Viscosity and Thermal Conductivity of Individual Substances in the Critical Region

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In Memory of
Professor D. I. Rabinovich
Techniques for measuring viscosity and thermal conductivity of individual substances and binary mixtures, which take into account specific features of their behavior in the critical region are briefly discussed. Some aspects of experimental investigations, related to these specific features, are considered. Accuracy of different techniques is estimated.

Measured and calculated exponents for viscosity and thermal conductivity are analyzed in detail. Some causes of divergence between theoretical and experimental results are discussed. The foundations of modern theory of transport phenomena in the vicinity of the liquid–gas critical point and procedures for calculating viscosity and thermal conductivity, based on this theory, are briefly presented. Some recommendations as to the analysis and processing of experimental data on viscosity and thermal conductivity in terms of modern theoretical approaches are given.

The relationship between equilibrium and nonequilibrium properties in the critical region is studied in order to develop reliable self-consistent tables of thermal properties of substances. In Supplement, viscosity and thermal conductivity of a number of commercially important substances in a broad vicinity of the liquid–gas critical point are calculated from the results obtained.

The book is addressed to specialists working in the field of power engineering and chemical technology for processing foodstuff as well as to engineers, students, post-graduates and researchers concerned with investigations of thermophysical properties of gases and liquids in the critical region.

A detailed analysis is given of the major and most frequently used methods and techniques of measuring viscosity and thermal conductivity of individual substances and binary mixtures in view of specific features of measurements in the critical region. The precision of the measuring techniques is estimated. Some topics related to the basic principles of performing and controlling the precision measurements of viscosity and thermal conductivity of supercritical fluids are considered. Technical problems due to the specific nature of thermophysical measurements near the critical point are discussed. The foundations of modern theory of the transfer phenomena near the critical point and methods for calculating viscosity and thermal conductivity are presented in an original form. Some practical recommendations are given as to the analysis and processing of experimental data on viscosity and thermal conductivity on the basis of modern theoretical models. The modern theory of crossover phenomena, extensively used for the description of transport properties of liquids and gases in a large vicinity of the critical point, is given in a form clear to specialists at large. The theory of dynamic "pseudospinodal" scaling is outlined, which is currently used for the description of critical anomalies in viscosity and thermal conductivity of both individual substances and binary mixtures near the liquid–gas and liquid–liquid critical points. The experimental and theoretical estimates of the critical exponents for viscosity and thermal conductivity are analyzed in detail. The causes of some discrepancies between theory and experiment are discussed. Some problems of interrelation between statistic properties (the equation of state) and transport properties (viscosity and thermal conductivity) near the critical point are also considered. In this connection, the problem of agreement between independent thermodynamic and transport properties is of great significance for the development of consistent tables of thermophysical properties of commercially important liquids and gases. For some of these liquids and gases, such as benzene, toluene, ethylbenzene, chlorobenzene, o-xylene, etc., tables of viscosity and thermal conductivity values in a large vicinity of the liquid–gas critical point are given in a form convenient for practical use.
Transport properties (viscosity and thermal conductivity) of individual substances and binary mixtures near the liquid–gas and liquid–liquid critical points are described in the monograph "Viscosity and Thermal Conductivity of Individual Substances in the Critical Region" from the viewpoint of a modern theory of dynamic critical phenomena and experimental techniques.

Rabinovich, V. A.
Abdulagatov, I. M.

Authors


Audience

Specialists in power engineering, chemical technology, oil and gas production and refining, supercritical technologies of food products processing, ecology, and other branches of industry; research workers; post-graduate students and students; and engineers concerned with fundamental research of thermophysical properties of liquids and gases near a critical point.
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This monograph is a continuation of the book 'Thermodynamics of the Critical State of Individual Substances' published by Energoizdat in 1990 and translated into English in 1994. Our original idea was to present the behavior of equilibrium and nonequilibrium properties of individual substances and mixtures in the critical region in a consistent manner in three books. By now, only the second book has been prepared for publication. Its scheme and structure can be inferred from the contents.

Unlike equilibrium properties, the experimental determination of the transport coefficients for liquids and gases encounters some difficulties because of effects caused by deviation of a system from the thermodynamic equilibrium. The transport coefficients in the system are well known to determine the relation between pressure, temperature and concentration gradients and the corresponding flows. The response of the system to the presence of finite gradients is extremely intricate; therefore, in certain cases the experimenter faces a complicated problem of taking into account all of the corrections that strongly affect the precision of measurements.

The pressure gradient, for example, which is bound to be present in investigations of dynamic viscosity, induces secondary flows and energy dissipation in addition to laminar flows of liquids and gases. The temperature gradient usually induces not only thermal conductivity but convection and radiation as well. To take account of these and other side effects, a special technique should be developed for measuring the transport coefficients, which
would minimize the effects that tend to increase as the critical point is approached.

In view of this fact, the first chapter deals with the most widely used techniques for measuring viscosity and thermal conductivity of liquids and gases, taking into account the specific features of their behavior in the critical region. The theoretical foundation for equations used to calculate transport coefficients, based on the results of measurements, is discussed, and possible errors in the final values are estimated for each of the measuring techniques. A list of works is given, which report experimental data on numerous individual substances and binary mixtures near liquid–liquid and liquid–gas critical points.

As experimental data accumulated, a theory of dynamic phenomena near the critical point was being developed. By now, some advances have been made in this field that allow one to calculate transport coefficients in the critical region. However, the accuracy of calculated data depends, to some extent, on the choice of equations and values of dynamic critical exponents. Moreover, an excess 'theoretization' brings about unwarranted difficulties, which can be avoided if a calculation procedure is chosen such as to give reliable final results in a simplest way.

Therefore, problems related to theoretical estimation of critical exponents for viscosity and thermal conductivity are discussed in the second chapter and the estimates are compared with experimental data. An outline of modern theory of transport phenomena near the critical point and procedures of calculating viscosity and thermal conductivity is presented. Some recommendations as to the analysis and processing of experimental data, based on modern theoretical approaches, are given. Special attention is paid to the theories of crossover phenomena and dynamic 'pseudospinodal' scaling, because these theories are competitive for describing anomalous behavior of different substances in the vicinity of the critical point.

An attractive idea of unifying the thermophysics of equilibrium and non-equilibrium phenomena in substances, because they are naturally interconnected, is steadily gaining recognition. This universality is most conspicuous in the behavior of substances as a critical point is approached. It can be hoped, therefore, that a description of this behavior by equations, that connect statistical and dynamic properties of liquids and gases near critical points, would provide further support to the idea and stimulate search for their rational interdependence in the whole region where liquids and gases exist.

The accuracy and self-consistency of equilibrium and nonequilibrium properties is central in developing tables of thermophysical properties. Therefore, in Chapter 3 we briefly present the theoretical principles that establish the connections between the equation of state and transport coefficients. The basic types of parametric equations of state are discussed that can be used in calcu-
lating thermodynamic properties of individual substances near the critical point, the equations following from the crossover theory and 'pseudospinodal' hypothesis included.

Tables of viscosity and thermal conductivity values in the vicinity of the liquid–gas critical point were calculated for some commercially important substances (such as benzene, toluene, ethylbenzene, o-xylene, chlorobenzene, fluorobenzene and carbon dioxide). The reliability of the calculated values is estimated. The results obtained are based on the data from numerous theoretical and experimental works of researchers in this country and abroad. The list of the works is presented.

When working at this book, we kept in mind what Einstein once noted. He said that no scientist thinks in formulas. Before starting calculations, a physicist should have a course of reasoning in his mind, and this, in most cases, can be formulated in simple words. Calculations and formulas are the next step.

Whether we succeeded in following this is for our readers to judge. We ourselves are far from considering the work a complete success lacking shortcomings. Therefore, we would greatly appreciate any comments and proposals, which can be used in our future work.

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January 1995

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Experimental determination of transport properties of liquids and gases involves some difficulties which are not encountered in investigations of their thermodynamic properties. These difficulties are related to some effects that arise when a system is not in the thermodynamic equilibrium. Transport properties of a system are known to determine the relationship between the gradients of thermodynamic variables, such as temperature, pressure, or concentration, and corresponding flows. However, these flows enter hydrodynamic equation which contain nonlinear terms. The response of the system to the presence of finite gradients is so intricate that it is difficult to take these gradients into account in experiments. For example, the temperature gradient usually gives rise not only to thermal conductivity, but to convection and radiation as well. The pressure gradient indices secondary flows and energy dissipation in addition to laminar flow. These difficulties challenge researchers to develop special techniques for measuring transport properties, which would diminish the effects to a minimum.

In this chapter, we present and consider some techniques most frequently
used for measuring viscosity and thermal conductivity of liquids and gases. Theoretical foundations for the equations involved in the determination of viscosity and thermal conductivity are given for each technique. Problem related to estimation of experimental errors, taking account of the specific features of the critical region where transport properties are measured, and applicability of individual techniques for measuring viscosity and thermal conductivity in the region of strong fluctuation are discussed. The data reported on viscosity and thermal conductivity of a great number of individual substances and binary mixtures near the liquid–gas and liquid–liquid critical point are summarized.

1.1 Specific Features of Measuring Thermal Properties Near the Liquid–Gas Critical Point

Experimental thermophysics belongs to classical engineering science. However, experimental and theoretical studies on the critical phenomena belong to one of the actively developing measuring areas of modern physics, because the development of experimental techniques for measuring thermal properties of liquids and gases near the critical point is intimately associated with working out the theoretical aspects of these phenomena.

Measurements of thermal properties near the critical point are characterized by some specific features which cause some difficulties and impose restrictions in performing experiments. These difficulties and restrictions are due to some factors that are to be found in any investigation near the critical point: (1) an exact determination of the parameters of a critical state, especially critical density; (2) the effect of small amounts of impurities upon the critical behavior of a system, i.e. the purity of a sample; (3) the accuracy of temperature determination; (4) the establishment of thermodynamic equilibrium in a system, namely, long times of the system relaxation; and (5) gravity effect on the critical anomalies of a system.

These factors were partially discussed in [1, 2]. Let us consider, in brief, the role of each effect in measurements near the critical point.

To determine critical parameters \((T_c, P_c, \text{ and } \rho_c)\), a system confined within a closed space is usually used. In real situation, the state with a density closed to the critical one can be determined by the weighing method or using an optical criterion, the critical opalescence. The weighing method requires knowledge on an exact value of \(\rho_c\). The values of \(\rho_c\) reported for ordinary liquids differ by about 1% in different works. The weighing procedure gives an error of the same order in the determination of \(\rho_c\) [3]. If a liquid is optically transparent, the appearance of a meniscus, when the liquid is cooled from a supercritical state, can be taken as a criterion in the determination of \(\rho_c\). A meniscus, appearing exactly in the middle of a vessel, corresponds to an
average density equal to \( \rho_c \). An error of this method is usually of the same order as in the weighing method. As a rule, the density of a system deviates from \( \rho_c \) by 2.5% at the phase-transition temperature, thus deviating from \( T_c \) by 0.001 K, i.e. \( T_c - T \equiv 0.001 \) K.

When comparing the results of calculations or of different experimental measurements near the critical point, liquids of high purity are commonly used. Most of the samples for the investigations of critical phenomena are 99.80–99.99% pure. Small amounts of impurities drastically affect critical phenomena. Straub [4] and Hastings et al. [5] studied the effect of small amounts of impurities (less than 1%) on the behavior of a system near the critical point. A theoretical analysis of the effect of random impurities on critical phenomena is given in [6].

The behavior of thermodynamic and transport properties of a system near the critical point is described by asymptotic power laws through the reduced temperature \( t = (T - T_c)/T_c \). An error in the determination of \( t \) results from the uncertainties in measuring relative temperature \( \Delta(T - T_c) \) and absolute critical temperature \( \Delta T_c \)

\[
\left| \frac{\Delta t}{t} \right| = \left| \frac{\Delta(T - T_c)}{T - T_c} \right| + \left| \frac{\Delta T_c}{T_c} \right| \quad (1.1.1)
\]

The last term in the equation does not markedly contributed to \( |\Delta t/t| \). The spread in the absolute values of \( T_c \) reported for known liquids is \( \pm 0.1 \) K. The first term in Equation 1.1.1 brings in some difficulties in the calculations near the critical point, because its denominator becomes very small. The accuracy of a relative-temperature measurement is usually by an order of magnitude higher than that of an absolute-temperature measurement. For example, the temperature 0.01 K measured with a thermocouple corresponds to 0.001 K when measured with a thermistor. Hence, a 10% error in \( |\Delta t/t| \) takes place at the temperature difference \( |T - T_c| = 0.1 \) K. The closer to the critical point, the greater should be the accuracy of a technique for measuring temperature.

The establishment of a thermodynamic equilibrium is required for thermal properties to be measured correctly. This is especially true of liquids near the critical point, where compression diverges greatly because fluctuations in this region become strong and decay slowly owing to small thermal diffusion. Hence, the characteristic relaxation times of a system increase indefinitely and usually reach a thousand of seconds or so. The relaxation times were measured in [4, 7–10] and found to be great, which agrees with theory.

In the presence of a gravitational field, the density of any compressible medium is known to be a function of the sample height \( h \). This dependence is especially strong near the critical point where isothermal compressibility is
subject of divergence. Hence, the density gradient near the critical point in liquids depends on $t$ and $\Delta \rho$. Straub showed [4] that changes in the density of $\text{N}_2\text{O}$ along the critical isochore amount to 15% in a sample 20 mm high. Hence, the gravity can hamper a correct measurement of density-dependent thermophysical properties.

It was assumed in [11, 12] that thermodynamic properties of a liquid at a level $h$ in a sample with density $\rho(h)$ are identical to the properties of a similar uniform system with the corresponding constant density. Because $\xi$ increases near the critical point, the density remains approximately constant up to a height $h \approx \xi$. This limit is usually reached under experimental conditions.

There are some experimental difficulties near the critical point because any measurements average a local density, thus averaging the density dependence of a property measured along the whole height of a sample. This averaging determines the experimental resolution limit. A quantitative analysis of this effect was made in [13], where the accuracy of measuring this thermophysical property was determined for a sample of height $h$ at certain $T$ and $\rho$ near the critical point. In other words, an estimate was made of an experimental error due to gravitation-induced averaging of local properties. The critical state at a reduced gravitation was studied in [14, 15].

Under the conditions of terrestrial gravitation, measurement of thermal conductivity in low-viscous liquids are hampered by convection. At a reduced gravitation, the Rayleigh and Nusselt numbers decrease greatly. An experimental set-up, which allows one to estimate convection, and a technique for measuring thermal conductivity of liquids under microgravity conditions are proposed in [16].

The method of local averaging of thermal properties [13] proved inadequate at distances of $t = 10^{-6}$ from the critical point. At these temperatures, the density gradient becomes very high ($d\rho/dz \to \infty$), and nonlocal effects are substantial. The influence of nonlocal effects on measurements of thermal properties is discussed in [12].

Table 1 lists the basic techniques for measuring thermal conductivity and viscosity of liquids and gases in wide temperature ($T$) and pressure ($P$) ranges, the critical region included. Also presented in the table are averaged measurement errors for each of the techniques, based on the data reported in different works.

1.2 Theoretical Foundations of Experimental Techniques for Measuring Viscosity Near the Critical Point

Techniques frequently used to measure viscosity of liquids and gases are those of (1) capillary flow; (2) oscillating discs; (3) oscillating cups; (4) falling body;
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