Critical exponents of liquids

M. A. Anisimov, A. T. Berestov, V. P. Voronov, Yu. F. Kiyachenko, B. A. Koval'chuk,
V. M. Malyshev, and V. A. Smirnov

*All-Union Research Institute of Physicotechnical and Radiotechnical Measurements
and Moscow Institute of Petroleum Chemical and Gas Industry*
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Results are presented of an experimental determination of the critical exponents α of the heat capacity of argon and of the solutions nitroethane–isoöctane and methanol–cyclohexane, the exponent β of the coexistence curve of argon and of a nitroethane–isoöctane solution, of the susceptibility γ, and of the correlation function η of a nitroethane–hexane solution. The obtained values ($\alpha = 0.108 \pm 0.010$, $\beta = 0.339 \pm 0.006$, $\gamma = 1.20 \pm 0.002$, and $\eta = 0.045 \pm 0.010$) offer evidence favoring universality of the critical exponents of nonconducting liquids and are closest to the results of a numerical solution of the renormalization-group equations for the three-dimensional Ising model.

1. INTRODUCTION

Modern theory of critical phenomena[1] groups all liquids, their solutions, as well the three-dimensional Ising model into a single universal class. According to the theory, the exponents of the power laws that characterize the asymptotic behavior of analogous physical quantities near the critical points should be the same. However, even for an object as well investigated theoretically as the Ising model, the uncertainty in the values of the critical exponents is too large to permit their use as fixed parameters of a universal equation of state.[2]

By way of an example we cite the values of the critical exponent α obtained by different methods for the three-dimensional Ising model: high-temperature expansions[1] -0.125, ε-expansion with terms $\sim\varepsilon^2$ taken into account -0.077, numerical solution of the renormalization-group equations[4] -0.1132, experiment (result of present study) -0.108 ± 0.010. Thus, the problem of experimentally obtaining the critical exponent with an error less than the uncertainty of the theoretical results remains a pressing one.

In this paper we present the results of an experimental determination of the critical exponents of the heat capacity (α), of the coexistence curve (β) of argon and a nitroethane–isoöctane solution, the susceptibility (γ) and the correlation function (η) of a nitorethane–hexane solution, and newly reduced data on the heat capacity of a methanol–cyclohexane solution.[5] The obtained values offer evidence in favor of universality of the critical exponents and are closest to results of the numerical solution of the renormalization-group equations.

2. ALLOWANCE FOR CORRECTIONS TO THE ASYMPTOTIC LAWS.

The simple power laws used to determine the critical exponents have an asymptotic character $t = (T - T_c)/T_c \to 0$. The region of the experimental determination of the critical exponent is usually $t = 10^{-1} - 10^{-5}$. In the region closer to the critical point, the experimental result is as a rule unreliable. Approximation of the experimental results by an asymptotic model in the far

(reliable) region leads to biased estimates of the critical exponents if the contribution of the non-asymptotic (correction) terms is of the order of and greater than the experimental errors.

Table I lists the result of the calculation of the non-asymptotic terms that arise when account is taken both of the next-order approximations of scaling theory,[3,6-8] and of the difference between a real liquid and the symmetrical model of a lattice gas, which we have calculated using the results of Refs. 1, 9, and 10.[1] In this table, μ is the chemical potential and ρ is the density. It is seen that for the coefficient of isothermal compressibility and the critical isotherm the corrections necessitated by asymmetry are of the same order as the non-asymptotic terms of scaling theory, and are small for the isochronous heat capacity.

3. REDUCTION OF EXPERIMENTAL DATA

The reduction was by a previously developed program[12] consisting of the following procedures: elimination of lapses, estimate of the sampling variances, estimate of the parameters and confidence regions by least squares, and a check on the adequacy of the model by the Fisher criterion. The parameters can be estimated simultaneously with their selection by the stepwise regression method. The program makes it possible to process a large class of models, both linear and nonlinear in the parameter, and monitor the calculation time; if necessary, it can be easily regulated.

TABLE I.

Thermodynamic quantity	Asymptotic behavior	Allowance for next approximation of scaling theory	Allowance for the deviation of a real liquid from the model of the lattice gas
Isochor heat capacity C_V	$\sim t^{-\alpha}$	$\sim t^{-\alpha+\Delta}$	$\sim t^{\gamma-2\alpha}$
Isothermal-compressibility coefficient	$\sim t^{-\gamma}$	$\sim t^{-\gamma+\Delta}$	$\sim t^{-\gamma+(\beta+\gamma-1)}$
Critical isotherm: $\mu(\rho, T_c) - \mu(\rho_c, T_c)$	$\sim \Delta\rho\,\lvert\Delta\rho\rvert^{\delta-1}$	$\sim \Delta\rho\,\lvert\Delta\rho\rvert^{\delta-1+\Delta/\beta}$	$(D_2'\Delta\rho + D_2''\lvert\Delta\rho\rvert)\cdot \\ \cdot\lvert\Delta\rho\rvert^{\delta-1+(\beta+\gamma-1)/\beta}$
$\left(\dfrac{\partial^2\mu}{\partial T^2}\right)_{\rho=\rho_c}$	const	—	$\sim t^{\gamma-1-\alpha}$
$\rho_{liq} - \rho_g$	$\sim \lvert t\rvert^{\beta}$	$\sim \lvert t\rvert^{\beta+\Delta}$	—
$(\rho_{liq} + \rho_g)/2$	ρ_c	—	$\sim \lvert t\rvert^{1-\alpha}$

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Let us dwell in greater detail on the check of the hypothesis of the adequacy of the model, for if the model is inadequate, then estimates of the parameters and of the confidence intervals may turn out to be biased. Inadequacy of the model can be due to two factors: non-correspondence of the model to the investigated physical process, and the presence of a systematic error. It is impossible to discriminate these causes within the framework of a statistical reduction. The answer is determined by the physical premises and by the researcher's experience.

For an adequate model, the residuals $[Y_i - \eta(x_i, B)]$ (Y_i is the experimental value at the point $x_i \eta(x_i, B_i)$ is the value determined from the model at the same point, and B is the parameter-estimate vector) must not contain systematic deviations, and a check on the hypothesis of the adequacy of a model reduces to a check of the hypothesis that $\Phi_{min} = \Phi_0$. Here Φ_{min} is the sum of the squares of the deviations at the minimum point, and Φ_0 is the sum of the squares of the deviations and is connected with the purely random error. The quantity

$$\frac{\Phi_{min} - \Phi_0}{\Phi_0} \frac{n-m}{m}$$

has a Fisher distribution, and the critical region for verifying the hypothesis of the adequacy of the model is determined by the inequality (see, e.g., Ref. 13)

$$\frac{\Phi_{min} - \Phi_0}{\Phi_0} \frac{n-m}{m} < F_{1-\varkappa}(m, n-m), \tag{1}$$

n is the number of experimental points, m is the number of the parameters of the model, and $\varkappa$ in (1) is the significance level, usually chosen equal to 0.05.

It is difficult to determine Φ_0 directly, for this calls for a large number of repeated measurements. We have used for an estimate the following considerations.[12] Let the true dependence $Y(x)$ be described by the model $\eta(x, B) + \eta^*(x, \beta^*)$, where $\eta^*(x, \beta^*)$ is a model supplementing the verifyied model and describing the residuals due to the inadequacy. Determining the estimates B_i^* of the parameters β_i^*, we can use as an estimate of Φ_0 the quantity

$$\Phi_{min}^* = \sum_{i=1}^{n} \frac{[Y_i - \eta(x_i, B) - \eta^*(x_i, B^*)]^2}{s^2(x_i)}. \tag{2}$$

If the inequality (1) holds, then the hypothesis that the model is adequate is accepted.

The experimental procedure used to obtain the data employed by us was improved over that of Voronel' et al.[14] The use of an improved construction of the adiabatizing screens and of the calorimeter has made it possible to decrease substantially the temperature gradients over the calorimeter and the sample. New high-sensitivity automatic regulators, developed for the system that maintained the adiabatic regime, and also a semi-automatic system of registration of the temperature dependences,[16] has made it possible to improve the temperature resolution to 2×10^{-5} K. The measures adopted decreased the random error of the experiment, which is now due only to the error in the measurement of the temperature in the thermometer's own scale, by about one order of magnitude compared with Ref. 14 (see, e.g., Refs. 17 and 18).

The remaining details of the reduction will be illustrated with argon as an example, since they are essentially the same for the remaining substances. Besides the new data[18] we used also our old results.[19]

The data on the heat capacity C_V on the critical isochor, in accordance with the results given in Sec. 2, were approximated expressions of the type

$$\frac{C_V}{T} = A_0 t^{-\alpha} + A_1 + A_2 t^{-\alpha+\Delta} + A_3 t^{\gamma-2\alpha}. \tag{3}$$

The result in the two-phase region was obtained for a density $\rho = 0.5344$ g/cm^3, which differs from ρ_c by 0.13% ($\rho_c = 0.5351$ g/cm^3, Ref. 18). The interval of temperature variation corresponds to $t = 10^{-2} - 10^{-4}$, and the indicated deviation of the density from the critical value in this temperature interval hardly influences the results of the reduction, which has shown that two terms in (3), A_1 and $A_3 t^{\gamma-2\alpha}$, are insignificant. The quantity Δ was fixed in the reduction at $\Delta = 0.45$.[20] The quantity γ was also fixed at $\gamma = 1.20$ in accord with the measurement results of Bale et al.[21] We point out also that in no case was the quantity T_c varied by us anywhere in the course of the reduction, since it was determined independently from thermograms. It was found as a result that in the two-phase region $\alpha = 0.117 \pm 0.001$. Such a narrow confidence interval is due to the fact that the data were reduced by an abbreviated model (partial confidence interval).

In the one-phase region, we first reduced our old data[19] on the critical isochor in the range $t = 10^{-2} - 10^{-3.8}$ (in the closer region, errors were observed in the experimental data on account of the hydrostatic effect[22,23]). It turned that the asymptotic dependence describes the experimental data, and the result $\alpha = 0.115 \pm 0.008$ was obtained. Next, at a fixed value of α, these data were reduced jointly with the more recent data[18] on an isochor of corresponding density $\rho = 0.5321$ g/cm^3, which differed from ρ_c by 0.56% ($t = 10^{-0.13} - 10^{-2.5}$. The values of Δ and γ, just as in the two-phase region, were fixed. The results of the reduction in the entire temperature interval have shown that the model is complete but not adequate. An analysis of the residuals has shown that the experimental points deviate systematically from the model in a region farther from T_c starting with $t \approx 10^{-0.4}$; this apparently limits the region of applicability of expression (1). The final values of the parameters in the temperature dependence of the heat capacity in (3) were obtained by reducing the data of Refs. 18 and 19 in the interval $t = 10^{-0.4} - 10^{-3.8}$ (the confidence intervals are given for 68% probability):

$A_0 = 0.265 \pm 0.002,$ $\alpha = 0.115 \pm 0.008,$ $A_1 = -0.264 \pm 0.005,$

$A_2 = 0.089 \pm 0.005,$ $\Delta = 0.45$ (fixed),

$A_3 = -0.060 \pm 0.006,$ $\gamma = 1.20$ (fixed).

The value of α in the single-phase region is 0.115 ± 0.008, which agrees within the limit of the confidence interval with the value obtained in the two-phase region. We call attention to the fact that in the expression for the heat capacity the quantity $A_2 t^{-\alpha+\Delta}$, which is connected with the next approximation of the scaling theory, is significant. A reduction of the experimental data

without this term not only leads to biased estimates for the parameters of the model, but also makes the description inadequate. The term $A_3 t^{\nu-2\alpha}$, which takes into account the asymmetry of the liquid, also turned out to be significant. However, a check by us has shown that the accuracy of the available data[18,19] is not enough to be able to distinguish this term in the expression (3) for the heat capacity from the quantity $\sim t$ that arises when the regular part is expanded in powers of t. However, in the analysis of the shape of the coexistence curve, the terms that take the asymmetry into account have a non-ambiguous interpretation.

Using the results given above, we approximate the data on the argon coexistence curve by the expression

$$\Delta\rho = \pm B_0 |t|^\beta \pm B_1 |t|^{\beta+\Delta} + B_2 |t|^{1-\alpha} + B_3 t. \tag{4}$$

The need for taking into account the term $B_3 t$ follows from the work of Fomychev and Khokhlachev.[10] The results of the reduction in the entire temperature interval have shown that the model is complete, i.e., all the terms in (4) are statistically significant, but is inadequate. An analysis of the residuals has shown that there are systematic positive deviations from the model in a region close to T_c; these deviations are typical of the hydrostatic effect, whose influence decreases with increasing distance from T_c. By successively decreasing the approximation interval we obtained the limit $|t| \gtrsim 10^{-3.2}$, which is close to its theoretical estimates,[22,23] where the model is adequate. The values of the parameters in the expression (4) for the coexistence curve of argon, following a reduction of the data of Ref. 18 in the interval $t = 10^{-1} - 10^{-3.2}$ (the confidence intervals are given for 68% probability), are the following:

$B_0 = 1.63 \pm 0.002$, $\quad \beta = 0.340 \pm 0.002$, $\quad B_1 = 0.593 \pm 0.047$,

$\Delta = 0.45$ (fixed), $\qquad B_2 = 1.65 \pm 0.08$

$\alpha = 0.115$ (fixed), $\qquad B_3 = -1.76 \pm 0.13$.

All the parameters in (4) are significant, i.e., an adequate description of the experimental data calls for inclusion of the term that accounts for the curvature (singularity) of the diameter of the coexistence curve as well as inclusion of higher-order approximation of scaling theory. Our analysis of the joint confidence region of the exponent β and of the coefficient B_1 of the non-asymptotic correction shows (see Fig. 1) that neglect of the nonasymptotic terms leads to an overestimate $\beta = 0.35 - 0.36$, which is characteristic of many experimental papers, over the correct value (see Ref. 2).

Similar results were obtained by us also in the reduction of the data on the coexistence curve of a nitroethane–isoöctane mixture. The measured quantity in this case is the ultrasound velocity as a function of the temperature in the two-phase region.[24] The ultrasound velocity on the coexistence curve is uniquely connected with the concentration of the phase. As a result of the reduction we obtained $\beta = 0.338 \pm 0.008$. We note also that the correlation coefficient of the exponent β and the coefficient of the nonasymptotic increment have the same sign as for argon, and the ellipsoid of the joint confidence region has the same elongated form.
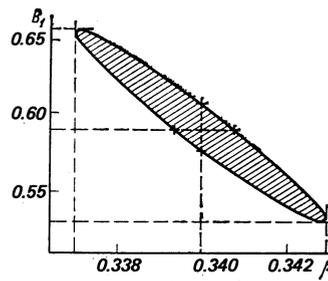
FIG. 1. Joint 95% confidence region of the coefficient B_1 and of the exponent β. Attention is called to the strong correlation of these parameters, which leads to an increase of β when B_1 is decreased.

We consider now the results of the reduction of the data on the heat capacity in the mixtures nitroethane–isoöctane (C_p and C_V) and methanol–cyclohexane (C_p). In view of the presence of a large regular part in the dependence of the heat capacity on the temperature in the mixtures, expression (1) was modified to

$$C = T(A_0 t^{-\alpha} + A_1 t^{-\alpha+\Delta}) + A_2 + A_3 t. \tag{5}$$

The value of Δ, just as in the reduction of the data on argon, was fixed. In the entire measured interval $t = 10^{-1.4} - 10^{-4}$ the model turned out to be complete and adequate. The obtained values $\alpha^- = 0.11 \pm 0.04$ and $\alpha^+ = 0.14 \pm 0.07$ agree with each other within the limits of their errors.

Estimates of the parameters obtained under the assumption $\alpha^- = \alpha^+ = 0.11$ yield good agreement of the constants A_2 and A_3 above and below the transition point. This means the absence of a jump or kink in the regular part. However, the reduction in a joint model of the data above and below T_c:

$$C(T < T_c) = T(A_0^- t^{-\alpha} + A_1^- t^{-\alpha+\Delta}) + A_2 + A_3 t,$$
$$C(T > T_c) = T(A_0^+ t^{-\alpha} + A_1^+ t^{-\alpha+\Delta}) + A_2 + A_3 t, \tag{6}$$

has led to an inadequate description of the experimental data. The description becomes adequate if the model is supplemented by the term $A_4 t^2$:

$$C(T < T_c) = T(A_0^- t^{-\alpha} + A_1^- t^{-\alpha+\Delta}) + A_2 + A_3 t + A_4 t^2,$$
$$C(T > T_c) = T(A_0^+ t^{-\alpha} + A_1^+ t^{-\alpha+\Delta}) + A_2 + A_3 t + A_4 t^2. \tag{7}$$

This model was used to reduce all the data on C_p and C_V for the nitroethane–isoöctane mixture and C_p for the methanol–cyclohexane model. As a result of the reduction it turned out that the order of magnitude and the sign of A agree with the behavior of the heat capacities of the individual components of the solution in this temperature interval.[23] Values $\alpha = 0.105 \pm 0.004$ for C_p and $\alpha = 0.107 \pm 0.007$ for C_V were obtained for the nitroethane–isoöctane mixture. For the methanol–isoöctane mixture. For the methanol–cyclohexane mixture, $\alpha = 0.103 \pm 0.007$.

We proceed now to consider the results of the reduction of the intensity of scattered light as a function of the temperature and of the scattering angle in a nitroethane–hexane mixture. This mixture is equivalent to the nitroethane–isoöctane mixture. The isoöctane was replaced by the hexane which has a lower refractive index in order to improve the scattering ability of

the object. The experimental procedure can be found in Ref. 26. The intensity of the scattering by the critical fluctuations, as is well known (see Ref. 2), is proportional to the correlation function $G(k, r_c)(k = 4\pi\lambda^{-1} \times \sin(\theta/2)$, r_c is the correlation radius).

The measurements were made in the temperature interval $t = 3 \cdot 10^{-2} - 10^{-5}$ and at scattering angles θ from 12 to 150°. The results were approximated by an expression of the type[27]

$$G(k, r_c) = A\frac{(\varphi^2 k^2 + r_c^{-2})^{\eta/2}}{k^2 + r_c^{-2}}. \qquad (8)$$

This expression leads to correct asymptotic forms of the correlation function $G(k, r_c) = r_c^{2-\eta}g(kr_c)$, and describes well the measurement results. According to Ref. 27, $\varphi^2 \sim 0.1$. The entire assembly of data was reduced (about 1000 points), and the coefficients A and φ, the exponent η in Eq. (8) as well as the intensity of the scattered light were all reduced and referred to zero angles (values corresponding to 54 temperature values). For the critical exponent of the correlation function we obtained in this case $\eta = 0.046 \pm 0.003$. The confidence interval was estimated here, as in the other cases, from the linearized model.

An additional analysis has shown, however, that the linear approximation exaggerates the accuracy in this case. A correct estimate of the confidence interval was obtained from the form of the dependence of the sum of the squares of the deviations near the minimum. This yielded $\eta = 0.038 - 0.050$. Allowance for the possible systematic errors in the measurement of the intensity of the scattered light (multiple scattering, finite aperture of the photoreceiver, etc.) yields a final result $\eta = 0.045 \pm 0.010$.

The intensity values referred to zero angles (obtained from the reduction of the initial assembly of data) was approximated by a formula that took into account the nonasymptotic terms

$$G(0, t) = \Gamma_0 t^{-\gamma} + \Gamma_1 t^{-\gamma+\Delta}. \qquad (9)$$

The reduction result is $\gamma = 1.19 \pm 0.06$. The coefficient of the nonasymptotic correction turned out to be insignificant. We have therefore performed several variants of the reduction at a fixed coefficient of the nonasymptotic increment ($\Gamma_1 = 0$ and $\Gamma_1 = 1$):

$\gamma = 1.19 \pm 0.01$, $\Gamma_1 = 0$; $\gamma = 1.21 \pm 0.01$, $\Gamma_1 = 1$.

Restriction of the interval of the values of the argument did not lead to a noticeable change of γ.

TABLE II.

	α	β	γ	η
Experimental results of present work	0.108 ± 0.010	0.339 ± 0.006	1.20 ± 0.02	0.045 ± 0.010
Ising model: computer experiment	0.125	0.3125	1.250	0.041
ε-expansion (with terms ~ε2 taken into account)	0.078	0.339	1.244	0.037
Numerical solution of the renormalization group equations.	0.1132	0.337 [²⁸]	1.238	0.046
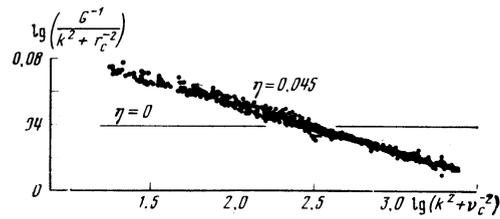
FIG. 2. Deviation of the experimentally obtained correlation function from the Ornstein-Zernike approximation.

4. CONCLUSION

In Table II are given the final result of our work. The critical exponents α for all the investigated objects are the same within the limits of their confidence intervals. The exponents β also practically coincided for argon and for the nitroethane—isooctane solution.

The averaged values $\alpha = 0.11$ and $\beta = 0.34$ we regard as established with a high degree of reliability. We think the value $\gamma = 1.21$ to be more probable than $\gamma = 1.19$. At any rate, the value $\gamma = 1.21$ follows from the relation $\alpha + 2\beta + \gamma = 2$ of the scaling theory (at $\alpha = 0.11$ and $\beta = 0.34$) and leads to a more acceptable value of the correlation radius $v = \gamma/(2 - \eta) = 0.62$.

The exponent $\eta = 0.05$ can also, in our opinion, be regarded as reliably established, and the deviation of the correlation function form the Ornstein-Zernike approximation can be regarded as experimentally proved (see Fig. 2).

As to the theoretical estimate, preference should be given on the whole to the results of a numerical solution of the renormalization-group equation,[4] although the accuracy of these calculations is difficult to estimate. The absence at the present time of reliable estimates of the accuracy of the calculation of the critical exponents restricts the possibility of practical applications of the theory.

The most realistic way of increasing the accuracy of the experimental critical exponents while using the existing procedure is to increase substantially the aggregate of the data (to several thousand points) in a reliable (i. e., free of systematic errors) temperature interval, followed by a statistical reduction based on complete models after checking the adequacy of the approximation.

[1])Detailed calculations are given in Berestov's dissertation.[11]

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Effect of pressure on the Fermi surfaces of the dioxides of molybdenum and tungsten

E. P. Vol'skii, A. G. Gapotchenko, E. S. Itskevich, and V. M. Teplinskii

Institute of High-Pressure Physics, USSR Academy of Sciences
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For the study of the properties of transition-metal dioxides it is important to know their electronic structure and the dependence of the latter on the lattice parameters. An investigation of the de Haas–van Alphen effect under pressure can yield these data. We measured the change of the size of the sections of some parts of the Fermi surfaces of single crystals of MoO$_2$ and WO$_2$, whose Fermi surfaces are similar.

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The electric and magnetic properties of the oxides of transition metals[1] are governed by a complicated system of relatively narrow (less than 1 eV) closely lying and partially overlapping electron bands connected with the d-levels of the metallic ions and preserving a rather distinctly pronounced d character in the crystalline state.[2] This leads to a definite similarity of their electronic spectra.

The structure of the d band in transition-metal oxides should be quite sensitive to the change of the interatomic distances and of the lattice symmetry. This manifests itself in a tendency to formation of distorted crystal structure, and in the role that small displacements of the atoms and the formation of the distorted structure play in the mechanism of the metal–insulator transition in a number of oxides (V$_2$O$_3$, VO$_2$, NbO$_2$).[1] For the same reasons one should expect the properties of

the oxides to be sensitive to the lattice deformation that is produced, in particular, by hydrostatic pressure. In fact, a rather strong influence of pressure on the metal–insulator transition temperature in V$_2$O$_3$ was observed in Ref. 3. However, analogous experiments[4] on VO$_2$ have shown that the influence of pressure on the metal–insulator transition in this oxide is much weaker.

In oxides that retain metallic conductivity at liquid-helium temperature, the influence of pressure on the electronic characteristics can be investigated in considerable detail by measuring the shape and dimensions of the Fermi surface (FS). So far, however, no such experiments were performed on any oxides. We report here the results of such an investigation on the metallic oxides MoO$_2$ and WO$_2$, whose FS at zero pressure was investigated quite in detail before.[5,6] Since MoO$_2$ and WO$_2$ have the same distorted rutile crystal structure as