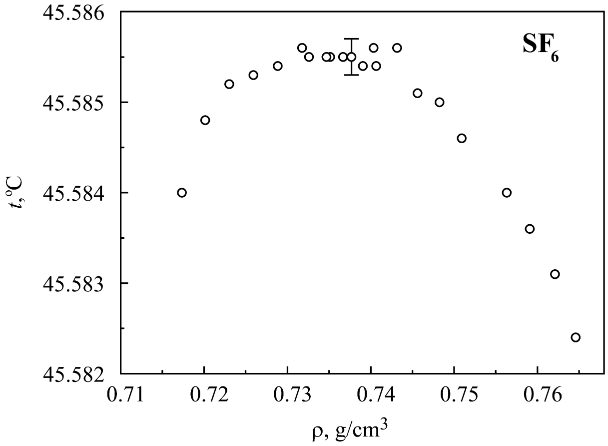

Figure 1.6 The top of the coexistence curve of SF_6 in the temperature range $(T_c - T) = 0.003$ K. The size of the vertical line corresponds to the temperature measurement error $\pm 2 \times 10^{-4}$ K [87, 91].

problem (see, e.g., [98, 121, 125, 129, 131, 145–151]). It should be said that during all these researches the existence of a singular diameter in nonconducting liquids was not experimentally confirmed, and moreover, no single reason for its possible appearance was proposed.

In Fig. 1.8, the data for the coexistence curve for pure SF_6 (see Figs. 1.4 and 1.5) are shown in the log–log scale. As all values of $\Delta\rho^*$ (see Eq. (1.5)) for this graph were calculated using as critical density the values ρ_c', determined by the rectilinear diameter rule, the fact that the experimental points corresponding to both branches

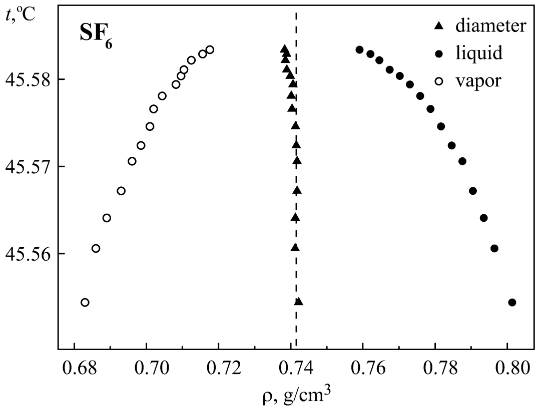

Figure 1.7 The top of the coexistence curve of SF_6 in the temperature range $(T_c - T) = 0.03$ K together with its "curvilinear diameter". For $(T_c - T) > 0.01$ K, $\rho_d = \rho_c' = 0.7416$ [87, 91].

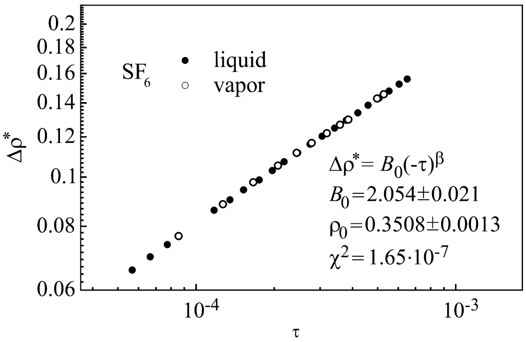

Figure 1.8 The coexistence curve of SF_6. The symmetry of the behavior of both branches of the curve in the interval $5 \times 10^{-5} < |\tau| < 7 \times 10^{-4}$ [141]. The curves are plotted using data from [87, 91].

of the coexistence curve form in the region $|\tau| > 3 \times 10^{-5}$ a common line definitely indicates that this rule is well fulfilled in this temperature range.

Figure 1.9 demonstrates the accuracy of the approximation of both branches of the coexistence curve in the interval $3 \times 10^{-5} < |\tau| < 7 \times 10^{-4}$ by simple scaling dependences (Eq. (1.5)) with $B_{0+} = B_{0-} = 2.054 \pm 0.021$ and $\beta_+ = \beta_- = 0.3508 \pm 0.0013$ [141]. It should be mentioned that these refined values agree wonderfully with the results of the "pre-computer era" coexistence curve analysis $B_0 = 2.05 \pm 0.01$ and $\beta = 0.350 \pm 0.006$ [89, 91, 126, 128]. Note again that Eq. (1.5) describes each branch of the coexistence curve separately in contrast to the more usual equation (1.4). From Fig. 1.9 it follows that in the "far" part of the mentioned temperature range errors are random and do not exceed 0.02–0.03%, while in the "near" part there can be observed small deviations (~0.06–0.07%) but systematic ones. As analysis showed, the addition of extra terms (such as a dependence like Eq. (1.4)) does not lead to a better description of the experimental data. A very detailed analysis of this problem was especially carried out in [153]; it was dedicated to the analysis of xenon. It was shown that the obtained coexistence curve data could be well described by the simplest one-term equation with a common index $\beta = 0.356$ for the whole temperature interval $2 \times 10^{-5} < |\tau| < 3 \times 10^{-2}$ studied. Moreover, applying in this case Eq. (1.4) in its full form could not, as well as for SF_6, improve this description. This result clearly shows that it is not necessary to apply the extended scaling for such small temperature intervals (see also [125]).

At the same time it is clear (Fig. 1.9) that the character of deviations near the critical point ($|\tau| > 3 \times 10^{-5}$) is such that they could probably be avoided by using the same small correction, adding it to the values on the liquid branch of the coexistence curve and subtracting it from the gas branch values. Opposite correction signs, here and in the area of strong asymmetry of the coexistence curve ($|\tau| < 10^{-5}$), can, in our opinion, be explained by the influence (naturally, weaker) of the gravitational effect. It is clear from the diagram that for SF_6 (vessel height 8 mm) the gravitational effect on the coexistence curve disappears completely,

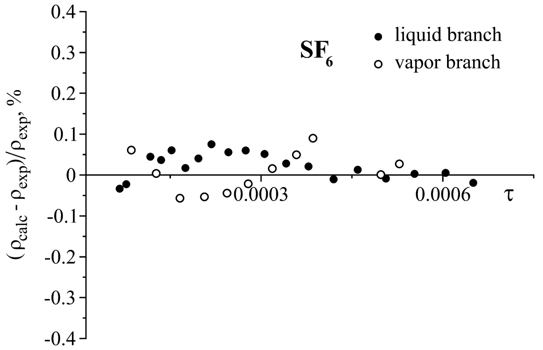

Figure 1.9 Coexistence curve of SF_6: reduced deviations of calculated density values (Eq. (1.5)) from experimental ones [141]. The curves are plotted using data from [87, 91].

beginning from $|\tau| > 4 \times 10^{-5}$. Considering the results for the different heights of the vessels used in two other papers [32, 98], where the gravitational effect was also found, this value agrees well with the ''old'' data [32] as well as with the ''new'' results [98].

1.3.3
Singularity of the Diameter of the Coexistence Curve

More than 100 years ago, Cailletet and Mathias experimentally established the so-called rectilinear diameter rule for the coexistence curve

$$\rho_d \equiv \frac{\rho_{\text{liq}} + \rho_{\text{vap}}}{2\rho_c} = 1 + A_1|\tau| + \cdots. \tag{1.6}$$

This rule remained correct even when the precision of the experiment and the degree of approach to the critical point already made it possible to find nonclassical values of the critical index β (see, for example, reviews of experimental work performed in the mid-1970s [39, 49], where the singular diameter problem did not even arise, or the papers of the same time, where this problem was especially looked at and it was shown that the experimental data for all substances, investigated by that time, agreed well within the margins of error with the rectilinear diameter rule). According to our data, this rule is well satisfied right up to $|\tau| \geq 3 \times 10^{-5}$ (see Figs. 1.7 and 1.8). In [98], which devoted particular attention to this problem, deviations from the rectilinear diameter rule were not found and it was used to determine the critical density.

There also appeared theoretical papers at the beginning of the 1970s, which suggested the possibility of incomplete symmetry between liquid and its vapor (particle–hole systems in terms of the lattice model) and consequently this rule was violated (see, e.g., [119, 120, 155, 156]). The singularity is not actually observed on the diameter itself but on its first derivative. It should be mentioned that these papers were only dealing with theoretical models. As a result, ''singular'' term was added to Eq. (1.6):

$$\rho_d^* \equiv \frac{\rho_{\text{liq}} + \rho_{\text{vap}}}{2\rho_c} = 1 + A_0|\tau|^{1-\alpha} + A_1|\tau| + \cdots, \tag{1.7}$$

where α is the critical index of isochoric heat capacity.

Application of the RG-representation to explain this problem in those cases, when the critical behavior of liquids was initially modeled with the addition of an asymmetrical term to the ϕ^4-Hamiltonian [149,150], really led to the appearance of a nonanalyticity like Eq. (1.7). In other cases, a rectilinear diameter was obtained [157]. In [121–124], which further developed this theme, the singular diameter arose by taking into account not only double interactions but also triple ones. It seems that for the first time this approach was applied in [121] as an immediate reaction to the results of our research [87]. Without going into details, it is worth mentioning one important circumstance: the gravitational effect was not taken into consideration in any of these theoretical investigations.

As for the paper [144] where, according to its authors, the singular diameter was first found on the coexistence curve of SF_6, we shall add just one remark. Despite the wide resonance this paper arose in that time (see, in particular [148–150, 158], the deviation of the diameter from rectilinearity (see Fig. 1.10) was found in this work so far from the critical point ($\Delta T = 0.3\,^\circ$C), where nobody before or since has observed such effects (see, e.g., [87, 98, 99, 151] and Figs. 1.6–1.8). In this connection, the detailed investigation [151] deserves special attention, since here the same substance (SF_6) was studied using the same dielectric method as in [144], but with greater precision (it is enough to mention that the thermostatting stability in this paper was $\sim 20\,\mu$K (!), against ~ 0.001 K in [144]). No deviations from rectilinearity were found and, according to the authors [151], the gravitational effect began to have a strong influence on the coexistence curve only in the range $|\tau| < 1 \times 10^{-4}$. It should be mentioned that with a height of the measuring cell (capacitor) of 0.5 mm it is impossible here as well as in [136] to completely exclude the influence of the surface tension forces. However, neither in [144] nor in any later work, including the masterly analysis carried out in [148] in order to prove that in [144] it was the singular diameter that was observed, the gravitation as a possible reason for the observed deviations was not even considered. Moreover,

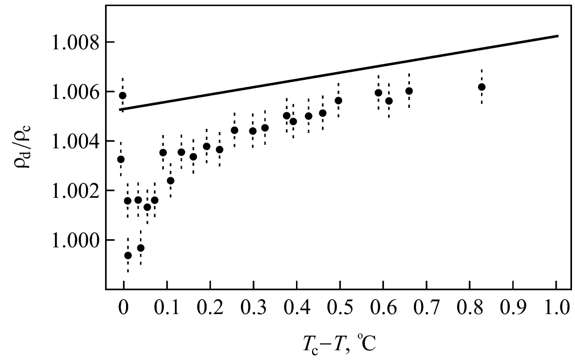

Figure 1.10 Behavior of the coexistence curve diameter for SF_6 [144].

the results of our paper [87], despite the suggested explanation related just to gravitation, were considered by other authors as direct experimental evidence of the diameter singularity of the coexistence curve (see, e.g., [121, 125]). Now, however, after the appearance of the papers [98, 99], there can be no doubt in our mind that gravitation is a cause of curve coexistence asymmetry. Without denying the existence of the diameter singularity for corresponding theoretical models [119, 120, 155, 156], we shall present below (see Chapter 2) a possible alternative explanation for the coexistence curve asymmetry, not for a model system but for a real liquid, where the gravitational field will be given the main role [87, 89, 91] (see Fig. 2.4).

1.3.4
The Critical Isotherm

Out of all the lines, which are usually investigated when looking at critical phenomena, the critical isotherm is of particular importance due to its most complex and labor-intensive experimental study. An indirect confirmation of this could be the fact that in vast reviews [39, 40] it was not practically discussed, while the coexistence curve had a separate paragraph dedicated to it and susceptibility (compressibility) a large table. This is a reflection of real difficulties, which arise when investigating the critical isotherm, whose direct (pVT)-measurements are extremely rare [88, 98, 159].

The most detailed critical isotherm of SF_6 [88] (~140 experimental points in the range of density change, $\Delta\rho^* = \pm 0.2$) is shown in Fig. 1.11. In the two other cited works on the critical isotherm of SF_6 [98] and Xe [159], about 25–30 experimental points were obtained. Figure 1.12 shows only a part of this isotherm immediately

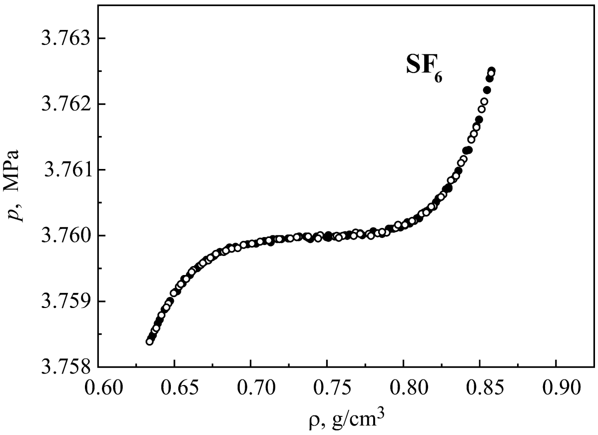

Figure 1.11 Critical isotherm of SF_6. The measurements were carried out at increasing (•) and decreasing (○) volume [88]. The absence of hysteresis shows that experimental data are obtained for equilibrium.

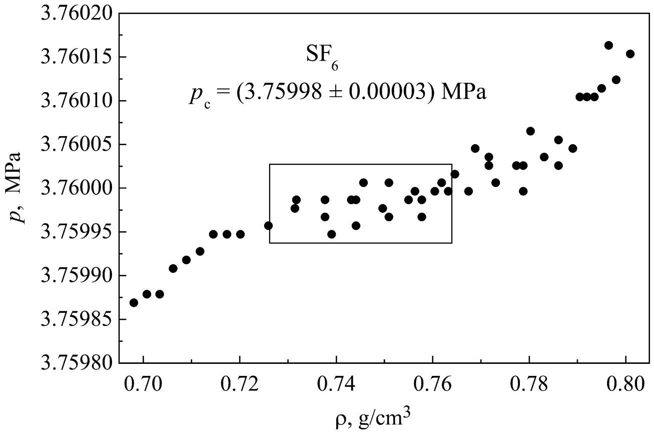

Figure 1.12 The horizontal part of the critical isotherm around the critical point: new analysis [141] of experimental data given in [88].

close to the critical point. Here, apart from the horizontal part, both the precision of the pressure measurement and thermostatting stability are clearly seen. The presence of a horizontal part of the isotherm and the flattening of the upper part of the coexistence curve are consequences of the gravitational effect [32, 115]. From the data it can be seen that its width on the critical isotherm (∼±2%) is wider than that on the coexistence curve (∼±1%). In our opinion this can be easily explained, as the "moving away" from the critical point along the coexistence curve takes place simultaneously with two parameters (ρ and T), and for the isotherm only with one parameter (ρ). It is therefore natural that gravitation in the second case is effective in a wider range of density changes than in the first case. The fact that there is a twofold difference in the dimensions of the flat parts on these curves does not seem to be an accidental coincidence and may also point to the gravitational nature of the horizontal part of the isotherm.

The experimental data relating to the critical isotherm [88] were treated in [90, 91, 126, 141] in terms of the similarity hypothesis both in $(\mu - \rho)$- and $(p - \rho)$-representations in accordance with Eqs. (1.8) and (1.10):

$$\Delta\mu^*_{\pm} = D_0 \Delta\rho^*_{\pm} \left|\Delta\rho^*_{\pm}\right|^{\delta-1} \left(1 + D_1^{\pm} \left|\Delta\rho^*_{\pm}\right|^{\Delta\pm/\beta}\right), \tag{1.8}$$

where μ is the chemical potential,

$$\Delta\mu^* \equiv \frac{\rho_c}{p_c}\left[\mu(\rho, T) - \mu(\rho_c, T_c)\right], \tag{1.9}$$

and the signs "+" and "−" refer to the liquid and vapor branches of the critical isotherm, respectively,

$$\Delta p^*_{\pm} = D_0 \Delta\rho^*_{\pm} \left|\Delta\rho^*_{\pm}\right|^{\delta-1} \left(1 + D_1^{\pm} \left|\Delta\rho^*_{\pm}\right|^{\Delta\pm/\beta}\right),$$

$$\Delta p^*_{\pm} \equiv \left(\frac{p_{\pm}}{p_c} - 1\right). \tag{1.10}$$

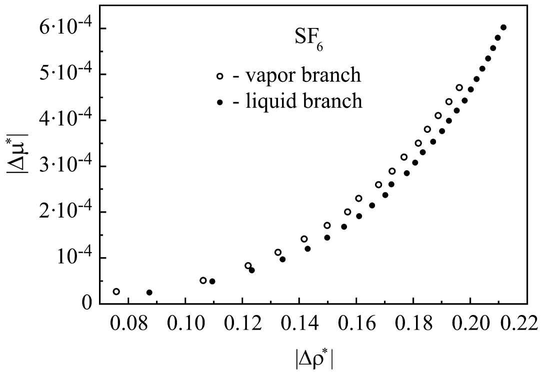

Figure 1.13 Comparative position of both branches of the critical isotherm of SF_6 [88, 90, 91].

From a theoretical point of view, the $(\mu - \rho)$-representation is more adequate as it is suggested that in this case the critical isotherm should be fully antisymmetrical. In experiments, the critical isotherm is measured in more natural $(p - \rho)$-coordinates. Wallace and Meyer, the authors of an extended research of static properties of ^{3}He near the critical point by the dielectric method [161, 162], expressed their surprise after they carried out numerical integration of experimental pressure values on the critical isotherm and were unable to obtain an equality of chemical potential values on its both branches, as was suggested by contemporary theory (see, e.g., [39]). Moreover, it turned out that $|\Delta\mu^*_{\text{gas}}| > |\Delta\mu^*_{\text{liq}}|$. To find this experimental fact requires high sensitivity and precise data, which does not actually happen very often. In the experiment on SF_6 (Fig. 1.13), the same result was obtained [88, 90, 91].

Concerning the discovered deviation from complete antisymmetry of the critical isotherm, the calculated $(\mu - \rho)$-data do not, to our opinion, have enough advantage over the initial $(p - \rho)$-representation. Therefore, the new analysis [141] of the critical isotherm of SF_6 was only carried out with Eq. (1.10). It turned out that just as in the case of the coexistence curve, to obtain the same critical index (δ) and amplitude (D_0) for both branches of the critical isotherm it was necessary to use, instead of the critical density value found by visual observation, the value which was determined by the "rectilinear diameter" rule. This gives an additional evidence of its validity.

The parameters of the main term (D_0 and δ) coincided with those for the $(\mu - \rho)$-representation found previously [90, 91], which are $D_0 = 1.70 \pm 0.01$ and $\delta = 4.30 \pm 0.01$. This result should have been, in principle, expected as the difference in the numerical values of $\Delta\mu^*$ and Δp^*, at worst, does not exceed $0.01\Delta p^*$. Moreover, due to the carried out analysis it was possible not only to fulfill the requirement of the equality $\Delta_+ = \Delta_- = \Delta$ [63], which had been already obtained earlier [90, 91], but also to achieve a quantitative coincidence of the obtained values $\Delta = 0.49 \pm 0.02$ with its RG-value, $\Delta = 0.493$ [103]. Thus, the full set of parameters of Eq. (1.10) for describing the critical isotherm of SF_6 "far" from the critical point

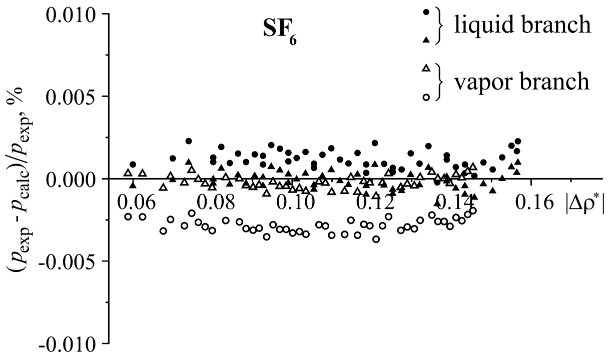

Figure 1.14 Critical isotherm of SF$_6$. The relative deviations of the calculated pressure values (Eq. (1.10)) from experimental ones [88]: $p_c = 3.75998$ MPa for both branches of the critical isotherm (•, ○); $p_c = 3.75988$ MPa for the gas (△) branch and $p_c = 3.76003$ MPa for the liquid (▲) branch [141].

($|\Delta\rho|^* > 0.08$) turned out to be as follows:

$$\begin{aligned}
&D_0 = 1.70 \pm 0.01, \qquad \delta = 4.30 \pm 0.01,\\
&\Delta_+ = \Delta_- = \Delta = 0.49 \pm 0.02,\\
&D_1^+ = 1.40 \pm 0.05, \qquad D_1^- = 0.06 \pm 0.02,\\
&\beta = 0.3508 \pm 0.0013.
\end{aligned} \tag{1.11}$$

The comparison of experimental and calculated, according to Eq. (1.10), taking into account Eq. (1.11), pressure values is presented in Fig. 1.14. Looking at this picture, we can see systematic deviations, although small and within the limits of ±(0.002–0.004)%, especially on the gas branch. We attribute this critical isotherm asymmetry, as well as the coexistence curve asymmetry (see Figs. 1.6 and 1.7), to gravitation. The asymmetry observed in both cases cannot be explained by a real difference between liquid and gas, as any difference between them should be decreased on approaching the critical point. As the analysis in [141] showed, the observed systematic deviations can only be removed by a special choice of the critical pressure. No changes in the critical indices and amplitudes led to the desired result (Fig. 1.14). Just like in the case of the coexistence curve (see Fig. 1.9) it is necessary to add to the measured pressure value (there, density) on the liquid branch and subtract from the gas branch some small correction which gets smaller as the system moves away from the critical point. It is remarkable that if the error in measurement of pressure, including critical, was higher by only two or three times, it was impossible to see the described peculiarities of the critical isotherm. Even in this case the measurement precision would have been better than 0.01% which is much higher than in most of the researches that we are aware of.

Finally, just as with the analysis of the coexistence curve, in the nearest vicinity of the critical point the change in the critical index toward its classical value was observed. The change here was also attributed to gravitation. Analogous results with the same interpretation were also presented in [98] (for a detailed and comparative analysis, see Chapter 2).

1.3.5
Isothermal Compressibility Along the Critical Isochore

This thermodynamic characteristic being a particular case of a more general property, the system susceptibility, plays a rather noticeable role in the physics of critical phenomena as well as in the physics of condensed state as a whole. It has been known since van der Waals that all the phenomena, united by the term ''critical,'' are directly related to singularity of the compressibility. This fact is also reflected in the variety of methods for its experimental determination using the temperature dependences of different quantities like the intensity of scattered light and X-rays, density, dielectric constant, etc. (see, e.g., [39, 40, 49, 65, 66, 125]). As the first and, for a long time, as the only one Habgood and Schneider's work [159] devoted to the thorough and detailed (pVT)-analysis of the critical region of xenon should be considered. The authors did not use their experimental data to find the compressibility critical index γ. This was, however, done subsequently by Kadanoff et al. [48] using the original data from [159] for the determination of the dependence of compressibility on temperature in accordance with Eq. (1.12):

$$p_c K_T \equiv \frac{p_c}{\rho_c}\left(\frac{\partial \rho}{\partial p}\right)_T = \Gamma_0^+ \tau^{-\gamma}. \tag{1.12}$$

The result is shown in Fig. 1.15: ''far'' from the critical point the value of γ was equal to 1.44, which is close to its Ising value, near the critical point $\gamma \sim 1$ holds, which is typical for the mean-field behavior. A similar result was obtained 20 years later on SF_6 [92, 163]. The paper [92] was a direct continuation of the research carried out in [163] and its intention was to extend this research by studying more carefully the nearest vicinity of the critical point. Although the experiment's precision, as described in [163], gave us no reason to doubt the validity of the obtained values of the critical index of compressibility, due to the unusual importance of this problem for critical phenomena further investigation of the temperature dependence of compressibility was carried out in the temperature interval $(0.02 < (T - T_c) < 0.33\,\mathrm{K})$, where in [163] was found $\gamma = 1.00 \pm 0.02$ (Fig. 1.17).

With this aim the same experimental setup as in [163] was used to study 16 isotherms (Fig. 1.16) lying higher than the critical one with an extremely small temperature step ($\sim$0.02 K). On each isotherm $\sim$20 experimental points were obtained within the range of volume changes of ±8% from the critical one with a decrease in the substance's density in the piezometer as well as with its increase. The absence of hysteresis (see Fig. 1.16) shows that the obtained data

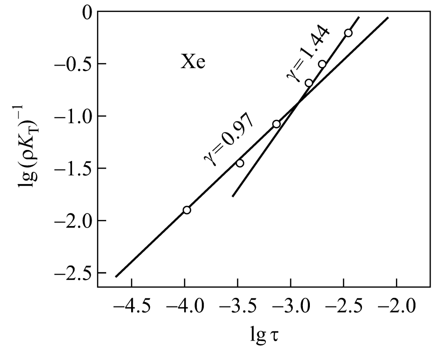

Figure 1.15 Data on the isothermal compressibility of xenon [159] as processed by Kadanoff et al. [48].

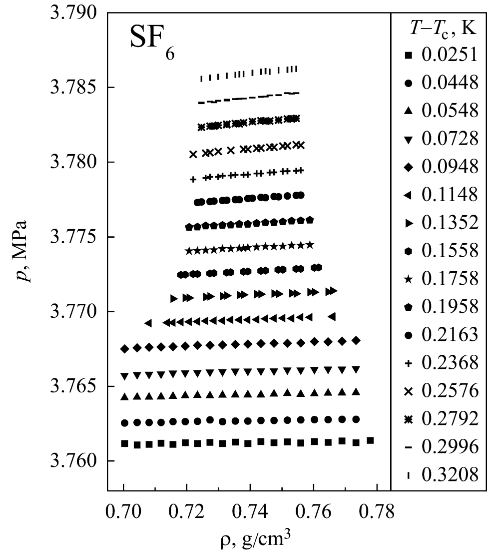

Figure 1.16 Linear sections of the $(p - \rho)$-isotherms in the single phase region of pure SF_6 in the temperature interval $0.02 < (T - T_c) < 0.33$ K [91, 92].

were measured for equilibrium states of the system under consideration. The data analysis carried out in [89, 91] confirmed the result obtained in [163] and showed that there are two regions in the vicinity of the critical point: "far" ($\tau > 10^{-3}$), where the critical index $\gamma = 1.16 \pm 0.03$ turned out to be close to the Ising value $\gamma = 1.24$, and "near" ($\tau < 10^{-3}$), where $\gamma = 0.96 \pm 0.02$ (see Fig. 1.17), which characterizes mean-field behavior. This does not exclude the fact that it should be looked at as a crossover from Ising to mean-field value of the critical index of compressibility.

The results obtained in [89, 91] and in [163] were fully identical, but the principal difference between these works is connected with their interpretation. The authors

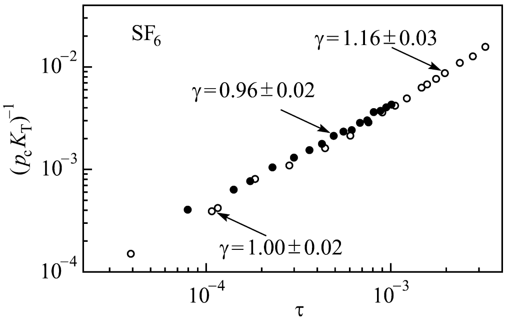

Figure 1.17 Dimensionless inverse isothermal compressibility dependent on the approach to the critical point (● [89, 91], ○ [163]).

of [163] suggested that such behavior was a natural consequence of the classical theory of critical behavior. Another point of view [89, 91] suggests that it is the gravitational effect which leads to a change in the index γ to its classical value in the discussed experiments. In fact, we deal here with that gravitational effect that could not be eliminated by stirring (see, e.g., [135]). It was subsequently called the *intrinsic gravitational effect* [181–183].

Subsequently, in the 1990s Wagner et al. obtained exactly the same result ($\gamma = 0.98 \pm 0.05$ at $\tau < 5 \times 10^{-4}$) and again on SF_6 [98] (it is surprising but historically true that all nontrivial results on the behavior of simple liquids near the critical point were obtained for the first time on SF_6; of course, this statement is true except of the first result, which discovered the critical point itself, where CO_2 was used [7, 8]). Later on, apparently in order to convince themselves of the universality of such behavior, Wagner's group carried out detailed comparative research on the isothermal compressibility behavior of SF_6 and CO_2 in vessels of different heights [99]. In fact, it was a set of the same vessels placed, as in the famous research [32], either horizontally ($h = 11\,\mathrm{mm}$) or vertically ($h = 30\,\mathrm{mm}$). This work showed that the change, in the presence of gravitation, of the compressibility critical index from the one close to the Ising value $\gamma \approx 1.2$ to the mean-field one, $\gamma \approx 1$, took place both for SF_6 and CO_2 (see Figs. 1.18 and 1.19) and, in all probability, represented a universal property of pure nonconducting fluids. Moreover, in this work as well as in [89, 91, 92] it was possible to confidently determine the temperature of transition from one γ value to another. The temperature values obtained in [99] ($\tau \sim 4 \times 10^{-3}$, $h = 11\,\mathrm{mm}$) agree well with those found in [91, 92] ($\tau \sim 1.2 \times 10^{-3}$, $h = 8\,\mathrm{mm}$). It also turned out that the difference, found in [99], in the distance of this transition from the temperature critical point for both heights and both substances (see Figs. 1.18 and 1.19) completely agree with their density difference:

$$\frac{\tau_{CO_2}}{\tau_{SF_6}} \cong \frac{\rho_{CO_2}}{\rho_{SF_6}} \cong \frac{2}{3}. \tag{1.13}$$

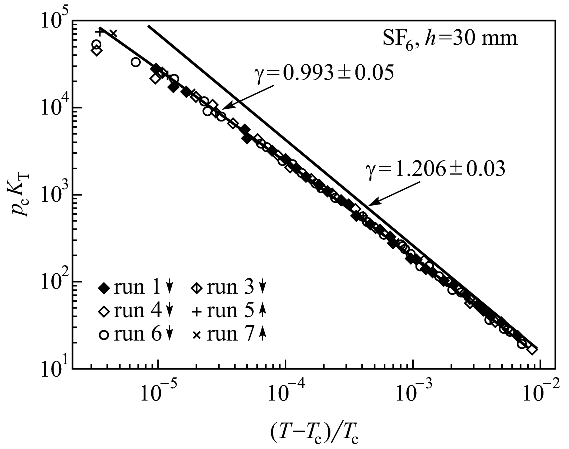

Figure 1.18 Compressibility of SF_6 [99].

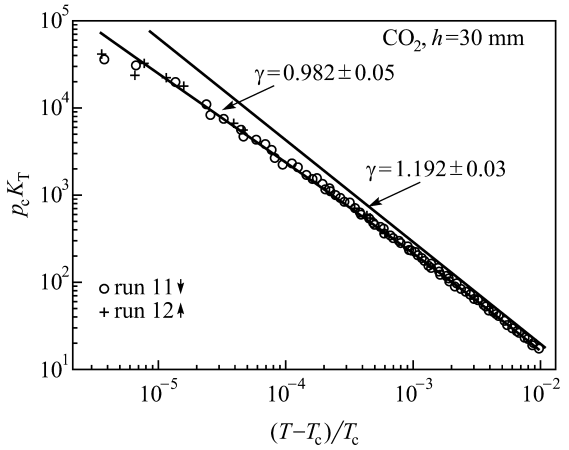

Figure 1.19 Compressibility of CO_2 [99].

It is difficult to disagree with the authors of [99] who suggested that this result is a very weighty argument in favor of the decisive role that gravitation plays in this effect.

Overall, these facts once more clearly show that, under conditions of unlimited growth of the system's compressibility as it approaches the critical point, sooner or later necessarily there will come such a moment when small, in the usual sense, gravitational effects become essential that lead to equally substantial consequences, namely, to the transformation of the fluctuation type of critical behavior to the mean-field, classical one. This effect was observed in [87, 89, 91, 92, 98, 99, 163] when not only compressibility but also all the other investigated thermodynamic characteristics of matter near the critical point were analyzed (see Chapter 2 for more on this).

1.3.6
($p - T$)-Dependence Along the Critical Isochore

For us the ($p - T$)-dependence is noteworthy mainly because its form makes it possible to judge the isochoric heat capacity (c_v)-behavior near the critical point and, therefore, the value of the critical index, α. This possibility is based on Eq. (1.14) which can be easily obtained by double temperature differentiation of Gibbs's thermodynamic potential

$$\frac{\rho c_v}{T} = \left(\frac{\partial^2 p}{\partial T^2}\right)_\rho - \rho \left(\frac{\partial^2 \mu}{\partial T^2}\right)_\rho . \qquad (1.14)$$

It is expected (see, e.g., [26, 40]) that the second temperature derivative of the chemical potential has not a singularity at the critical point, so only $(\partial^2 p/\partial T^2)_{\rho_c}$ is responsible for the heat capacity singularity. Several experimental attempts were undertaken to use this equation for determining the value of the critical index α by experimental ($p - T$)-dependence along the critical isochore [91, 132, 152]. In Kierstead's work [132], the ($p - T$)-dependence along the critical isochore of ^{4}He was analyzed with very high accuracy. Meanwhile, to avoid using double differentiation, the derivative $(\partial p/\partial T)_{\rho_c}$ was directly measured. The ^{4}He studied in this work was high purity grade (99.999%), and its critical parameters were defined independently on the same experimental (pVT)-setup.

The authors of [152] in their extensive (-6 K< ($T - T_c$ < 46 K) research on CO_2 also used the (pVT)-method with an experimental setup like in [159], but without the possibility of visual observations. The accuracy of these measurements was considerably lower than in [132]. Data analysis, carried out in these works, actually led to the same result: $-0.2 \leq \alpha \leq 0.2$ [132] and $0 \leq \alpha \leq 0.15$ [152]. In other words, it turned out that neither of these attempts was, unfortunately, successful.

Our (pVT)-investigation was carried out on pure (99.9995%) SF_6 in [91, 92]. The motivation for research was the following. First, the experimental setup accuracy was significantly higher than that in [152]. Second, as for the negative result obtained for ^{4}He, then it, a quantum liquid, could, in principle, have a special behavior. What is more, if success is achieved, then in the same experiment the full set of critical indices (α, β, γ, and δ), which are needed to describe static critical phenomena, could be simultaneously obtained. In the course of this experiment [91], within a fairly narrow temperature interval near the critical point ($-7 \times 10^{-4} \leq \tau \leq 3 \times 10^{-3}$) ~ 220 experimental points were found (Fig. 1.20). Particular attention was paid to studying the region ± 0.005 K from the critical point. More than 40 pressure values for different temperatures within this range were registered (Fig. 1.21). Ideal linearity of the dependence near zero makes it possible to state that here, just as in [132, 152], $\alpha = 0$.

It would be natural to suggest that, just as for other critical indices, the obtained value of α is a consequence of the gravitational effect. It is known that gravitation distorts the heat capacity anomaly (see, e.g., [40]), which makes it similar to a jump that is typical for classical theory for which $\alpha = 0$. Thus, in the precise (pVT)-experiments described above [87, 89, 91, 92, 98, 99, 163] it was found every

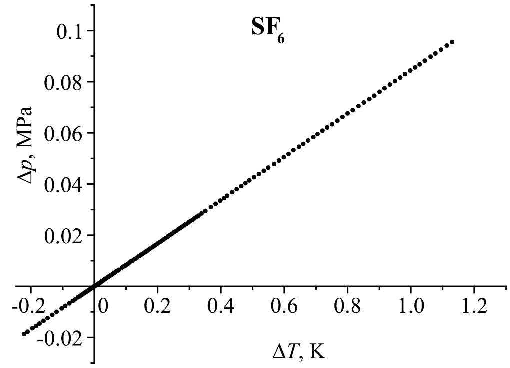

Figure 1.20 $(p-T)$-dependence along the critical isochore of SF$_6$ [91, 126].

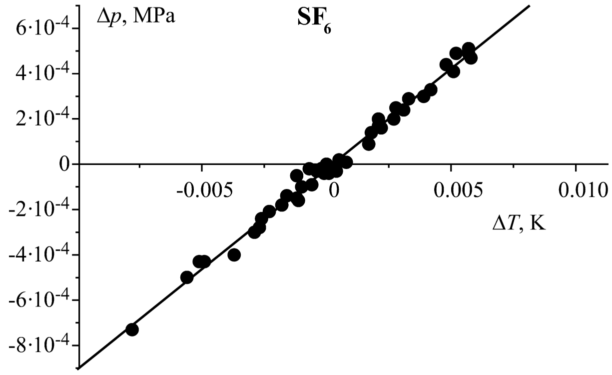

Figure 1.21 The nearest to the critical point part of the $(p-T)$-dependence along the critical isochore of SF$_6$ [91, 126].

time that critical indices took on their "classical" values, beginning with a definite degree of approach to the critical point with respect to temperature (density).

Let us repeat: the compressibility critical index turned out to be equal to $\gamma \approx 1$ for $\tau \le 10^{-3}$, the coexistence curve critical index $\beta \approx 0.5$ for $|\tau| \le 10^{-5}$, while on the critical isotherm $\delta \approx 3$ for $|\Delta\rho|^* < 0.08$. Such a type of behavior was first found in [87, 88, 91, 92], and for the first time explained by the strong specific influence of the Earth's gravitational field on different properties of matter under conditions of unlimited growth in the system's susceptibility. In [89] a nontrivial analogy in the critical behavior of pure liquids and magnets was noted consisting in the tendency of the index β to tend to its classical values common for both systems (see Chapter 2 for more). Also, the idea was put forward, which has only been confirmed in recent years, according to which "near to the phase transition points, independent of interaction details, external factors of different nature can in the same way influence the behavior of similar physical quantities" [89].

The mentioned paper can be considered as the first, maybe heuristic, formulation of this book's central idea: the nearest vicinity of the critical point is, in fact, the region of deformed (suppressed) fluctuations, whose further increase under conditions of unlimited growth in the system's susceptibility is restrained by the action of macroscopic fields of different (depending on the type of system) physical nature. As a result *the nearest vicinity of the critical point is transformed from a fluctuation region, where Ising model results are justified, to a region where classical, mean-field behavior should be once more re-established* [2, 126, 141, 142].

When this idea was first mentioned, just as a logical noncontradictory (at least, according to the author) suggestion [87, 89, 91], it had no other basis. Today the situation has changed significantly. And although everything that has been said above shows that, with rare exceptions, the problem of critical behavior of real systems in the presence of different disturbing factors has still not been definitely solved, recent experimental and theoretical researches, some of which we have already mentioned, add quite weighty arguments in favor of this idea.