

# Thermodynamic and Transport Properties of Supercritical Fluids. Part 2: Review of Transport Properties

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**Abstract**—The experimental foundations and some aspects of the theory and modeling of transport properties (thermal conductivity, viscosity, heat-transfer coefficient) of fluids in the critical and supercritical regions are considered. The theoretical and experimental information on the critical anomaly of thermal conductivity is analyzed in detail. A brief historical reference is given to the first experiments on the thermal conductivity in the critical region, which were carried out mainly by Soviet researchers. The features of measuring the thermal conductivity in the critical region and various interpretations of its critical anomalies are considered. Various approaches to describe the critical anomaly of the transport properties of supercritical fluids, primarily the crossover approach, are discussed. It is shown that the critical anomalies of thermal conductivity, which are described using the mode coupling theory of dynamic critical phenomena, can be represented by a simplified model with two critical amplitudes and one cutoff parameter  $\bar{q}_D$  (the boundary value of the wavenumber), which is characteristic of a particular fluid. A procedure to determine these specific parameters is developed based on the principle of corresponding states. This makes it possible to develop a universal method for describing the critical anomalies of transport properties of supercritical fluids. In a pulse experiment, conditions were found under which anomalies of properties do not manifest themselves.

**Keywords:** thermal conductivity, critical amplitudes, critical point, supercritical fluid, crossover model, heat-transfer coefficient

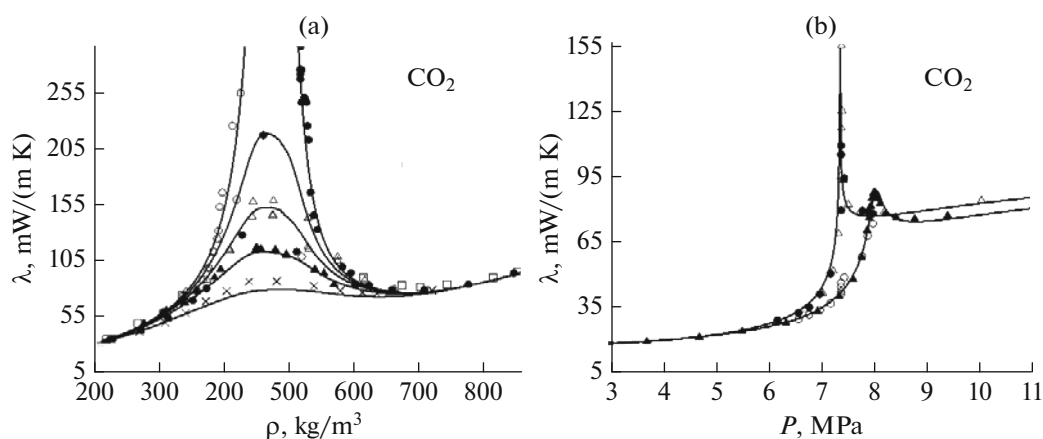
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## INTRODUCTION

In determining thermal conductivity as the typical transfer coefficient, higher standards are demanded of the choice of the experimental conditions and their maintenance during long-term measurements. This is dictated by the procedure of measuring the thermal conductivity of a substance. In this context, the reliability of the results is determined not only by the accuracy of measuring the variables (stationary methods used in the critical region measure the lengths of segments and the potential differences, which are used to determine the temperature difference), but also by the degree of approximation of the experimental conditions to the requirements of the model within which the primary data are converted to the thermal conductivity values. The key requirement in this context is to ensure the immobility of the medium in the measuring volume. Meeting this requirement in the vicinity of the critical point is a challenge, which was noted by most of the researchers (see, e.g., [1, 2] and references there). The search for a way to suppress convection has

been reduced to a tendency of decreasing the characteristic size of the measuring cell and the temperature difference. The highest consistency of matching the experimental conditions with the model requirements was ensured, in our opinion, by Michels and Sengers [3]. Their three articles on the measurement of the thermal conductivity of carbon dioxide [3–5] became classical. It is not improbable that the complete solution of this problem is beyond the responsibility of the experimenter. The fundamental inevitability of the motion of the medium in the vicinity of the critical point was indicated, in particular, by Polezhaev and his colleagues [6]. Their conclusions were based on the results of a sophisticated work done under orbital flight conditions [7].

A natural result of the multiplicity of factors affecting the experimental integrity in the vicinity of the critical point became the multiyear discussion on the presence or absence of the peak of the thermal conductivity in the near supercritical region [2, 8–10]. An intermediate outcome of the discussion was the acceptance of the correction of the tabular standards of the



**Fig. 1.** Measured and calculated values of the thermal conductivity of CO<sub>2</sub> along supercritical isotherms as functions of (a) density and (b) pressure. The points represent the experimental values from the NIST database [35], the continuous curves were calculated by the equation [36] (REFPROP [37]).

transfer coefficients for water and carbon dioxide, primarily, thermal conductivity [11, 12]. Because of the correction, the values of the Prandtl number in the critical region turned out to be significantly (by a factor of two or more) decreased. Thus, the new standard required the revision of the approaches developed by thermophysicists, including Soviet ones (see, e.g., Kurganov et al.'s fundamental work [13]), to evaluate the heat transfer at supercritical pressures in such practically important fields as heat power engineering.

Below, we successively considered data on the thermal conductivity of water, carbon dioxide, ammonia [9, 14–20], and some other substances, as well as data on the heat transfer under natural convection<sup>1</sup> of carbon dioxide and sulfur hexafluoride at sub- and supercritical parameters of a substance [21–24]. Unlike the data on the thermal conductivity of supercritical fluid, the peak of the heat-transfer coefficient in supercritical isobars/isotherms was detected by virtually all researchers. Its existence cannot be doubted and is conventionally related to the phenomena of the increase in the thermal conductivity and the convective mobility of the medium in the vicinity of the critical point considered above. The discussion of the experimental data given below on heat transfer is mainly aimed at determining the possibility of using this phenomenon in practical applications.

#### *Critical Anomalies of the Thermal Conductivity of Molecular Liquids in the Critical Region*

The stationary experiments [4, 8, 9, 16–20, 25–27] and theoretical studies [28–33] demonstrated that the thermal conductivity of liquids significantly increases near their liquid–vapor critical point (Fig. 1). To

<sup>1</sup> The state of the art of studies of the heat transfer under forced convection of a heat-transfer medium at supercritical pressures was analyzed by Kurganov et al. [13].

explain this phenomenon, the experimentally observed thermal conductivity  $\lambda$  is represented as the sum of the anomalous component  $\Delta\lambda_C$  and the background, or regular, part  $\lambda_b$  [34]:

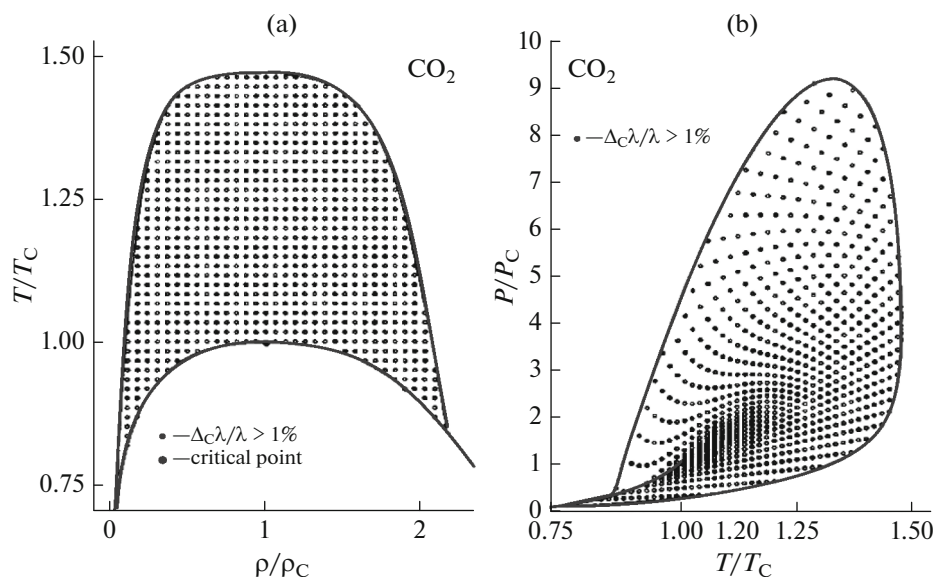
$$\lambda = \Delta\lambda_C + \lambda_b. \quad (1)$$

Here,  $\Delta\lambda_C$  is due to large-scale critical fluctuations, and  $\lambda_b$  is the thermal conductivity and is the value that should be expected in the absence of critical fluctuations.

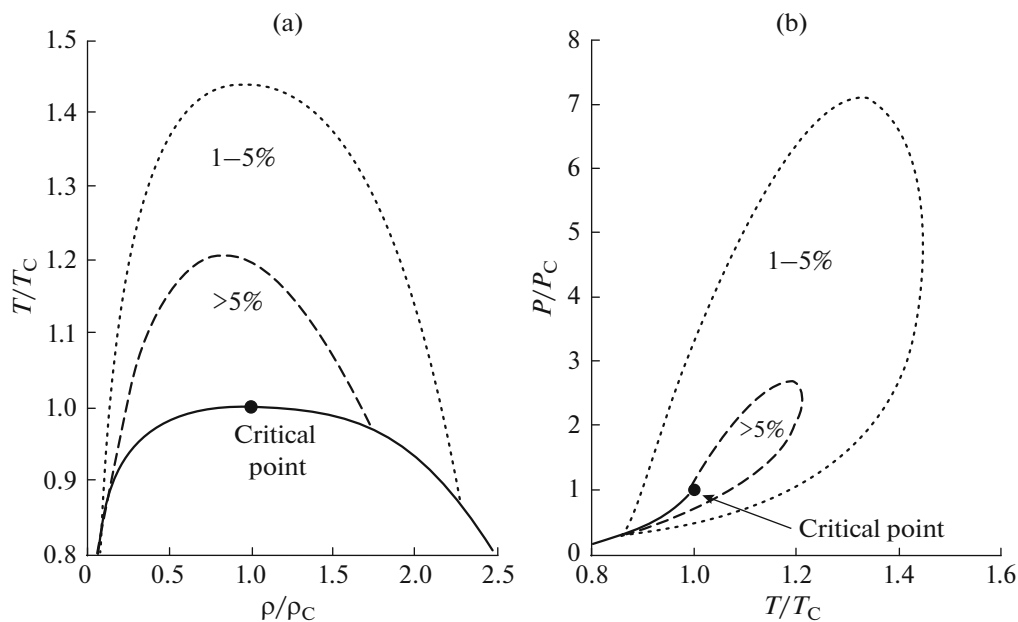
The contribution of the critical part  $\Delta\lambda_C$  of the thermal conductivity is significant over quite a wide range of densities and temperatures in the supercritical region. This phenomenon is illustrated in Figs. 2 and 3, which, as an example, show the ranges of densities, temperatures, and pressures in which the critical increase in the thermal conductivity contributes more than 1% of the actual thermal conductivity for CO<sub>2</sub> [38] and H<sub>2</sub>O [39].

As is seen from Figs. 2 and 3, the critical increase in the thermal conductivity in the supercritical region is significant over a wide range of reduced densities  $0.06 < \rho/\rho_C < 2.27$  and temperatures  $0.81 < T/T_C < 1.44$ . The phenomenon of the critical increase in the thermal conductivity over a wide range of  $T$  and  $P$  in the supercritical region was observed for all pure substances. Consequently, the phenomenon of the critical anomaly of thermal conductivity not only is of scientific interest but also should be taken into account in practical applications of supercritical fluids, e.g., in cycles of electricity generation and cooling, and in supercritical fluid technologies [40].

A theoretical description of the critical anomalies  $\Delta\lambda_C$  of thermal conductivity was performed by a number of researchers [25, 28, 29, 41–46]. The developed methods were applied to generalize the experimental data on the thermal conductivity of various substances in the critical and supercritical regions. Perkins et al.



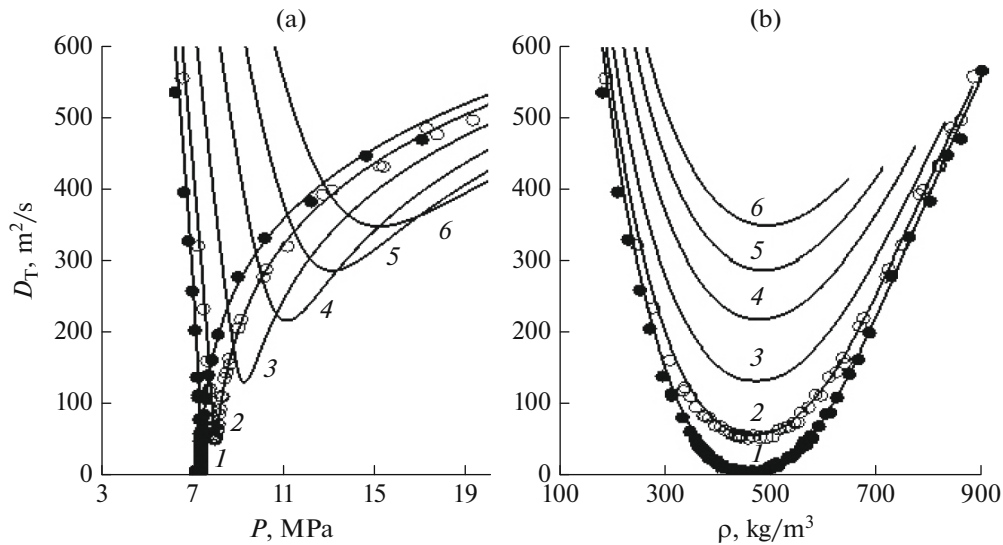
**Fig. 2.** Contribution of the critical anomalies to the thermal conductivity of supercritical carbon dioxide in the ranges of densities  $\rho$ , temperatures  $T$ , and pressures  $P$  reduced to their critical values  $\rho_C$ ,  $T_C$ , and  $P_C$ , respectively, where the contribution of the critical anomalies to the thermal conductivity exceeds 1% of the observed value [38].



**Fig. 3.** Ranges of densities  $\rho$ , temperatures  $T$ , and pressures  $P$  reduced to their critical values  $\rho_C$ ,  $T_C$ , and  $P_C$ , respectively, where the contribution of the critical anomalies to the thermal conductivity exceeds 1 and 5% of the observed value [39].

[41] presented a general procedure to describe the critical anomalies of the thermal conductivity of a large number of molecular liquids for practical applications, including liquids on which only limited experimental information is available. In particular, Perkins et al. [47] considered a simplified solution, which was originally developed by Olchowy and Sengers [28], and relates the critical anomalies of the thermal

conductivity to the thermodynamic properties of the liquid, to the correlation length of long-range critical fluctuations, and to the cutoff parameter  $\bar{q}_D$  (the boundary value of the wave number). This parameter is determined as follows: the wavenumber ranging from 0 to  $\infty$  in the case of critical fluctuations is limited (cut off) by a certain value, which characterizes a specific liquid.



**Fig. 4.** Measured and calculated values of the thermal diffusivity of carbon dioxide along supercritical isotherms as functions of (a) pressure and (b) density. The points represent the experimental values of the thermal diffusivity from the NIST database [35]; the continuous curves were calculated by the equation [36] (REFPROP [37]): (1) 304.45 K, (2) 307.97 K, (3) 315.15 K, (4) 325.15 K, (5) 335.15, (6) 345.15 K.

The rate of decay of critical fluctuations in fluids near the liquid–vapor critical point is determined by their thermal diffusivity  $D = \lambda/\rho C_p$ , where  $\rho$  is the density, and  $C_p$  is the heat capacity at constant pressure. According to the representation of the thermal conductivity as the sum of the critical and regular components (see Eq. (1)), the thermal diffusivity can also be expressed as the sum of the critical contribution  $\Delta D_C = \Delta\lambda_C/\rho C_p$  and the regular contribution  $D_b$  [34]:  $D = \Delta D_C + D_b$ .

At the critical point, both contributions and, hence, the  $D$  value become zero. This phenomenon was called the critical fluctuations slowing down (Fig. 4).

The regular term  $D_b$  is a classical contribution to the critical fluctuation slowing down at which the diffusion coefficient decreases proportionally to  $C_p^{-1}$ :  $D_b = \lambda_b/\rho C_p$ . The shear viscosity can also be written as the sum of the critical component  $\Delta\eta_C$  and the regular component  $\eta_b$  components:

$$\eta = \Delta\eta_C + \eta_b.$$

Unlike the critical increase  $\Delta\lambda_C$  in the thermal conductivity, the critical anomalies of viscosity are weak and are restricted to a narrow temperature range near the critical point [48] (Fig. 5).

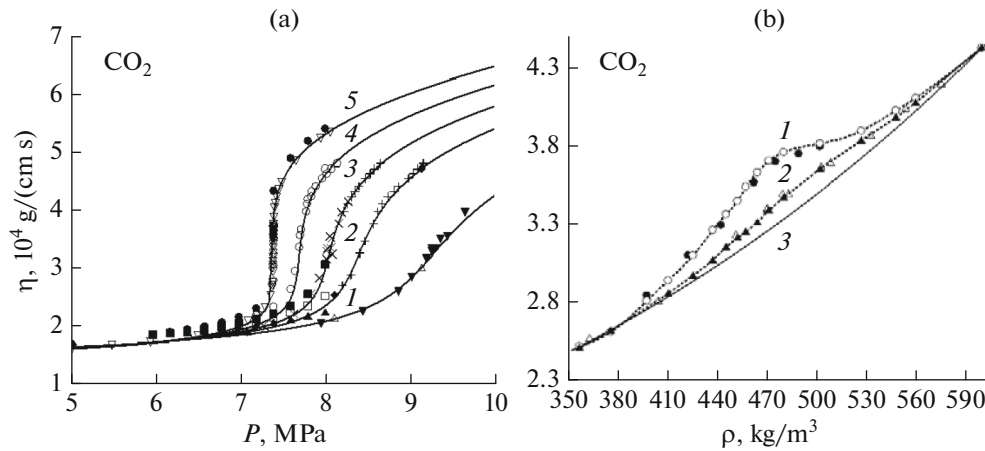
The mode coupling theory of dynamic critical phenomena [30, 31] predicts the behavior of the critical contributions to the thermal diffusivity and the shear viscosity as a system of coupled integral equations:

$$\Delta_C D(q) = \frac{\Delta_C \lambda(q)}{\rho C_p(q)} = \frac{k_B T}{(2\pi)^3 \rho} \int_0^{q_D} d\mathbf{k} \left[ \frac{C_p(|\mathbf{q} - \mathbf{k}|)}{C_p(q)} \right] \times \frac{\sin^2 \theta}{k^2 \eta(k)/\rho + |\mathbf{q} - \mathbf{k}|^2 D(|\mathbf{q} - \mathbf{k}|)}, \quad (2)$$

$$\Delta_C \eta(q) = \frac{1}{2q^2} \frac{k_B T}{(2\pi)^3} \int_0^{q_D} d\mathbf{k} C_p(k) C_p(|\mathbf{q} - \mathbf{k}|) \times \left[ \frac{1}{C_p(k)} - \frac{1}{C_p(|\mathbf{q} - \mathbf{k}|)} \right] \frac{k^2 \sin^2 \theta \sin^2 \phi}{k^2 D(k) + |\mathbf{q} - \mathbf{k}|^2 D(|\mathbf{q} - \mathbf{k}|)}, \quad (3)$$

where  $k_B$  is the Boltzmann constant;  $T$  is temperature; and  $\theta$  and  $\phi$  are the azimuthal and polar angles, respectively, of the wavevector  $\mathbf{k}$  with respect to  $\mathbf{q}$ .

Because of the long-range action of critical fluctuations, it is necessary to take into account the dependence of  $\Delta D_C$  and  $\Delta\eta_C$  on the wavenumber  $q$  of the fluctuations. The integration is taken over all the values of the wavevector  $k = |\mathbf{k}|$  up to the maximum value  $q_D$  corresponding to the scale of the length that divides long-range critical fluctuations, which obeys the mode coupling theory of dynamic critical phenomena, and short-range fluctuations. As we can note,  $D$ ,  $\eta$ , and  $C_p$  depend only on the wavevector of the critical fluctuations. To calculate the critical contributions to the experimentally observed thermal diffusivity, thermal conductivity, and the shear viscosity, it is necessary to solve the system of Eqs. (2) and (3) in the hydrodynamic limit  $q \rightarrow 0$ . As the critical point is asymptotically approached, the expression for  $\Delta D_C$  transforms into the Stokes–Einstein equation:



**Fig. 5.** Measured and calculated values of the viscosity of carbon dioxide along supercritical isotherms. The points represent the experimental values of the viscosity of CO<sub>2</sub> from the NIST database [35]; the continuous curves were calculated by the standard Laesecke–Muzny equation [49] (REFPROP [37]): (a) the dependence on pressure at (1) 315.15 K, (2) 310.15 K, (3) 308.15 K, (4) 306.15 K, and (5) 304.19 K; (b) the dependence on density at (1) 304.25 K, (2) 305.15 K, and (3) 343.15 K.

$$\Delta D_C(q) = \Delta D_C(0) \approx \frac{R_D k_B T}{6\pi\eta\xi}, \quad (4)$$

where  $\xi$  is the correlation length, and  $R_D$  is the universal ratio between the dynamic amplitudes [31, 32]. According to various theoretical estimates,  $R_D$  are within the range from 1.0 [30, 31] to 1.065 [46, 50–52]. In the asymptotic vicinity of the critical point, the viscosity behaves as [53]:

$$\eta = \eta_a(Q\xi)^z, \quad (5)$$

where  $z$  is the universal dynamic critical exponent, and  $Q$  is the system-dependent coefficient.

Asymptotic estimation using Eq. (3) gives  $z = 8/15\pi^2 = 0.054$  [42]. The currently accepted value of the dynamic critical exponent is  $z = 0.068$  [54, 55]. The critical anomalies of viscosity are quite weak; therefore, in practical problems, they can be neglected. Hence, in Eq. (2), the variable  $\eta(k)$  can approximately be replaced by  $\eta \approx \eta_b$ , which is independent of the wavenumber  $k$ . This approximation decouples two integrals of the coupled modes, and Eq. (2) in the limit  $q \rightarrow 0$  reduces to the form

$$\Delta D_C(q) = \frac{\Delta\lambda_C}{\rho C_P} \approx \frac{R_D k_B T}{(2\pi)^3 \eta} \int_0^{\bar{q}_D} d\mathbf{k} \left[ \frac{C_P(k)}{C_P(0)} \right] \times \frac{k^{-2} \sin^2 \theta}{1 + \rho D(k)/\eta}. \quad (6)$$

We introduced the universal dynamic amplitude  $R_D$  in Eq. (6); therefore, Eq. (6) now represents the asymptotic behavior of  $\Delta D_C$  near the critical point. Near the critical point,  $\rho D(k)/\eta$  in the integrand in Eq. (6) becomes very small because the thermal diffusivity becomes zero at the critical point. Far from the critical point, its contribution is positive. Hence,

neglecting this term leads to an overestimation of the integral. Because this term is never large, the overestimation can be compensated by integration to a lower wavenumber  $\bar{q}_D < q_D$ :

$$\Delta D_C(q) = \frac{\Delta\lambda_C}{\rho C_P} \approx \frac{R_D k_B T}{(2\pi)^3 \eta} \int_0^{\bar{q}_D} d\mathbf{k} \left[ \frac{C_P(k)}{C_P(0)} \right] \frac{\sin^2 \theta}{k^2}. \quad (7)$$

Interestingly, Eq. (6) is identical to the simple coupled-mode integral, which was originally considered by Kawasaki [30] and Ferrell [56], except for the presence of the finite upper wavenumber  $\bar{q}_D$ . The preservation of the finite upper limiting number is a significant and necessary condition for obtaining a physically realistic description of the nonasymptotic critical behavior of thermal conductivity. To integrate relation (7), the dependence of the specific heat  $C_P(k)$  on the wavenumber was determined through the isothermal compressibility  $\chi = \rho(\partial\rho/\partial P)_T$  using a well-known thermodynamic relation (see Eq. (16) below) and the Ornstein–Zernike equation. Under some approximations, Olchowy and Sengers [29] represented the critical anomaly of thermal conductivity in the form

$$\Delta\lambda_C = \rho C_P \Delta D_C(q) \approx \frac{\rho C_P R_D k_B T}{6\pi\eta\xi} Y(\bar{q}_D \xi), \quad (8)$$

where  $Y(\bar{q}_D \xi)$  is the crossover function defined as

$$Y(y) = \frac{2}{\pi} \left\{ \left[ (1 - k^{-1}) \arctan(y) + k^{-1} y \right] - \left[ 1 - \exp\left(-\frac{1}{y^{-1} + y^2 \rho_c^2 / 3\rho^2}\right) \right] \right\}, \quad (9)$$

and  $k = C_P/C_V$ .

In the limit  $y = \bar{q}_D \xi \rightarrow \infty$ , Eq. (6) reproduces the asymptotic behavior of  $\Delta\lambda_C$  according to Eq. (4).

The integrals of coupled modes (2) and (3) do not become zero far from the critical point because the coupled modes take into account the so-called contributions of the long tail of the integral to the transport properties far from the critical point, which are contained in the regular part  $\lambda_0$  of thermal conductivity. The second term in Eq. (9) is to subtract this residual contribution to guarantee that the critical thermal conductivity tends to zero in the limit  $y = \bar{q}_D \xi \rightarrow \infty$ , i.e., far from the critical point. Note that the expression for the critical anomaly of thermal conductivity depends on the heat capacities  $C_p$  and  $C_v$ , the shear viscosity  $\eta$ , the correlation length  $\xi$ , and the system-dependent parameter  $\bar{q}_D$ . The asymptotic behavior of these properties near the critical point is governed by the simple scaling power laws

$$\begin{aligned} \bar{C}_v &\approx \bar{A}_0 (\Delta \bar{T})^{-\alpha}, \quad \bar{\chi} \approx \bar{\Gamma}_0 (\Delta \bar{T})^{-\gamma}, \\ \xi &\approx \xi_0 (\Delta \bar{T})^{-\nu}, \quad \Delta \bar{\rho}_{\text{exc}} \approx \pm \bar{B}_0 |\Delta \bar{T}|^\beta, \end{aligned} \quad (10)$$

where the critical amplitudes obey the universal relation  $\frac{\alpha \bar{A}_0 \bar{\Gamma}_0}{\bar{B}_0^2} = 0.058 + 0.001$  predicted by the theory of critical phenomena [61–64] (see also Part 1 of this review [57]). According to the principle of two-factor universality,  $\xi_0 (\alpha \bar{A}_0 N_A \rho_C)^{1/3} = 0.266 \pm 0.003$ . The amplitudes  $\bar{A}_0$  and  $\bar{B}_0$  are directly related to the experimental data on the heat capacity and the coexistence curve (see Eq. (10)).  $\bar{A}_0$  and  $\bar{B}_0$  were previously used as the main information source for developing the empirical dependences of the amplitudes  $A_0$  and  $B_0$  on the acentricity factor [47]:

$$\bar{A}_0 = 5.58 \pm 7.94\omega, \quad \bar{B}_0 = 1.45 \pm 1.21\omega \quad (11)$$

The critical amplitude  $\bar{\Gamma}_0$  can be calculated as  $\bar{\Gamma}_0 = \frac{0.058 \bar{B}_0^2}{\alpha \bar{A}_0}$ . Using the obtained correlation (Eq. (11)) for the critical amplitude  $\bar{A}_0$  of heat capacity, the critical amplitude  $\xi_0$  of correlation length can be estimated at  $\xi_0 = 0.266 \left( \frac{v_C}{\alpha \bar{A}_0} \right)^{1/3}$ , where  $v_C = (N \rho_C)^{-1}$  is the molecular volume at the critical point.  $\xi_0$  is seen to depend on not only  $v_C$  but also the acentricity factor through the critical amplitude  $\bar{A}_0$  of heat capacity.

To describe the critical part of thermal conductivity, it is necessary to estimate the parameter  $\bar{q}_D$  (the boundary value of the wavenumber) in Eq. (8). As was shown previously [47], the dependence of  $\bar{q}_D^{-1}$  on  $v_C^{1/3}$  can be represented as

$$\bar{q}_D^{-1} = -0.0240 + 0.863 v_C^{1/3}, \quad (12)$$

where the values  $\bar{q}_D^{-1}$  and  $v_C^{1/3}$  are expressed in nanometers.

Thus, for practical applications, the critical part  $\Delta \lambda_C$  of thermal conductivity can be represented by expression (8) with the universal parameters  $R_D = 1.02$ ,  $\bar{T}_R = 1.5$ ,  $\nu = 0.630$ , and  $\gamma = 1.239$ . The critical amplitude  $\bar{\Gamma}_0$  of susceptibility can be calculated from the relation  $\bar{\Gamma}_0 = \frac{0.058 \bar{B}_0^2}{\alpha \bar{A}_0}$  with the amplitudes  $\bar{A}_0$  and  $\bar{B}_0$  taken from relations (11) or (12). The amplitude  $\xi_0$  of the correlation length can be calculated as  $\xi_0 = 0.266 \left( \frac{v_C}{\alpha \bar{A}_0} \right)^{1/3}$  using the values of the critical amplitude  $\bar{A}_0$  of the heat capacity from Eq. (11). Finally, the parameter  $\bar{q}_D^{-1}$  is calculated from relation (12).

This procedure describes the critical part of thermal conductivity without using any fitting parameters; in particular, it can be calculated from the fundamental equation of state for the thermodynamic properties, provided that there are equations for the regular parts of viscosity and thermal conductivity. As an example, Figs. 6 and 7 present the results of calculating the thermal conductivity of water and isobutane in the critical region according to this procedure together with the published experimental data [58].

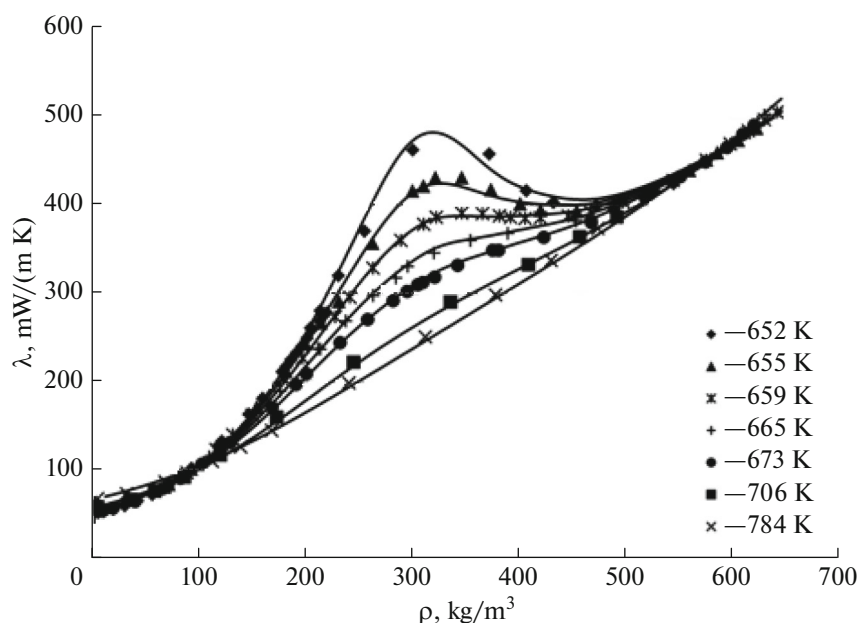
The parameter  $\bar{q}_D^{-1}$  is sensitive to the equation for the regular part of thermal conductivity because it is very difficult to exactly separate the critical part caused by large-scale fluctuations in the critical region. For this reason, the parameter  $\bar{q}_D^{-1}$  is often found by simultaneous optimization of the equations for the critical and regular parts of thermal conductivity. Applying this theory to liquids for which there is sufficient experimental information on the thermal conductivity in the critical region, we can determine the effective value of the parameter  $\bar{q}_D^{-1}$ . However, we propose to use the universal representation of  $\Delta \lambda_C$  and merely derive an equation for the regular component of thermal conductivity. Moreover, in the absence of the experimental data on the thermal conductivity in the critical region, the proposed universal representation gives a realistic estimate of the critical contribution to thermal conductivity, depending on temperature and density.

As relations (4) and (8) show, in the asymptotic region near the critical point, the critical part of thermal conductivity can be written as

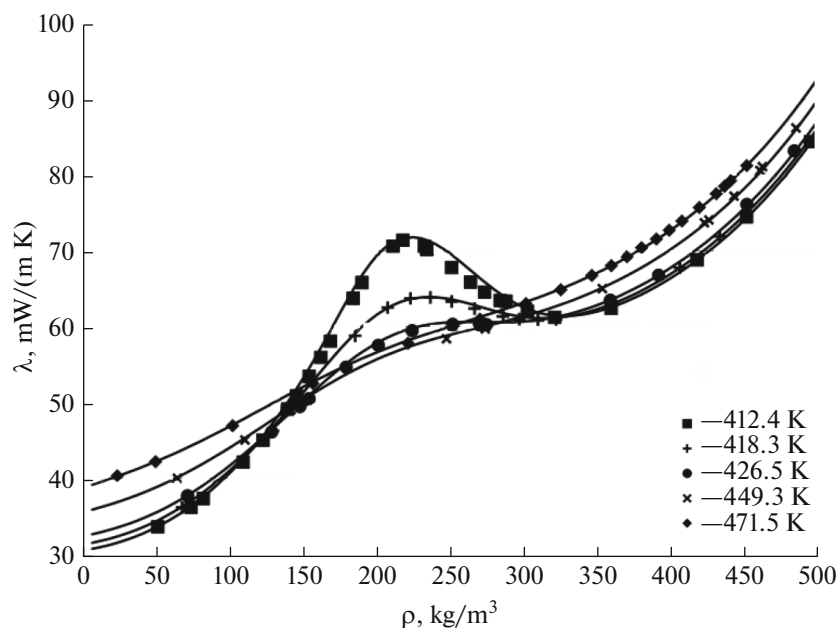
$$\Delta \lambda_C \approx \frac{\rho C_p R_D k_B T}{6\pi \eta \xi}. \quad (13)$$

Similar expressions were proposed by a number of researchers [28, 42–44]. All these equations include the asymptotic limit (13) of the Stokes–Einstein equation but also contain more complete expressions for the crossover function  $Y(\bar{q}_D \xi)$  in Eq. (8). The solution





**Fig. 6.** Thermal conductivity of water in the critical region as a function of density along supercritical isotherms. The points represent the experimental values of the thermal conductivity [58]; the continuous curves were calculated using the universal representation of the critical part  $\Delta\lambda_C$  of thermal conductivity and the equation for the regular component  $\lambda_b$  [39].



**Fig. 7.** Thermal conductivity of isobutane in the critical region as a function of density along supercritical isotherms. The points represent the experimental values of the thermal conductivity [59]; the continuous curves were calculated using the universal representation of the critical part  $\Delta\lambda_C$  of thermal conductivity and the equation for the regular component  $\lambda_b$  [26].

of coupled-mode equations (2) and (3) has the form [28, 42]

$$Y(y) = \frac{2}{\pi}(1 - k^{-1}) \arctan(y) + \dots \quad (14)$$

Consequently, the first correction term to the asymptotic Stokes–Einstein equation coincides with

expression (9). Nonetheless, it contains many additional terms, which were approximated through  $(2/\pi)k^{-1}y$ . Expression (9) for  $Y(\bar{q}_D\xi)$  is a simplified version of the published expression [28, 42]. Kiselev and Kulikov [43, 44] also separated Eq. (2) from Eq. (3), neglecting the dependence of viscosity on the wavenumber.

Mathias et al. [60] proposed a very simple empirical estimate of the critical part of thermal conductivity for practical calculations:

$$\Delta\lambda_C = a \left( \frac{RT}{\rho} \chi \right)^b, \quad (15)$$

where  $a$  and  $b$  are fitting parameters determined from the experimental data on thermal conductivity. According to this approach, as the critical point is asymptotically approached, the critical part  $\Delta\lambda_C$  of thermal conductivity diverges as  $\Delta\lambda_C \propto \chi^b$ . It is of interest to compare the asymptotic behavior  $\Delta\lambda_C \propto \chi^b$  with the prediction of relation (13), which follows from the mode coupling theory of dynamic critical phenomena.  $C_V$  diverges weakly at the critical point,  $C_V \propto (T - T_C)^{-\alpha}$ , and, hence, depends weakly on the wavevector  $k$ . In this case, the  $(\partial P/\partial T)_\rho$  remains finite at the critical point. Therefore, in the Ornstein–Zernike approximation for susceptibility,  $\chi(k) = \chi(0)/(1 + k^2\xi^2)$  [65], as applied to the heat capacity  $C_V$  as a function of the wavevector, we have

$$\begin{aligned} C_p(k) &= C_V(k) + \frac{T}{\rho^3} \left( \frac{\partial P}{\partial T} \right)_\rho^2 \chi(k) \\ &\approx C_V + \frac{T}{\rho^3} \left( \frac{\partial P}{\partial T} \right)_\rho^2 \frac{\chi(0)}{1 + k^2\xi^2}. \end{aligned} \quad (16)$$

Hence, we have  $\rho C_p = \rho C_p(0)$  and diverges as  $\chi$ , whereas the correlation length  $\xi$  according to the equation

$$\begin{aligned} \xi &= \xi_0 (\bar{\Gamma}_0^{-1} \Delta\bar{\chi})^{v/\gamma}, \quad \Delta\bar{\chi} = \bar{\chi}(\bar{T}, \bar{\rho}) - \bar{\chi}(\bar{T}_R, \bar{\rho}), \\ \bar{T}_R &= 1.5-2.5, \end{aligned}$$

diverges as  $\chi^{v/\gamma}$ . Because the viscosity diverges weakly, this divergence can be neglected (by replacing the viscosity by a regular term). Then, from relation (13), we have  $\Delta\lambda_C \propto \chi^{1-v/\gamma}$ . Consequently, the exponent  $b$  in Eq. (15) should be a universal parameter  $b = 1 - v/\gamma = 0.49$  rather than a fitting parameter. The value of this parameter that was calculated by Mathias et al. [60] differs significantly from the universal value.

Thus, we showed that crossover model (8) together with Eq. (9) predicts the behavior of the critical anomaly of the thermal conductivity of supercritical fluids. This approach requires us to know the equation of state for thermodynamic properties and the equation for viscosity. The equation of state should ensure the correct description of the compressibility and capacity heat of fluids in the critical region (typically, they are scaling-type crossover equations). Systematic errors in the compressibility and heat capacity in the equation of state lead to systematic errors in predicting the critical part of thermal conductivity. In this context, in this model, it is not recommended to use a cubic equation of state, such as the Peng–Robinson equation, in the critical region. Moreover, to use this model, it is necessary to know two critical amplitudes ( $\bar{A}_0$  and  $\bar{B}_0$ ),

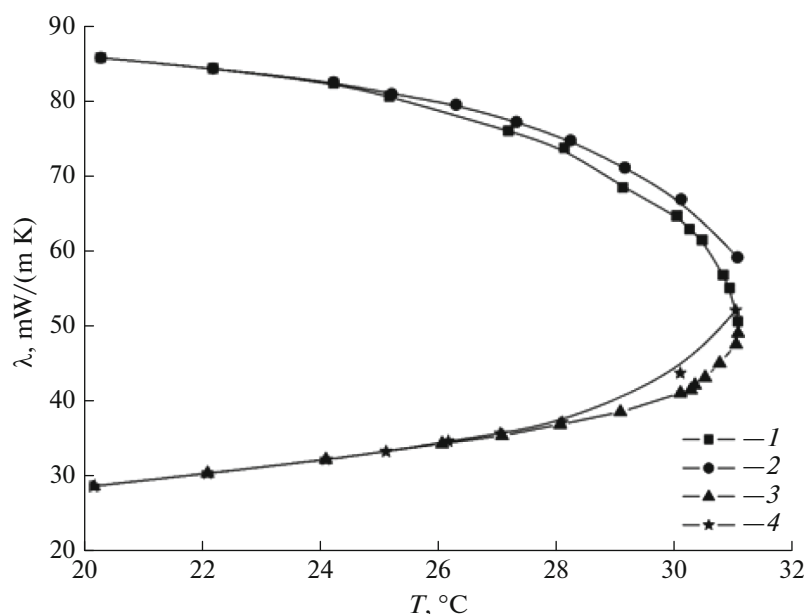
which is characteristic of the liquid, and one boundary value  $\bar{q}_D$  of the wavenumber. In the absence of reliable experimental data on the critical amplitudes, they can be estimated using relation (11). In the presence of reliable experimental data on the thermal conductivity in the critical region, the boundary value of the wavenumber can, in principle, be found by fitting them to the crossover model expressed by Eqs. (8) and (9). However, for practical applications, the  $\bar{q}_D$  value can be sufficiently accurately estimated from Eq. (12). Consequently, the procedure described in this work (see also [47]) can be used to quantitatively describe the critical anomalies of the thermal conductivity of many molecular liquids even in the absence of reliable experimental data on the thermal conductivity in the critical region.

#### EXPERIMENTAL STUDIES OF THE CRITICAL ANOMALIES OF THE THERMAL CONDUCTIVITY OF SUPERCRITICAL FLUIDS: A HISTORICAL REFERENCE

Probably, one of the first studies in which all efforts were made to suppress the effect of convective transfer was performed by Kh.I. Amirkhanov, Corresponding Member of the Academy of Sciences of the USSR, with his colleagues at the Dagestan Branch, Academy of Sciences of the USSR, Makhachkala, Dagestan, USSR [14, 15]. The data on the thermal conductivity of carbon dioxide [14] (and later water [15]) were obtained by two complementary methods, namely, the absolute method of a parallel-plate and the relative method of concentric cylinders. Experimental setups allowed us to vary the characteristic size of the measuring cell (gap width) and the temperature difference and were tested in experiments with substances with known properties. Special attention was given to the purity of carbon dioxide, which was 99.96%. The experiments were carried out along the saturation line and detected no anomalous phenomena: in the critical state, two branches of the thermal conductivity smoothly merged. More precisely, an increase in the heat transfer in the critical region did occur, but only after decreasing the requirements for the suppression of convective transfer. Indeed, whereas at a gap width of 0.3 mm, no dependence of the measured data on  $\Delta T$  was observed, at a gap width of 0.59 mm, an increase in the heat transfer was detected above  $\Delta T \approx 0.2$  K (Fig. 8).

Sirota and other researchers who obtained data on the characteristic  $\lambda$ -shaped curve of the thermal conductivity as a function of the density of a substance along close supercritical isotherms [8, 9, 11], in discussing the smoothness of Amirkhanov's data, indicated the following methodological feature of his experiments. The discussed measurements [14] were made along the saturation line, i.e., at temperatures that were very close to the critical value, but, nonethe-





**Fig. 8.** Thermal conductivity of carbon dioxide along the saturation line; the parameter is  $\Delta T$  at a gap width of 0.59 mm: (1, 3) 0.07–0.15°C and (2, 4) 0.2–0.5°C.

less, somewhat lower. Under such conditions, the phenomenon of excess thermal conductivity might not occur. Moreover, the density in the saturation line changes significantly with a shift in temperature by tenths of a degree, which corresponds to the temperature difference detected in the experiments. In this context, two things are perplexing: first, the width of the range in the supercritical region in which there are critical anomalies of thermal conductivities (Figs. 2 and 3), and second, the impossibility to directly control the density of the substance under the experimental conditions.

A systematic study of the thermal conductivity of water was conducted by Sirota and colleagues at the Dzerzhinsky All-Union Thermal Engineering Institute, Moscow, USSR (see summarizing works [16, 27] and references there). They used the parallel-plate method with an original design of the measuring unit for the purpose of decreasing the distortions of the temperature fields. The nonisothermality at the boundaries of the layer was estimated [9] as the most probable source of convection. To increase the reliability of the results, the design of the setup and the measurement procedure were revised as the data were accumulated. Particular attention was given to checking the isothermality of the lower plate, the angle between the plate and the horizon, the calibration of thermocouples, their readings in the course of the experiment lasting many hours and determining the so-called zero readings of the thermocouples as sources of systematic errors. The gap width was 1.4 mm, but in some sets of experiments in the critical region, it was decreased to 0.4 mm. The sign of the

absence of convection, as before [3], was considered the absence of the dependence of the measurement results on the gap width (from 1.4 to 0.4 mm and taking into account the corresponding change in the correction for radiant heat transfer), and also on the angle between the plates and the horizon (at small angles) [17].

In the supercritical isobars, sharp peaks of the thermal conductivity of water near its critical isochore were detected. The fact of their existence was confirmed by repeated versatile check of the experimental results. The peaks of the thermal conductivity with increasing pressure smoothed more rapidly than the known maximums in the  $C_p$  curves and virtually ceased to be resolved at pressures of about 25 MPa. The lines of the maximums of the thermal conductivity as a function of the calculated density  $\lambda(\rho)$  in isobars and isotherms did not coincide with each other. They also did not coincide with each other in the  $\rho$ – $T$  diagram or with the lines of maximums of the specific heat capacity  $C_p$ , which suggested the absence of a simple correlation between the data on thermal conductivity and heat capacity.

It proved that, in this region of the phase diagram, the discussed results (see Fig. 9 and [58]) differ significantly from the values recommended by the reference books based on the 1964 International Skeleton Steam Table, an international table of thermal conductivity data. This contradiction favored the acceptance of the new standards mentioned above [13]. In discussing the results, the complexity of the dependence of the line of maximums on density was indicated. Note also the scale of the change in the density of a substance in the critical region, the core of the remarks on Amirkha-

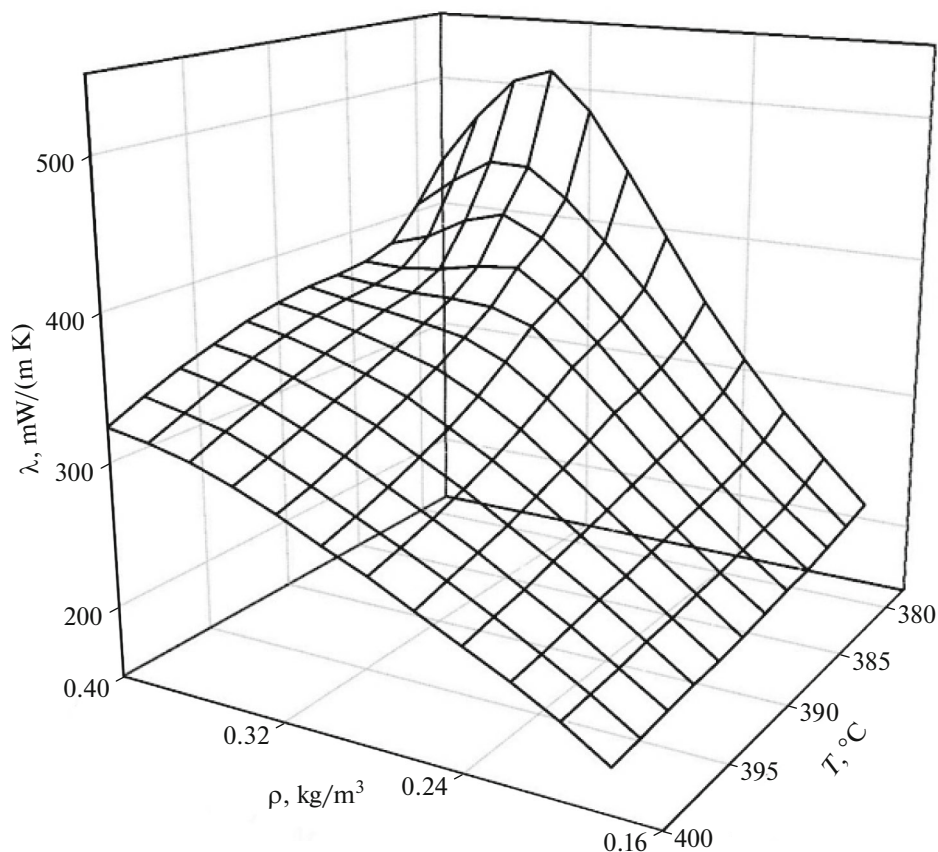


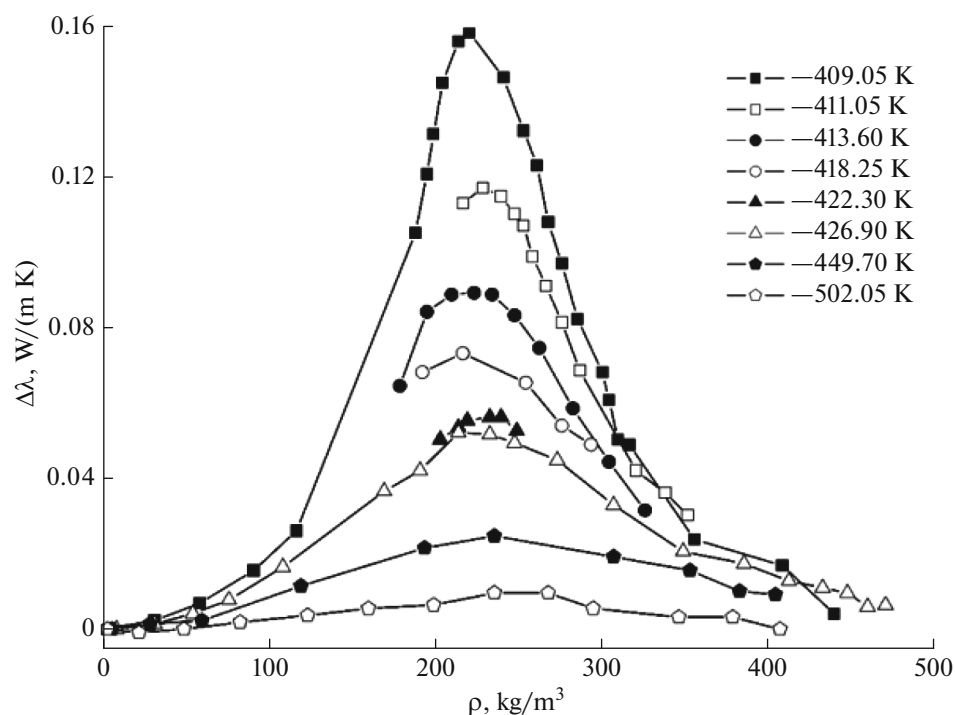
Fig. 9. Thermal conductivity of water along supercritical isotherms as a function of density.

nov's results [14], and the impossibility of the experimental determination of the measuring-cell-section-average density of a substance. In view of all these circumstances, the form of the representation of the results on the thermal conductivity as a function of density, a parameter that is most difficult to determine in the critical region [20], appears to be debatable.

Let us further consider the thermal conductivity of polar substances in the critical region. This problem was studied in detail by Ivanov [20, 67] by the example of ammonia using both the results of the direct measurements of the thermal conductivity [19], and the static light scattering data [68]. Investigation of static light scattering is not accompanied by introducing gradients of whatever physical quantity to the system, which is extremely important in experiments near the critical point. As a result, the combination of the two methods increased the informativeness of the conclusions in comparison with the pioneering works [14–18]. In particular, Ivanov succeeded in obtaining the data on the critical amplitudes and exponents that are necessary to describe the thermal conductivity in the critical region. An assumption was made of the common dynamic critical behavior of polar and nonpolar pure liquids under a noticeable effect of various disturbing factors.

Tufeu et al. [19] performed their studies in 1978–1979 at the Laboratory of Materials Science and High Pressures (Laboratoire d'Ingénierie des Matériaux et des Hautes Pressions, LIMHP), Université Paris 13, Villetaneuse, France. The thermal conductivity was measured by the method of concentric cylinders in stationary mode. The setup on which the measurements were made has received worldwide recognition due to the investigation of the thermal conductivity of many substances at high and superhigh pressures [69, 70]. The gap width between the cylinders was 0.26 mm. The temperature difference between the cylinders decreased at the critical point to 0.15 K. The correction for convection, which was calculated using the properties of ammonia (the purity of the sample was no less than 99.96%) and the measuring cell, was maximum in the isotherm closest to the critical point and did not exceed 2.5%. The behavior of the thermal conductivity of ammonia was explored over a wide range of variables, including along the critical isochore, namely, in the temperature range  $3 \times 10^{-5} \leq \tau \leq 0.18$ , where  $\tau = (T - T_C)/T_C$  and  $T_C = 405.4$  K.

In experiments [20, 71], as previously for water, carbon dioxide, and some other substances [4, 8–12, 72–74], the maximum of the thermal conductivity was detected. In subsequent processing of the results [20,



**Fig. 10.** Dependence of the excess thermal conductivity of ammonia on its density at various temperatures according to the published data [20, 71].

67], attention was paid to the fact that the nonmonotonicity of the curve of the thermal conductivity in the vicinity of the critical isochore occurs quite far from the critical point, actually, as far as one hundred degrees (see Fig. 10, and also Figs. 2 and 3). This result was obtained after eliminating the background part of the thermal conductivity from the experimental data. The determination of specific mechanisms transferring the effect of the critical point to the static and dynamic characteristics of a substance sufficiently far from this point was assigned by Ivanov [67, 71] to the key issues determining the understanding of the nature of critical phenomena.

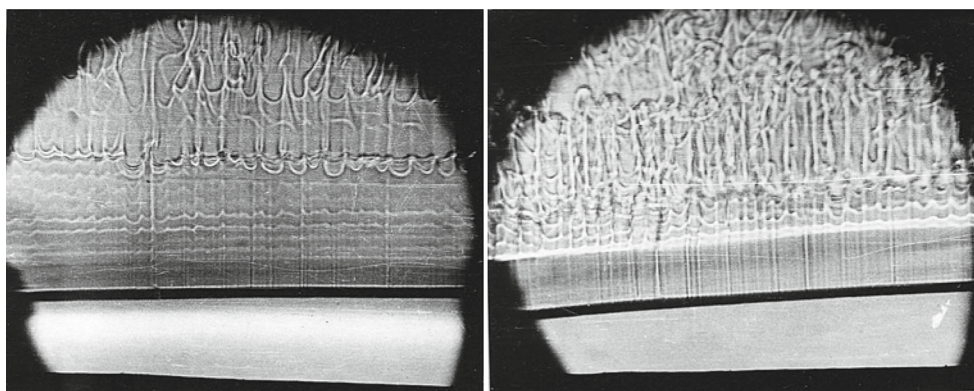
At the same laboratory (LIMHP) by the same method, several studies were made of the thermal conductivity of pure substances in the sub- and supercritical regions of parameters [70], also with the participation of researchers of the Laboratory of Theoretical Foundations of Thermal Engineering, Kazan Chemical Technological Institute, now Kazan National Research Technological University, Kazan, Russia [75]. The thermal conductivity of HFC-134a fluorocarbon [73] and hexane [74] was studied in detail in fairly many isotherms. By analyzing the results, the singular part of the thermal conductivity was separated, its behavior in the critical isochore and noncritical isochores was described, and also the critical exponent of thermal conductivity was estimated. In this context, note two significant issues. First, the determination of the background part of thermal conductivity is diffi-

cult because it requires us to use a large body of experimental data over a wide temperature range of manifestation of excess properties [71, 76]. Second, fluorocarbons are considered as promising supercritical fluid extractants, and the knowledge of their properties over a wide range of variables is important for modeling the relevant technological processes [40].

By and large, the investigation favored the development of the theory of critical phenomena and also showed the possible way to increase the efficiency of heat exchangers. To determine practically important details, it was necessary to allow the convective heat transfer, which is suppressed in the thermal conductivity experiments. The features of the heat transfer in the critical region under natural convection in a substance are discussed below.

#### HEAT-TRANSFER COEFFICIENT IN THE CRITICAL REGION

A pioneering work aimed at measuring the heat-transfer coefficient along isotherms and isobars in the region of continuous supercritical transition and visually observing the free-convection heat transfer was done by Academician V.P. Skripov in the 1960s [21–24]. A variant of the method of thin wire probe heated by direct current was used [77]. The method proved to be sufficiently convenient to use and informative and was developed at the Ural Thermal Physics School [78], in particular, to determine the critical parameters



**Fig. 11.** Convective motion of supercritical carbon dioxide in the isotherm 305.15 K at a pressure of 7.56 MPa over the surface of a probe 100  $\mu\text{m}$  in diameter at a temperature difference of 0.5 K (left) and 6.4 K (right) [84].

of thermally unstable liquids [79, 80] and study the supercritical heat transfer at the scale of short characteristic times and sizes [81–83]. A combination of this method with shadow photography enabled one not only to determine the shape of the curve for the heat-transfer coefficient along supercritical isotherms but also to identify the structure of convective flows in the case of the horizontal (Fig. 11) and vertical positions of the heater [22, 24].

The experiments were carried out under the following conditions. The length of a wire probe—resistance thermometer—was 80 mm. Probes of five thicknesses from 20 to 200  $\mu\text{m}$  in diameter were used. Most of the measurements were performed with a probe 29  $\mu\text{m}$  in diameter. The measuring system of the setup comprised an electric power supply circuit of the probe as a heat source and a potentiometric circuit of the probe as a resistance thermometer. The heating power was chosen so that the temperature difference once the stationary mode was established was about 0.5°C. The primary experimental data (the voltage drops across the probe and a reference resistor) were converted to the probe temperature, the specific heat flux, and the heat-transfer coefficient. The parameter was the pressure in the thermostated cell with temperature  $T > T_C$ . The samples were carbon dioxide and sulfur hexafluoride ( $T_C = 318.71$  K,  $P_C = 3.76$  MPa). The purity of the samples was 99.8 and 99.7%, respectively.

It was found that the heat-transfer coefficient passes through a maximum. This is due to the extremal change in the thermophysical properties, first of all, the heat capacity and the volumetric expansion coefficient in the supercritical region. To the maximum values, a developed fine-structural convection throughout the observable space corresponded (Fig. 11). As in the case of heat capacity, as the critical temperature receded, the height of the maximum decreased, and the peak shifted toward higher pressures (Fig. 12). The convection was localized near the heater.

The detection of the characteristic peaks of the heat capacity, the heat-transfer coefficient, and, under certain assumptions, the thermal conductivity stimulated the exploration of new applications of supercritical phenomena. At the same time, specific features of the supercritical heat transfer manifested themselves in the fact that an increase in the temperature difference at a constant temperature in the cell leads to a decrease in the detected heat-transfer peak (Fig. 13). This was observed at all the diameter values and all the spatial orientations of the probe. Within a phenomenological approach, such a result was explained based on the structure of the free-convection heat-transfer equation in dimensionless variables [21–24, 84]. Finally, the following challenge was identified: low heat fluxes, at which the peak occurs, are not difficult to remove; the problem is the guaranteed removal of high-density heat fluxes [13].

## DISCUSSION

Let us now return to the discussion of the behavior of the thermal conductivity in the critical region. Let us list out some arguments for the existence of the peak:

- the results of sets of careful experiments performed by stationary methods at various laboratories worldwide;

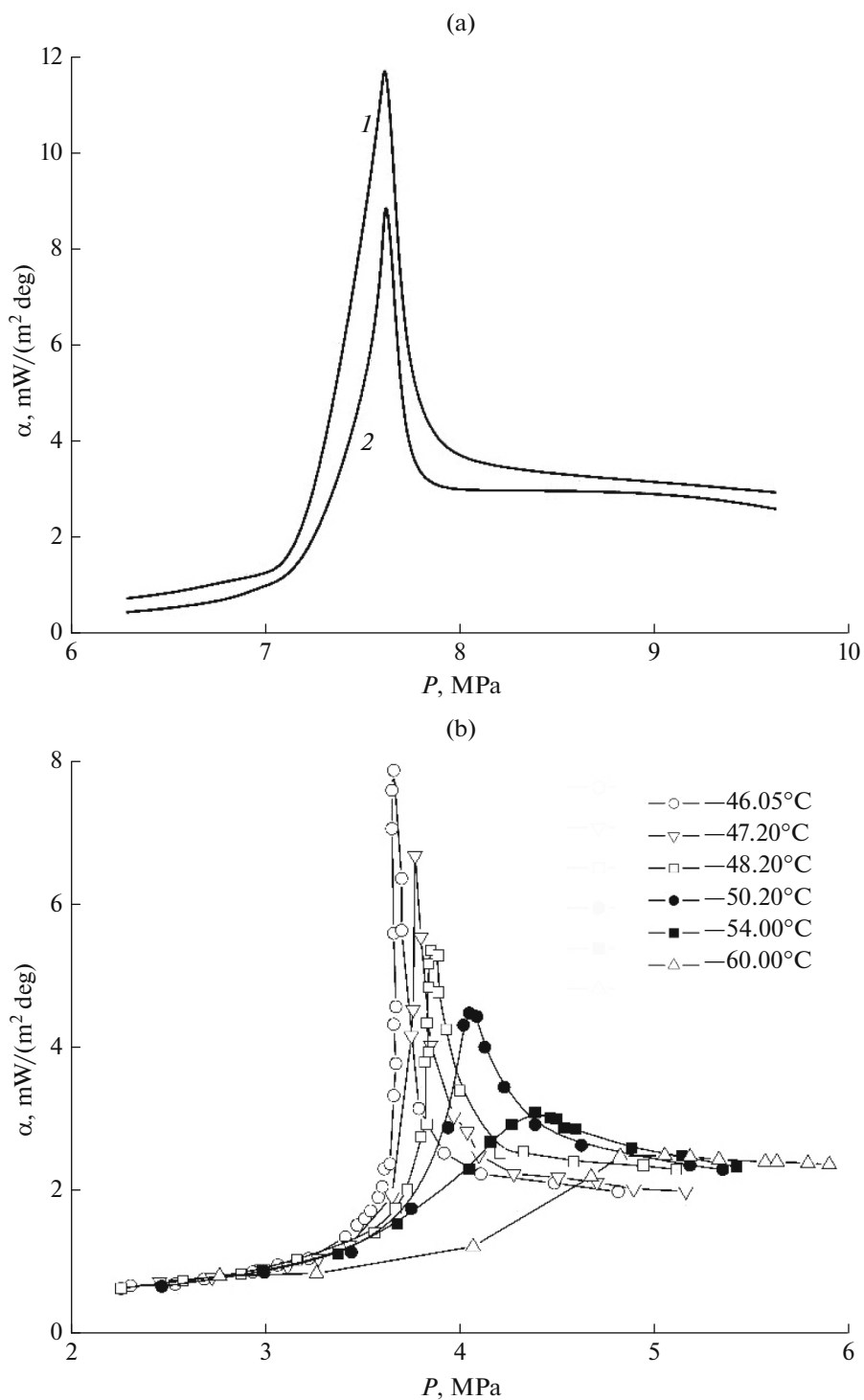
- the consistency of the theory of dynamic critical phenomena [1, 20];

- the indirect support by the results of free-convection heat-transfer experiments in the stationary mode [21–23, 84], which were represented as equations in dimensionless variables.

Let us also present arguments for other options:

- the absence of anomalies of the thermal conductivity in the vicinity of the liquid–liquid critical point of solutions capable of phase separation, which was





**Fig. 12.** Heat-transfer coefficients  $\alpha$  along supercritical isotherms of (a) carbon dioxide at 304.65 K and (b) sulfur hexafluoride at  $\Delta T \approx 0.5$  K. The parameters are the position of the probe with respect to the horizon ((1) horizontal and (2) vertical) and temperature, respectively.

detected using a precision scheme of compensation measurements [85], against the background of the characteristic peak of the specific heat in this vicinity [86];

—the hypothesis of the impossibility of suppression of the convective motion under actual experimental conditions [87];

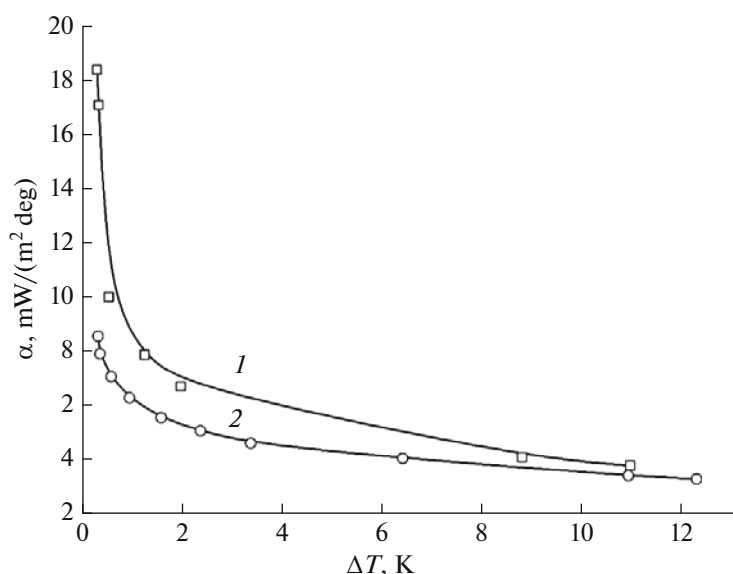


Fig. 13. Heat-transfer coefficients  $\alpha$  along supercritical isotherms of (1) carbon dioxide (cell temperature 307.15 K, pressure 8.0 MPa) and (2) sulfur hexafluoride (319.2 K, 3.86 MPa) as functions of temperature difference.

—the detection of a decrease in the heat-transfer intensity during the rapid transition of a compressed liquid ( $P > P_C$ ,  $T < T_C$ ) to the region of supercritical temperatures along an isobar in conductive heat-transfer experiments during powerful local heat release, which were performed at the scales of short times and sizes (such an approach allowed us to eliminate the effect of convection and gravitation on the results of the experiments).

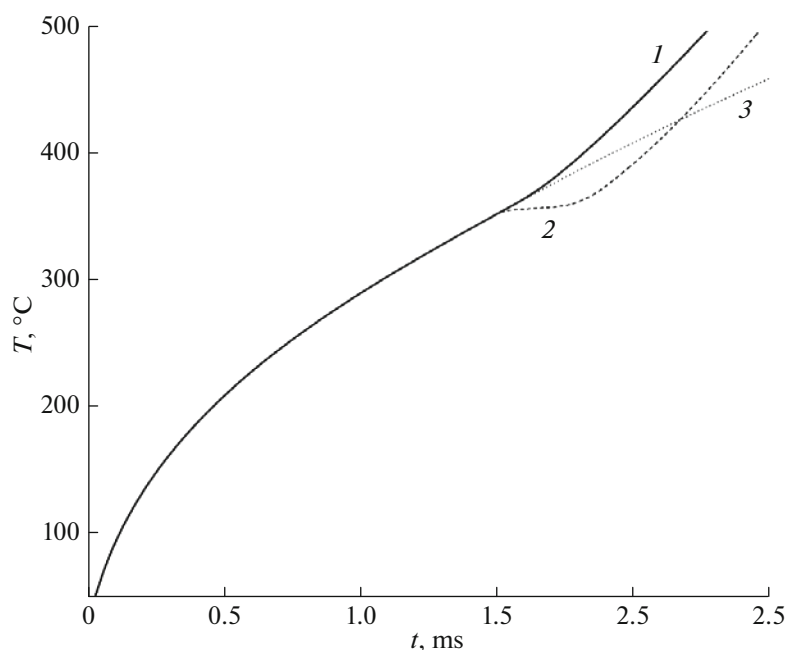
The last phenomenon has a threshold nature in the vicinity of the critical temperature and is observed up to pressures of  $3P/P_C$  for all the studied substances [83, 88] over a wide range of rates of crossing the critical region [89–91]. This result was proposed to be taken into account as a criterion for choosing the working pressure for equipment with a supercritical-pressure heating medium the operating conditions of which do not rule out the possibility of a powerful local heat release [92].

As an example, Fig. 14 presents the results of the pulsed experiment mentioned above. The primary data are the results of measuring the change with time in the voltage drops across the probe and a series “current” resistor [81, 93]. From these data, the integral-average temperature of the probe at each time is calculated. As judged from Fig. 14, the chosen experimental conditions do not feel the contribution made to the heat transfer by the maximum of the thermal conductivity, let alone the maximum of the heat capacity. Conversely, crossing the vicinity of the critical temperature from below gives rise to an additional thermal resistance, whereas crossing it in the opposite direction (Fig. 15) leads to the restoration of the normal heat transfer.

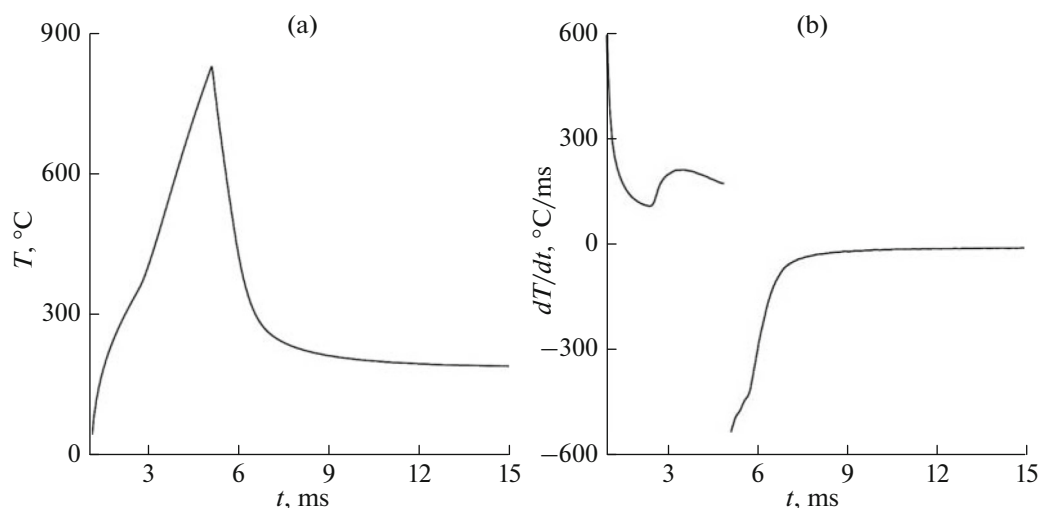
Such behavior of the critical heat transfer does not cancel out the existence of the maximums of thermophysical quantities, which are known from stationary measurements. Rather, it suggests the significant complexity of the phenomenon under discussion and the diversity of its manifestations, depending on specific experimental conditions [90, 91]. It is natural to take into account, first, the remark of the fragility of fluctuations in the presence of gravity, boundaries, gradients, etc. [67, 71]; and second, the Filippov–Kravchun hypothesis [94] of the emergence of additional thermal resistance in the transition from a one- to a two-component system and the results of experiments based on this hypothesis, which were carried out in the more general case of the transition of a homogeneous to an inhomogeneous system [95–98]. It is known (see, e.g., [10, 99–101] and Part 1 of this review [57]) that a supercritical fluid is not a homogeneous medium; consequently, it can exhibit a low intensity of conductive heat transfer as compared to the case of a compressed liquid.

Interestingly, the fact of the propagation of this decrease into the high-pressure range ( $1-3P/P_C$  [88–92]) resonates with Ivanov’s observations [71] discussed above in the context of Fig. 10. Thus, it is logical to assume that, at high heat flux densities, high temperature gradients, and short times of response of the heat-release surface, long-range critical correlations do not form. Hence, the anomalies of the properties [102], which are known from stationary measurements, do not manifest themselves. The possibility to reach a state with a low fluctuation amplitude and, as a consequence, with nonsingular thermodynamic functions in the case of sufficiently rapid propagation into the near-critical region was assumed by Y.B. Zel’dovich





**Fig. 14.** Change in the probe temperature in water (23 MPa, 25°C) while heating the probe by a constant-power pulse into the supercritical temperature range: (1) experiment, (2) calculation from reference data with taking into account the peaks of the thermal conductivity and the heat capacity [82], and (3) the expected shape of the curve if the properties of the substance are constant.



**Fig. 15.** Change in (a) the probe temperature in water and (b) its time derivative in the regions of heating and cooling of the probe. The powers in these regions are 11.8 and 2.3 W, respectively; a supercritical transition is observed at  $t \approx 2.5$  ms in the heating region and at  $t \approx 5.7$  ms in the cooling region.

[103]. He considered a rarefaction shock wave, which was experimentally observed [104] as a convenient tool to study such states of matter. It is important to determine the spatial-temporal scale that is characteristic of the suppression of anomalies, such as the Frenkel line dividing “the solid-like hard liquid and quasi-gaseous fluid” (cited from [105]) according to the physically substantiated sign.

The discussion above showed that the acceptance of the new tabular standards of transfer coefficients of water and carbon dioxide and the development of the universal method to describe critical anomalies of transport properties of supercritical fluids do not put an end to the investigation of the thermal physics of critical and supercritical phenomena. Indeed, “the behavior of matter near ... the liquid–vapor critical point turned out to be much more complex than it was

assumed by van der Waals and Landau" [103]. The literally first change in the scales of time and size of the experimentally system led to a qualitative change in the results. The clarity of the results was ensured by processing the primary experimental results free of model restrictions. The fact of their existence is hardly mentioned in reviews of studies of the heat transfer in supercritical fluids, in particular, the problem of heat transfer weakening [106], which has been debated since 1960s [107]. Nonetheless, the results of nonstationary experiments are expediently taken into account in designing industrial units the working medium in which is a supercritical medium, and the operation of which do not rule out the possibility of a powerful local heat release. Due to the general tendencies toward the intensification of technological processes and the mitigation of their environmental impact, the knowledge of the picture of a nonstationary heat transfer can be required for improving the equipment of nuclear power stations [13] and implementing various supercritical fluid technologies [40, 108].

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#### REFERENCES

1. M. A. Anisimov, *Critical Phenomena in Liquid Crystals* (Nauka, Moscow, 1987) [in Russian].
2. V. P. Skripov, *Metastable Liquid* (Nauka, Moscow, 1972) [in Russian].
3. A. Michels and J. V. Sengers, *Physica* (Amsterdam, Neth.) **28**, 1238 (1962).
4. A. Michels, J. V. Sengers, and P. S. van der Gulik, *Physica* (Amsterdam, Neth.) **28**, 1201 (1962).
5. A. Michels, J. V. Sengers, and P. S. van der Gulik, *Physica* (Amsterdam, Neth.) **28**, 1216 (1962).
6. V. I. Polezhaev and E. B. Soboleva, *Priroda*, No. 10, 17 (2003).
7. A. V. Zyuzgin, A. I. Ivanov, V. I. Polezhaev, G. F. Putin, and E. B. Soboleva, *Cosmic Res.* **39**, 175 (2001).
8. J. V. Sengers, in *Proceedings of the Conference on Phenomena in the Neighborhood of Critical Points*, Ed. by M. S. Green and J. V. Sengers (NBS Misc, Washington, DC, 1966), p. 165.
9. A. M. Sirota, V. I. Latunin, and G. M. Belyaeva, *Teplotenergetika*, No. 8, 6 (1973).
10. V. P. Skripov, *Critical Phenomena and Fluctuations in Solutions*, Ed. by M. I. Shakhparonov (Akad. Nauk, Moscow, 1960) [in Russian].
11. V. Vesovic, W. A. Wakeham, G. A. Olchowy, J. V. Sengers, J. T. R. Watson, and J. Millat, *J. Phys. Chem. Ref. Data* **19**, 763 (1990).
12. W. Wagner and A. Pr u , *J. Phys. Chem. Ref. Data* **31**, 387 (2002).
13. V. A. Kurganov, Yu. A. Zeigarnik, G. G. Yan'kov, and I. V. Maslakova, *Heat Transfer and Resistance in Pipes at Supercritical Coolant Pressures. Research Findings and Practical Recommendations* (OIVT RAN, Moscow, 2018) [in Russian].
14. Kh. I. Amirkhanov and A. P. Adamov, *Teplotenergetika*, No. 7, 77 (1963).
15. Kh. I. Amirkhanov and A. P. Adamov, *Teplotenergetika*, No. 10, 69 (1963).
16. A. M. Sirota, V. I. Latunin, and N. E. Nikolaeva, *Teplotenergetika*, No. 4, 72 (1981).
17. A. M. Sirota, V. I. Latunin, and G. M. Belyaeva, *Teplotenergetika*, No. 5, 70 (1976).
18. I. F. Golubev and V. P. Sokolova, *Teplotenergetika*, No. 11, 64 (1964).
19. R. Tufeu, D. Y. Ivanov, Y. Garrabos, and B. le Neindre, *Ber. Bunsen-Ges. Phys. Chem.* **88**, 422 (1984).
20. D. Yu. Ivanov, *Critical Behavior of Non-Idealized Systems* (Fizmatlit, Moscow, 2003) [in Russian].
21. V. P. Skripov and P. I. Potashev, *Inzh.-Fiz. Zh.* **5** (2), 30 (1962).
22. E. N. Dubrovina and V. P. Skripov, *Zh. Prikl. Mekh. Tekh. Fiz.*, No. 1, 115 (1965).
23. E. N. Dubrovina and V. P. Skripov, *Zh. Prikl. Mekh. Tekh. Fiz.*, No. 5, 152 (1969).
24. E. N. Dubrovina, V. P. Skripov, and N. A. Shuravenko, *Teplofiz. Vys. Temp.* **7**, 730 (1969).
25. R. Mostert, H. R. van den Berg, P. S. van der Gulik, and J. V. Sengers, *J. Chem. Phys.* **92**, 5454 (1990).
26. R. A. Perkins, *J. Chem. Eng. Data* **47**, 1272 (2002).
27. A. M. Sirota, in *Experimental Thermodynamics. III. The Measurement of Transport Properties of Fluids*, Ed. by W. A. Wakeham, A. Nagashima, and J. V. Sengers (Blackwell Scientific, Oxford, 1991), p. 142.
28. G. A. Olchowy and J. V. Sengers, *Phys. Rev. Lett.* **61**, 15 (1988).
29. G. A. Olchowy and J. V. Sengers, *Int. J. Thermophys.* **10**, 417 (1989).
30. K. Kawasaki, *Ann. Phys. (N.Y.)* **61**, 1 (1970).
31. K. Kawasaki, *Phase Transitions and Critical Phenomena*, Ed. by C. Domb and M. S. Green (Academic, New York, 1976), Vol. 5a.
32. P. C. Hohenberg and B. I. Halperin, *Rev. Mod. Phys.* **49**, 435 (1977).
33. V. Privman, P. C. Hohenberg, and A. Aharony, in *Phase Transitions and Critical Phenomena*, Ed. by C. Domb and M. S. Green (Academic, New York, 1991), Vol. 14, p. 1.
34. J. V. Sengers, *Int. J. Thermophys.* **6**, 203 (1985).
35. M. Frenkel, R. Chirico, V. Diky, C. D. Muzny, A. F. Kazakov, J. W. Magee, I. M. Abdulagatov, and J. W. Kang, *NIST Thermo Data Engine, NIST Standard Reference Database 103b: Pure Compound, Binary Mixtures, and Chemical Reactions, Vers. 5.0* (Natl. Inst. Standards Technol., Boulder, CO, 2010).
36. M. L. Huber, E. A. Sykioti, M. J. Assael, and R. A. Perkins, *J. Phys. Chem. Ref. Data* **45**, 013102 (2016).
37. E. W. Lemmon, M. L. Huber, and M. O. McLinden, *NIST Standard Reference Database 23, NIST Reference Fluid Thermodynamic and Transport Properties*,

- REFPROP, Version 10.1* (Natl. Inst. Standards Technol., Gaithersburg, MD, 2018).
38. J. M. H. Levelt Sengers, in *Supercritical Fluids. Fundamentals and Applications*, Ed. by E. Kiran and J. M. H. Levelt Sengers (Kluwer, Dordrecht, 1994).
  39. M. L. Huber, R. A. Perkins, D. G. Friend, J. V. Sengers, M. J. Assael, I. N. Metaxa, K. Miyagawa, R. Hellmann, and E. Vogel, *J. Phys. Chem. Ref. Data* **41**, 033102 (2012).
  40. F. M. Gumerov, *Supercritical Fluid Technologies. Economic Expediency* (AN RT, Kazan', 2019) [in Russian].
  41. R. A. Perkins, H. M. Roder, D. G. Friend, and C. A. Nieto de Castro, *Phys. A (Amsterdam, Neth.)* **173**, 332 (1991).
  42. J. Luettmer-Strathmann, J. V. Sengers, and G. A. Olchowy, *J. Chem. Phys.* **103**, 7482 (1995).
  43. S. B. Kiselev and V. D. Kulikov, *Int. J. Thermophys.* **15**, 283 (1994).
  44. S. B. Kiselev and V. D. Kulikov, *Int. J. Thermophys.* **18**, 1143 (1997).
  45. S. B. Kiselev and M. L. Huber, *Fluid Phase Equilib.* **142**, 253 (1998).
  46. R. Folk and G. Moser, *Phys. Rev. Lett.* **75**, 2706 (1995).
  47. R. A. Perkins, J. V. Sengers, I. M. Abdulagatov, and M. L. Huber, *Int. J. Thermophys.* **34**, 191 (2013).
  48. J. V. Sengers, R. A. Perkins, M. L. Huber, and D. G. Friend, *Int. J. Thermophys.* **30**, 374 (2009).
  49. A. Laesecke and C. D. Muzny, *J. Phys. Chem. Ref. Data* **46**, 013107 (2017).
  50. H. C. Burstyn, J. V. Sengers, J. K. Bhattacharjee, and R. A. Ferrell, *Phys. Rev. A* **28**, 1567 (1983).
  51. G. Paladin and L. Peliti, *J. Phys. Lett. (Paris)* **43**, 15 (1982).
  52. G. Paladin and L. J. Peliti, *J. Phys. Lett. (Paris)* **45**, 289 (1984).
  53. J. K. Bhattacharjee, R. A. Ferrell, R. S. Basu, and J. V. Sengers, *Phys. Rev. A* **24**, 1469 (1981).
  54. H. Hao, R. A. Ferrell, and J. K. Bhattacharjee, *Phys. Rev. E* **71**, 021201 (2005).
  55. R. F. Berg, M. R. Moldover, and G. A. Zimmerli, *Phys. Rev. E* **60**, 4079 (1999).
  56. R. A. Ferrell, *Phys. Rev. Lett.* **24**, 1169 (1970).
  57. I. M. Abdulagatov and P. V. Skripov, *Russian Journal of Physical Chemistry B*, **14** (7), 1178 (2020).
  58. R. Tufeu and B. le Neindre, *Int. J. Thermophys.* **8**, 283 (1987).
  59. J. C. Nieuwoudt, B. le Neindre, R. Tufeu, and J. V. Sengers, *J. Chem. Eng. Data* **32**, 1 (1987).
  60. P. M. Mathias, V. S. Parekh, and E. J. Miller, *Ind. Eng. Chem. Res.* **41**, 989 (2002).
  61. F. Nicoll and P. C. Albright, *Phys. Rev. B* **31**, 4576 (1985).
  62. C. Bervillier, *Phys. Rev. B* **34**, 8141 (1986).
  63. H. Behnejad, J. V. Sengers, and M. A. Anisimov, in *Applied Thermodynamics of Fluids*, Ed. by A. R. H. Goodwin, J. V. Sengers, and C. J. Peters (IUPAC, 2010), Chap. 10, p. 321.
  64. C. Bagnuls and C. Bervillier, *Phys. Rev. B* **32**, 7209 (1985).
  65. M. E. Fisher, *J. Math. Phys.* **5**, 944 (1964).
  66. D. Yu. Ivanov, L. A. Makarevich, and O. N. Sokolova, *JETP Lett.* **20**, 121 (1974).
  67. D. Yu. Ivanov, *Critical Behavior of Nonideal Systems* (Wiley-VCH, Weinheim, 2008).
  68. R. Tufeu, A. Letaief, Y. Garrabos, and B. le Neindre, in *Proceedings of the 8th Symposium on Thermal Properties*, Ed. by J. V. Sengers (ASME, New York, 1982), p. 451.
  69. N. B. Vargaftik, L. P. Filippov, A. A. Tarzimanov, and E. E. Totskii, *Handbook of Thermal Conductivity of Gases and Liquids* (Energoatomizdat, Moscow, 1990; CRC, Boca Raton, 1994).
  70. B. le Neindre and R. Tufeu, *Measurement of the Transport Properties of Fluids. Experimental Thermodynamics*, Ed. by W. A. Wakeham, A. Nagashima, and J. V. Sengers (Blackwell Scientific, Oxford, 1991), Vol. 3, p. 111.
  71. D. Yu. Ivanov, *Vestn. SibGUTI*, No. 3, 94 (2009).
  72. B. le Neindre, R. Tufeu, P. Bury, and J. V. Sengers, *Ber. Bunsen-Ges. Phys. Chem.* **77**, 262 (1973).
  73. B. le Neindre, Y. Garrabos, F. Gumerov, and A. Sabirzianov, *J. Chem. Eng. Data* **54**, 2678 (2009).
  74. B. le Neindre, G. Lombardi, P. Desmarest, M. Kayser, T. R. Bilalov, F. M. Gumerov, and Y. Garrabos, *Fluid Phase Equilib.* **481**, 66 (2019).
  75. *Department of Theoretical Foundations of Heat Engineering (1934–2004)*, Ed. by D. G. Amirkhanov and L. G. Shevchuk (Idel-Press, Kazan', 2004) [in Russian].
  76. J. M. H. Levelt Sengers, in *Supercritical Fluids: Fundamentals for Application, NATO ASI*, Ed. by E. Kiran and J. M. H. Levelt Sengers (Kluwer, Dordrecht, Netherlands, 2000), p. 3.
  77. L. P. Filippov, *Prib. Tekh. Eksp.*, No. 3, 86 (1957).
  78. P. V. Skripov and A. P. Skripov, *Int. J. Thermophys.* **31**, 816 (2010).
  79. E. D. Nikitin, *High Temp.* **36**, 305 (1998).
  80. A. A. Igolnikov, S. B. Rutin, and P. V. Skripov, *AIP Conf. Proc.* **2174**, 020104 (2019).
  81. S. B. Ryutin and P. V. Skripov, *Russ. J. Phys. Chem. B* **7**, 943 (2013).
  82. S. B. Rutin, A. D. Yampol'skii, and P. V. Skripov, *High Temp.* **52**, 465 (2014).
  83. S. B. Rutin, A. D. Yampol'skiy, and P. V. Skripov, in *Advanced Applications of Supercritical Fluids in Energy Systems*, Ed. by L. Chen and Y. Iwamoto (IGIGlobal, Hershey, PA, 2017), p. 271.
  84. E. N. Dubrovina, *Cand. Sci. (Phys. Math.) Dissertation* (Kirov Ural Polytech. Inst., Sverdlovsk, 1971).
  85. I. G. Gerts and L. P. Filippov, *Zh. Fiz. Khim.* **30**, 2424 (1956).
  86. V. P. Skripov and V. K. Semenchenko, *Zh. Fiz. Khim.* **29**, 174 (1955).
  87. E. B. Soboleva, *Russ. J. Phys. Chem. B* **8**, 1009 (2014).
  88. P. V. Skripov and S. B. Rutin, *Interfacial Phenom. Heat Transf.* **5**, 187 (2017).
  89. S. B. Rutin, D. V. Volosnikov, and P. V. Skripov, *Int. J. Heat Mass Transfer* **91**, 1 (2015).
  90. S. B. Rutin and P. V. Skripov, in *Proceedings of the 14th International Conference on Heat Transfer, Fluid*

- Mechanics and Thermodynamics (HEFAT'2019)*, Ed. by J. Meyer (Wicklow, Ireland, 2019), p. 773.
91. S. B. Rutin, A. A. Igolnikov, and P. V. Skripov, *J. Eng. Thermophys.* **29**, 67 (2020).
  92. S. B. Rutin and P. V. Skripov, *J. Eng. Thermophys.* **25**, 166 (2016).
  93. S. B. Rutin and P. V. Skripov, *Thermochim. Acta* **562**, 70 (2013).
  94. L. P. Filippov and S. N. Kravchun, *Zh. Fiz. Khim.* **56**, 2753 (1982).
  95. A. V. Baginsky, D. V. Volosnikov, P. V. Skripov, and A. A. Smotriskii, *Thermophys. Aeromech.* **15**, 373 (2008).
  96. S. B. Rutin and P. V. Skripov, *Int. J. Thermophys.* **37** (9), 102 (2016).
  97. D. V. Volosnikov, I. I. Povolotskiy, A. A. Igolnikov, and D. A. Galkin, *J. Phys.: Conf. Ser.* **1105**, 012153 (2018).
  98. P. Warrier, Y. Yuan, M. P. Beck, and A. S. Teja, *AIChE J.* **56**, 3243 (2010).
  99. Yu. E. Gorbatiy and G. V. Bondarenko, *Sverkhkrit. Flyuidy: Teor. Prakt.* **2** (2), 5 (2007).
  100. Y. E. Gorbatiy and G. V. Bondarenko, *J. Supercrit. Fluids* **14**, 1 (1998).
  101. V. K. Semenchenko, in *Application of Ultrasound to the Study of Matter* (MOPI, Moscow, 1956), No. 3, p. 51 [in Russian].
  102. V. K. Semenchenko, *Zh. Fiz. Khim.* **21**, 1461 (1947).
  103. Ya. B. Zel'dovich, *Sov. Phys. JETP* **53**, 1101 (1981).
  104. Al. A. Borisov, A. A. Borisov, S. S. Kutateladze, and V. E. Nakoryakov, *JETP Lett.* **31**, 585 (1980).
  105. V. V. Brazhkin, A. G. Lyapin, V. N. Ryzhov, K. Trachenko, Yu. D. Fomin, and E. N. Tsiok, *Phys. Usp.* **55**, 1061 (2012).
  106. H. Wang, L. K. H. Leung, W. Wang, and Q. Bi, *Appl. Therm. Eng.* **142**, 573 (2018).
  107. M. E. Shitsman, *Teplofiz. Vys. Temp.* **1**, 267 (1963).
  108. N. N. Veryasova, A. E. Lazhko, D. E. Isaev, E. A. Grebenik, and P. S. Timashev, *Russ. J. Phys. Chem. B* **13**, 1079 (2019).

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