current, as shown above, and consequent resonant behavior of the response. Therefore, it is clear that other mechanisms of phase fixation can hardly change anything in principle, apart from resulting in, for example, some renormalization of the frequency ω_1 of free oscillations. The frequency ω_2 is found to be relatively insensitive to the additional interaction fixing the phase, because this frequency corresponds (as pointed out in Sec. 3) to an oscillation mainly of the modulus of Δ.

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Experimental determination of the critical exponent and of the asymmetric and nonasymptotic corrections to the equation of the coexistence curve of Freon-113

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The coexistence curve (CC) of Freon-113 was experimentally investigated in a wide range of temperatures, including the vicinity of the critical point, for the purpose of checking on new theories of critical phenomena, the results of which are presented in the form of extended expansions. It is shown that the CC can be described by a formula with not less than four terms, having different forms for the liquid and gas branches. Statistical reduction of the experimental data on the CC yields the exponents and the coefficient of such a formula. It is established that the expressions for the symmetric and asymmetric terms are the same for the liquid and gas branches. The validity of zero-order symmetric scaling is proved. A singularity is found in the CC "diameter." From a comparison of the experimental data with the extended nonanalytic theories it is deduced that the existing theories agree with experiment only qualitatively.

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1. INTRODUCTION

In the last decade much progress was made in the theoretical research into the critical state[1] and this stimulated a number of experimental studies, which are reviewed in Refs. 2 and 3. Methods were developed[4-10] for the construction of an extended nonanalytic theory of critical phenomena. The results are presented in the form of series whose leading terms correspond to zero-order scaling. The asymmetrical terms take into account the difference between a real liquid + gas system and idealized models, and when used together with nonasymptotic symmetrical terms they enlarge the describable vicinity of the critical points. Various suggestions are encountered in the theoretical papers concerning the numerical values of the exponents of the correction terms, but the values of the coefficients do not lend themselves so far to theoretical calculation. To find the true equation of state in a large vicinity of the critical point it becomes urgent, besides the experimental determination of the leading (limiting, zero-order) terms, to obtain by experiment the succeeding terms of the expansion, and this calls for a highly accurate study of the behavior of the medium in a larger vicinity of the critical point. In particular, in the study of the liquid–vapor coexistence curve (CC), besides the determination of the leading terms,[2,3,11-15] attempts were already made to find the first nonasymptotic and asymmetric corrections.[16-20] It is obvious that the experimentally determined form of the correction terms can be strongly influenced by even an insignificant error made when choosing the leading term of the expansion. However, in the experimental determination of the limiting laws frequent use is made of finite intervals of the state parameters, so that as a rule one obtains not the limiting zero-order scaling exponents, but certain effective ones. Furthermore, most investigators do not measure and do not take properly into account the gravitational effect, and this also affects the values of the exponents and of the coefficients.

This circumstance and the fact that different experimenters use different intervals of the state parameters in the vicinity of the critical point makes it difficult to reconcile the results and compare them with the theory.

There is not enough logical justification for a procedure wherein certain theoretical exponents are used when the correction terms are determined from experimental data, and what are determined in fact are the coefficients of the extended equation.[21-23] A procedure in which some of the exponents are fixed is used also in an experimental study[24] which in all other respects has been performed in accord with the highest contemporary standards.

We have undertaken, by experimental study of the coexistence curve in a wide range of temperatures (including the immediate vicinity of critical point, where the gravitational effect is significant), and by statistical computer reduction of the curve, to obtain both the limiting laws that describe this curve and the first three correction terms.

2. EXPERIMENTAL RESULTS AND THEIR REDUCTION PROCEDURE

The chosen object of investigation was Freon-113 (trifluorotrichlorethane $C_2F_3C_{13}$) with purity better than 99.9%. The CC of Freon-113 was investigated by a procedure developed in our laboratory.[25-29] The Toepler shadow method was used in conjunction with the reference-prism method and with the microflat flotation method. The Toepler method in conjunction with reference prisms permit measurements of the absolute values of the refractive indices at any point of the chamber; these indices are next recalculated into densities with the aid of the Lorenz-Lorentz formula, with account taken of the temperature dependence of the refraction, determined by us by the microflat method. The refractive indices were measured at $\lambda = 579.1$ nm. The relative error of the refractive index was 0.01%, and the average error in the determination of the density was 0.1%. The possible systematic errors in the determination of the density ρ did not exceed the random errors. Double thermostatting was used with accuracy ±0.001°, and the temperature-measurement accuracy was ±0.0003° in the scale of the employed platinum resistance thermometer. A zero temperature gradient over the height of the chamber was achieved by regulating the current through the heating windings of the oven and was monitored with a differential copper-constantan thermocouple connected to an R-348 potentiometer.

A distinguishing feature of the employed procedure is that besides permitting the study of $\rho = \rho(\tau)$ in a wide temperature interval, it yields reliable data on the density along the height of the vessel when the gravitational effect manifests itself. In particular, at $T \leqslant T_{cr}$ the method makes it possible to measure the density at the liquid–gas interface itself, permitting thereby the study of the top of the true CC very close to the critical point.

We report in this communication the result of a study of the CC of Freon-113 in a wide range of temperatures ($1.5\times10^{-4} \leqslant |(T-T_{cr})/T_{cr}| \leqslant 0.39$) and densities ($0.102 \leqslant (\rho_l - \rho_{cr})/\rho_{cr} \leqslant 0.177$; $0.0969 \leqslant |(\rho_g - \rho_{cr})/\rho_{cr}| \leqslant 0.997$), where T_{cr} and ρ_{cr} are the critical temperature and density.

The experimental data on the CC of Freon-113 are given in Table I. On each of the experimental CC branches we measured 67 points pairwise corresponding to the same temperature. At low temperatures quite far from critical, when there is no gravitational effect, as well as in the region where the effect is insignificant, the measurements were performed only with reference prisms without the use of the Toepler method (points 1–50). With increasing temperature, the appearance of negligible density gradients along the

TABLE I. Experimental data along the Freon-113 saturation curve.

Point No.	T, K	ΔT	$\lvert\tau\rvert$	ρ_l^{exp}, g/cm³	ρ_l^{exp}, g/cm³
1	294.252	−192.716	0.39575	1.5715	0,0018
2	354.269	−132.699	0,27250	1.4213	0.0169
3	365.258	−121.710	0,24993	1.3931	0.0212
4	376.711	−110.257	$2,26\cdot10^{-1}$	1.3595	0,0260
5	388.524	−98.444	$2,02\cdot10^{-1}$	1.3228	0.0384
6	391.789	−95.179	$1.95\cdot10^{-1}$	1.3138	0,0393
7	400.727	−86.241	$1.77\cdot10^{-1}$	1,2834	0.0509
8	405.576	−81.392	$1.67\cdot10^{-1}$	1.2670	0,0562
9	412.980	−73.988	$1,52\cdot10^{-1}$	1,2413	0,0658
10	417.351	−69.617	$1.43\cdot10^{-1}$	1.2244	0.0722
11	425.409	−61.559	$1.26\cdot10^{-1}$	1.1942	0.0872
12	426.892	−60.076	$1.23\cdot10^{-1}$	1.1884	0.0902
13	428.505	−58.463	$1.20\cdot10^{-1}$	1.1824	0,0927
14	432.603	−54,365	$1.12\cdot10^{-1}$	1.1641	0,1004
15	439.649	−47.319	$9.72\cdot10^{-2}$	1.1322	0.1166
16	440.126	−46.842	$9.62\cdot10^{-2}$	1,1305	0,1182
17	444.120	−42.848	$8,80\cdot10^{-2}$	1,1119	0.1276
18	446,952	−40.016	$8.22\cdot10^{-2}$	1,0994	0,1358
19	450.365	−36.603	$7.52\cdot10^{-2}$	1,0825	0,1462
20	450.793	−36.175	$7,43\cdot10^{-2}$	1.0762	0,1467
21	452.972	−33,996	$6.98\cdot10^{-2}$	1.0686	0.1547
22	456.570	−30,398	$6.24\cdot10^{-2}$	1,0465	0.1674
23	457,409	−29.559	$6.07\cdot10^{-2}$	1,0408	0,1715
24	461.662	−25.306	$5.20\cdot10^{-2}$	1.0139	0.1881
25	463,142	−23.826	$4.89\cdot10^{-2}$	1.0021	0,1929
26	466.005	−20.963	$4.31\cdot10^{-2}$	0,9821	0.2077
27	472,343	−14,625	$3,00\cdot10^{-2}$	0.9296	0,2445
28	472.904	−14.064	$2.89\cdot10^{-2}$	0.9239	0.2488
29	472,957	−14.011	$2.88\cdot10^{-2}$	0.9248	0.2486
30	474.474	−12.494	$2.57\cdot10^{-2}$	0,9090	0.2606
31	477,121	−9,847	$2,02\cdot10^{-2}$	0,8822	0,2810
32	477.641	−9.727	$1.92\cdot10^{-2}$	0,8756	0.2855
33	478.231	−8,737	$1.79\cdot10^{-2}$	0.8684	0.2914
34	478,703	−8.265	$1.70\cdot10^{-2}$	0,8620	0.2966
35	478.816	−8.152	$1.67\cdot10^{-2}$	0,8607	0,2969
36	479.273	−7.695	$1.58\cdot10^{-2}$	0,8550	0.3019
37	479,642	−7,326	$1,50\cdot10^{-2}$	0,8506	0,3068
38	479.687	−7,281	$1,49\cdot10^{-2}$	0,8492	0,3073
39	480.305	−6.663	$1.37\cdot10^{-2}$	0,8400	0,3145
40	480,727	−6,241	$1.28\cdot10^{-2}$	0,8338	0,3195
41	481.235	−5.773	$1.18\cdot10^{-2}$	0,8268	0,3254
42	481.236	−5.732	$1.18\cdot10^{-2}$	0,8263	0,3261
43	481,804	−5,164	$1.06\cdot10^{-2}$	0.8157	0,3354
44	482.149	−4,819	$9.90\cdot10^{-3}$	0,8109	0.3401
45	482.658	−4,310	$8,85\cdot10^{-3}$	0,8016	0,3478
46	483.159	−3.809	$7,82\cdot10^{-3}$	0.7926	0.3555
47	483.395	−3.573	$7,54\cdot10^{-3}$	0.7875	0,3602
48	483.759	−3.209	$6.59\cdot10^{-3}$	0.7791	0.3679
49	484,029	−2,939	$6.03\cdot10^{-3}$	0.7738	0.3729
50	484.303	−2,665	$5,47\cdot10^{-3}$	0.7647	0,3815
51	484,588	−2.380	$4.89\cdot10^{-3}$	0.7570	0,3887
52	484.872	−2,096	$4,30\cdot10^{-3}$	0,7494	0,3967
53	485,117	−1.851	$3.80\cdot10^{-3}$	0.7412	0.4032
54	485,396	−1,572	$3.23\cdot10^{-3}$	0.7317	0,4113
55	485,672	−1,296	$2,66\cdot10^{-3}$	0,7213	0.4212
56	485,852	−1.116	$2.29\cdot10^{-3}$	0,7130	0,4286
57	485,993	−0,975	$2,00\cdot10^{-3}$	0,7073	0.4343
58	486,062	−0,906	$1.86\cdot10^{-3}$	0,7035	0.4383
59	486.221	−0,747	$1.53\cdot10^{-3}$	0.6953	0,4458
60	486,387	−0.581	$1,19\cdot10^{-3}$	0.6842	0.4559
61	486,518	−0,450	$9.20\cdot10^{-4}$	0.6737	0.4653
62	486,682	−0.286	$5,90\cdot10^{-4}$	0.6592	0,4795
63	486.817	−0,151	$3.10\cdot10^{-4}$	0.6410	0.4950
64	486,842	−0.126	$2.60\cdot10^{-4}$	0.6385	0,4982
65	486,894	−0,074	$2.00\cdot10^{-4}$	0.6244	0,5107
66	486.896	−0,072	$1,50\cdot10^{-4}$	0,6262	0.5110
67	486.897	−0.071	$1.50\cdot10^{-4}$	0.6244	0.5116

height of the chamber, due to the manifestation of the gravitational effect, was noted at $|\tau| = 1.6 \times 10^{-2}$. The gravitational effect was measured by the shadow method and was taken into account in the determination of the densities of the coexisting liquid and vapor starting with $|\tau| = 5.5 \times 10^{-3}$ (points 51–67).

A small scale plot of the CC of Freon-113 has the usual appearance: the "diameter" is almost a straight line; the half-sum $\rho_d = (\rho_l + \rho_g)/2$ decreases with increasing temperature (Fig. 1a). The temperature dependence of the half-sums of the liquid and gas densities near the critical point, in a scale that reflects the accuracy of the experiment, is shown in Fig. 1b. It is seen from this figure that the values of $\rho_d = (\rho_l + \rho_g)/2$ fit a certain curve. The "diameter" of the CC bends towards the higher densities, and the slope of this curve increases gradually as the critical point is approached. The deviation of the true values of the half-sum of the densities from the straight line extrapolated from the low-temperature region to the critical temperature amounts to 0.9%.

This preliminary analysis of the experimental data offers evidence that the CC cannot be described in a finite vicinity of the critical point by the zero-order scaling theory, and not even by extended symmetrical expansions, for the diameter should be horizontal and straight in both cases. For a mathematical representation of the results it is necessary to use extension series with allowance for asymptotic terms. In view of the lack of estimates of the convergence range of these series, it is usually assumed that it is equal to the region of the entire actually observable CC. Owing to the differences between the theoretically predicted values of the exponents, we consider it inadvisable to specify their values beforehand. For an unbiased check on the theoretical predictions it seems more correct to determine the exponents and the coefficients of the series terms directly from the experimental data and then compare the obtained values with various theoretical models. However, the determination of all the terms of an infinite series is unrealistic under the indicated conditions. It is necessary instead to approximate the experimental results by a polynomial. This substitution undoubtedly distorts the theoretical model, and additional assumptions must be made so as to reconcile at least the leading terms of the experimental polynomials with the theoretical model in which the CC is represented by an infinite series.

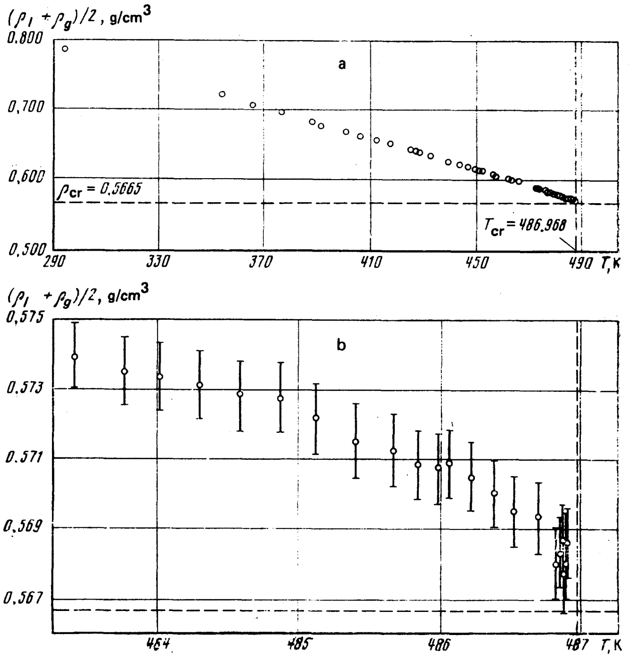

FIG. 1. Dependence of the diameter $\rho_d = (\rho_l + \rho_g)/2$ of the coexistence curve of Freon-113 on the temperature: a—over the entire investigated temperature interval, b—near the critical temperature.

We have reduced our experimental data on the CC of Freon-113 by a four-term formula that takes the following forms for the liquid and gas branches

$$(\rho_l - \rho_{cr})/\rho_{cr} = B_0|\tau|^{\beta_0} + B_1|\tau|^{\beta_1} + B_2|\tau|^{\beta_2} + B_3|\tau|^{\beta_3}, \tag{1}$$

$$(\rho_g - \rho_{cr})/\rho_{cr} = -B_0|\tau|^{\beta_0} + B_1|\tau|^{\beta_1} - B_2|\tau|^{\beta_2} + B_3|\tau|^{\beta_3}, \tag{2}$$

where $B_0|\tau|^{\beta_0}$ is the leading symmetrical term, $B_1|\tau|^{\beta_1}$ takes into account the asymmetry of the CC, and the terms $B_2|\tau|^{\beta_2}$ and $B_3|\tau|^{\beta_3}$ are corrections to the principal symmetric and asymmetric terms. In addition, we have assumed that none of the exponents or coefficients are known beforehand.

Since formulas (1) and (2) contain quite many parameters that must be determined, it is convenient to use also the half-difference and half-sum of these equations:

$$(\rho_l - \rho_g)/2\rho_{cr} = B_0|\tau|^{\beta_0} + B_2|\tau|^{\beta_2}, \tag{3}$$

$$(\rho_l + \rho_g - 2\rho_{cr})/2\rho_{cr} = B_1|\tau|^{\beta_1} + B_3|\tau|^{\beta_3}. \tag{4}$$

The symmetrical and asymmetrical terms are now contained in different equations, and this facilitates their determination, particularly because the procedure employed enables us to measure simultaneously ρ_l and ρ_g at the same temperature, rather than take them from smoothed curves, as many experimenters were forced to do (in traditional PVT measurements, when the thermogram method is used, etc.).

Figures 2 and 3 show in logarithmic scale the experimental data for the discussed four Eqs. (1)–(4).

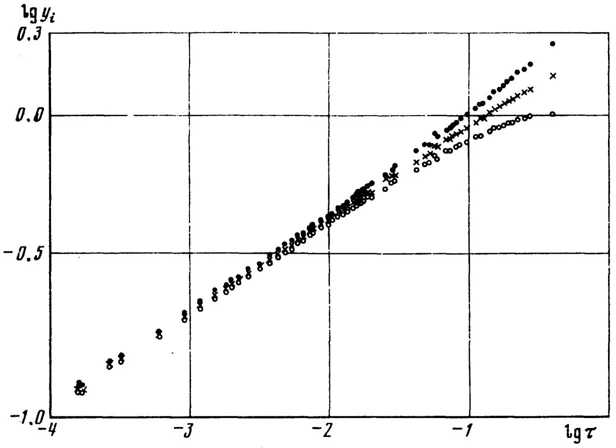

FIG. 2. Plots, against the reduced temperature $\tau = (T - T_{cr} / T_{cr}$ of the following functions: ●) $y_1 = (\rho_l - \rho_{cr})/\rho_{cr}$, ×) $y_2 = (\rho_l - \rho_g)/2\rho_{cr}$, ○) $y_3 = (\rho_{cr} - \rho_g)/\rho_{cr}$, in doubly logarithmic scale.

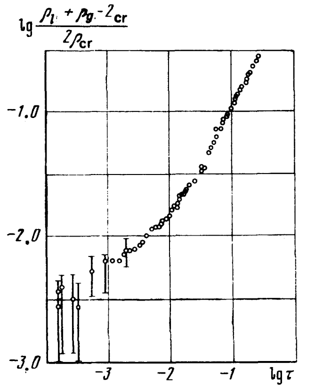

FIG. 3. Dependence of the function $y=(\rho_l+\rho_g-2\rho_{cr})/2\rho_{cr}$ on the reduced temperature $\tau=(T-T_{cr})/T_{cr}$ in doubly logarithmic scale.

As seen from Figs. 2 and 3, not only the plots of

$$\lg\frac{\rho_l-\rho_{cr}}{\rho_{cr}}=f(\lg|\tau|),\quad \lg\frac{|\rho_g-\rho_{cr}|}{\rho_{cr}}=f(\lg|\tau|),$$

but also the plots of

$$\lg\frac{\rho_l-\rho_g}{2\rho_{cr}}=f(\lg|\tau|),\quad \lg\frac{\rho_l+\rho_g-2\rho_{cr}}{2\rho_{cr}}=f(\lg|\tau|)$$

differ from straight lines, thus indicating that it is impossible to describe these relations by single-term expressions. These plots show that the function $\rho=\rho(T)$ must be described by at least four terms. However, a correct allowance for the succeeding terms is possible if the principal (leading) term $B_0|\tau|^{\beta_0}$ is determined exactly.

To find the limiting values of β_0 and B_0 we first attempted to reduce the experimental data by using for each of the branches the single-term formulas

$$(\rho_l-\rho_{cr})/\rho_{cr}=B_l|\tau|^{\beta_l}, \tag{5}$$

$$(\rho_g-\rho_{cr})/\rho_{cr}=-B_g|\tau|^{\beta_g} \tag{6}$$

and accordingly

$$(\rho_l-\rho_g)/2\rho_{cr}=B|\tau|^{\beta}. \tag{7}$$

Comparing these formulas with the experimental data in various temperature intervals produced by successively excluding the low-temperature points, we investigated in this manner the temperature dependences of certain effective values of the exponents and of the coefficients. We took 13 temperature intervals including the following experimental points: 1–67, 6–67, 11–67, 16–67, 21–67, 26–67, 31–67, 36–67, 41–67, 46–67, 51–67, 56–67, and 61–67 (see Table I).

The entire reduction of the experimental data [determination of the reference values of n, integration of the function $dn/dz=f(z)$, determination of the values r of the refractions and of the densities ρ_l and ρ_g of the coexisting phases, and others] was carried out with a computer in accord with a specially developed FORTRAN-IV program. The sought values of the critical exponents and coefficients in the case of four-parameter and two-parameter approximations for formulas (3)–(7) were estimated by the FUMILI program, based on a linearization method used to find the minima of the functionals that depend on the sought parameters only through their own functional argument.[30,31]

The following were specified in the FUMILI program: the experimental values of the temperature T, the densities of the coexisting phases ρ_l and ρ_g, the errors in the measured quantities, the form of the first derivatives of the investigated relations (3)–(7) with respect to the determined parameters, expressions for the errors Δy_i of the investigated dependences with account taken of the formula for the error transfer in accord with Ref. 32.

A comparison of the estimates for the various temperature interval was based on the χ^2 criterion:

$$\chi^2=\frac{2S}{N-M},\quad S=\frac{1}{2}\sum_{i=1}^{N}W_i[y_i(\mathbf{a}_i,\tau_i)-Y_i]^2,$$

where N is the number of experimental points, M is the number of the sought parameters, $y_i(\mathbf{a}_i,\tau_i)$ is the value calculated from the right-hand side of the expression (3) or (4)–(7) taken for the calculation at the i-th point, $\mathbf{a}_i$ is the vector of the sought parameters a_i, Y_i is the experimental value of the left-hand side of the corresponding expression for the i-th point, and $W_i=1/\Delta y_i^2$ is the statistical weight of the i-th point.

When this program was used to estimate the effective exponents and coefficients from (5)–(7) for the temperature intervals indicated above, it turned out that close to the critical temperature these parameters are very sensitive to very slight variations of the critical parameters T_{cr} and ρ_{cr} within the limits of the errors of the measurement of these parameters. A correct determination of the values of T_{cr} and ρ_{cr} and the establishment of the limiting values of β_0 and B_0 from the temperature dependences of the effective values of β_l, β_g and B_l, B_g are interrelated problems. Special attention was therefore paid to the analysis of the determination of T_{cr} and ρ_{cr}.

3. DETERMINATION OF THE CRITICAL PARAMETERS OF FREON-113

In this experiment we determined a tentative value of T_{cr} by visually observing the vanishing of the meniscus. However, owing to the gravitational effect and to the appearance of large density gradients near the meniscus, the accuracy with which T_{cr} can be determined in the experiment by this method is not better than $\Delta T=\pm 0.005-0.01$ K. A more accurate value of T_{cr} was obtained by analyzing the behavior of the temperature dependences of the effective values of β and B of Eq. (7) for different temperature intervals, with T_{cr} varied within the limits of the indicated experimental error ΔT_{cr} [the numerical value of ρ_{cr} does not play an important role here, inasmuch in formula (7) ρ_{cr} does not enter in the difference $(\rho_l-\rho_g)$].

After computing β with T_{cr} varied within the experimentally determined error interval ΔT_{cr}, we choose a value of T_{cr} such that the plot of $\beta=f(\log|\tau|)$ becomes horizontal within the limit of errors near the critical state. It was this value of T_{cr} which was taken to be the true critical temperature. In the scale of the platinum resistance thermometer, the critical temperature of Freon-113 determined by this method was $T_{cr} = (213.808 \pm 0.003)$°C.

The experimentally observed bending of the CC diameter indicates that ρ_{cr} should be less than the 0.571 g/cm^3 obtained from the intersection of the extrapolated linear plot of the "diameter" with the vertical line $T = T_{cr} = 213.808$ °C. On the other hand, the character of the motion of the meniscus with increasing temperature, in an experiment where the acerage density of the chamber content was $\bar{\rho} = 0.563$ g/cm^3, indicates that it is less than ρ_{cr}. The final determination of ρ_{cr} was similar to the determination of T_{cr} by computer calculation of the critical exponents β_1 and β_g and of the critical coefficients B_1 and B_g [formulas (5) and (6)] when the values of ρ_{cr} were varied.

By varying the critical density in the range $\rho = 0.571 - 0.563$ g/cm^3 it is possible to make the temperature dependences of $\beta_1(T)$ and $\beta_g(T)$ converge at a value $\rho_{cr} = 0.5665$ g/cm^3. It was this value which we took to be the true critical density of Freon-113. The absolute error in the determination of ρ_{cr} was taken by us to be the error in the determination of the density in layer-by-layer measurements of the near-critical regimes, namely $\Delta\rho = \pm 0.0010$ g/cm^3. We have thus $\rho_{cr} = 0.5665 \pm 0.0010$ g/cm^3.

4. DETERMINATION OF THE PARAMETERS OF THE LIMITING LAW THAT DESCRIBES THE CREST OF THE COEXISTENCE CURVE OF FREON-113

Simultaneously with selecting the true values of T_{cr} and ρ_{cr} we obtained the values of β_0 and B_0 as the limiting values of β, β_1, and β_g, and accordingly B, B_1, and B_g. To elucidate the character of the change of the effective exponents and coefficients obtained for 20 different temperature intervals, referred to the midpoints of these intervals.

The effective exponent β_1 decreases with increasing temperature, while β_g increases. When the critical point is approached, the plots of the exponents β_1 and β_g merge with the plot of β against $\log\tau_{av}$, and starting with $\log\tau_{av} = -3$ all three curves coincide within the accuracy limits of β, β_1, and β_g. The errors in the calculations of β_1 and β_g in all temperature intervals almost coincide with the error in the calculation of β. An analysis yields the following values of the limiting critical exponents and their errors:

$$\lim_{\tau\to 0} \beta = 0.342 \pm 0{,}003, \quad \lim_{\tau\to 0} \beta_l = 0{,}343 \pm 0.003, \quad \lim_{\tau\to 0} \beta_g = 0{,}341 \pm 0.003.$$

Thus:

$$\beta_0 = \lim_{\tau\to 0} \beta = \lim_{\tau\to 0} \beta_l = \lim_{\tau\to 0} \beta_g = 0.342 \pm 0{,}004.$$

The values of χ^2 for the temperature interval in which the limiting values are determined are respectively 1.2, 1.5, and 1.2.

We note that when we attempted to use the single-term formulas (5)–(7) to describe the CC branches and $(\rho_1 - \rho_g)$ in the entire invesitgated temperature interval we obtained the following effective exponents: $\beta = 0.3340 \pm 0.0003, \chi^2 = 24$; $\beta_1 = 0.3700 \pm 0.0003, \chi^2 = 87$; $\beta_g = 0.29000 \pm 0.003, \chi^2 = 450$. Obviously the effective exponents have nothing in common with the limiting values.

The temperature dependences of the effective values of the coefficients B, B_1, and B_g are analogous in a wide temperature range to those of the effective values $\beta(T)$, $\beta_1(T)$, and $\beta_g(T)$. A somewhat worse convergence of B_1 and B_g to the limiting value determined by B is observed, however. For the temperature interval closest to the critical temperature $1.5 \times 10^{-4} < |\tau| < 9.2 \times 10^{-4}$ the respective values of the coefficients are

$$B = 2.021 \pm 0.048, \quad B_l = 2.100 \pm 0.049, \quad B_g = 1.938 \pm 0.048.$$

Consequently it must be considered here, too, that

$$B_0 = \lim_{\tau\to 0} B = \lim_{\tau\to 0} B_l = \lim_{\tau\to 0} B_g$$

and that $B_0 = 2.02 \pm 0.13$, whereas the effective values for the entire temperature interval are

$$B = 1.943 \pm 0{,}002, \quad B_l = 2{,}390 \pm 0{,}002, \quad B_g = 1{,}515 \pm 0{,}001.$$

Consideration of the temperature dependences of the effective exponents are coefficients leads to one more conclusion: Within the limits of the calculation errors, if the critical parameters T_{cr} and ρ_{cr} are correctly chosen, the following equations are valid in the entire temperature interval:

$$\beta = (\beta_l + \beta_g)/2, \quad B = (B_l + B_g)/2.$$

The effective values of the exponents and of the coefficients were calculated also for "moving" intervals by successive selection of nine temperature points. The results agree qualitatively with the described relations, except that at low temperatures we obtained larger differences between β, β_1, β_g and B, B_1, and B_g.

It follows from the foregoing results that the effective values of β and B are temperature-independent, within the limits of experimental error, in the region $|\tau| < 10^{-2}$, as are also β_1, β_g and B_1, B_g in the region $|\tau| < 10^{-4}$. We can accordingly use in this regions, for calculations at the indicated accuracy, single-term formulas, but to determine the true form of the CC we must find for an equation that describes correctly its singularities in the entire range of the coexistence conditions.

5. EXPERIMENTAL CONFIRMATION OF THE VALIDITY OF SYMMETRIC SCALING THEORY

In the investigation of the temperature dependence of the effective values of the exponents and of the coefficients we have found, as noted above, that for the last temperature interval, which includes seven experimental points in the temperature range $1.5 \times 10^{-4} < |\tau| < 9.2 \times 10^{-4}$ we have within the limits of errors $\beta_1 = \beta_g$ but $B_1 > B_g$. It follows therefore that either the last investigated temperature interval is not yet asymptotic, or that in principle the gas and liquid branches of the CC are described by different limiting laws.

Assume that near the critical point we have for the limiting (zero-order) critical exponents and coefficients the inequalities $\beta_{01} > \beta_{0g}$ and $B_{01} > B_{0g}$, and consequently $\Delta\beta = \beta_{01} - \beta_{0g} \neq 0$ and $\Delta B = B_{01} - B_{0g} \neq 0$. Then in the asymptotic limits the liquid and gas branches of the CC satisfy the equations

$$(\rho_l - \rho_{cr})/\rho_{cr} = B_{0l} |\tau|^{\beta_{0l}}, \tag{7a}$$

$$(\rho_g - \rho_{cr})/\rho_{cr} = -B_{0g} |\tau|^{\beta_{0g}}. \tag{7b}$$

The difference between these equations, recognizing that $\beta_{01}=\beta_{0g}+\Delta\beta$, yields

$$\rho_l-\rho_g=\left[1+\frac{B_{0l}}{B_{0g}}|\tau|^{\Delta\beta}\right]\rho_{cr}-\left[1+\frac{B_{0l}}{B_{0g}}|\tau|^{\Delta\beta}\right]\rho_g \tag{8a}$$

an analogously, recognizing that $\beta_{0g}=\beta_{01}-\Delta\beta$,

$$\rho_l-\rho_g=-\left[1+\frac{B_{0g}}{B_{0l}}|\tau|^{\Delta\beta}\right]\rho_{cr}+\left[1+\frac{B_{0g}}{B_{0l}}|\tau|^{\Delta\beta}\right]\rho_l. \tag{8b}$$

These equations yield a linear connection between $(\rho_1-\rho_g)$ and ρ_g (or ρ_1) if the coefficients of ρ_{cr}, and hence of ρ_1 and ρ_g, do not vary with temperature, i.e., if $\Delta\beta=0$. Then $|\tau|^{\Delta\beta}=1$ and Eqs. (8) take the form

$$\rho_l-\rho_g=\left(\frac{B_{0l}+B_{0g}}{B_{0g}}\right)\rho_{cr}-\left(\frac{B_{0l}+B_{0g}}{B_{0g}}\right)\rho_g, \tag{9a}$$

$$\rho_l-\rho_g=-\left(\frac{B_{0l}+B_{0g}}{B_{0l}}\right)\rho_{cr}-\left(\frac{B_{0l}+B_{0g}}{B_{0l}}\right)\rho_l. \tag{9b}$$

The linearity of these equations near ρ_{cr} is confirmed by the experimental data for the investigated Freon-113 and other substances, namely heptane,[12] benzene,[33] F-23,[15] and CO$_2$.[34] From the plot of $(\rho_1-\rho_g)=f(\rho)$ it is seen directly that $\Delta\beta=0$ or $\beta_{01}=\beta_{0g}$. It is of interest to note the fact that ρ_{cr} is closest to the experimental points of the substances for which the gravitational effect was measured (heptane, hexane, Freon-113).

For each of the substances, the slopes of the linear sections of the "gas" and "liquid" branches are not equal. The intercepts on the ordinate axes are related as

$$|(B_{0l}+B_{0g})/B_{0g}|:|(B_{0l}+B_{0g})/B_{0l}|.$$

It is convenient to check on the equality of this ratio to (or its deviation from) unity for all the substances simultaneously. To this end we can derive a single "universal" equation for all substances, by dividing Eqs. (9a,b) by ρ_{cr}:

$$\frac{\rho_l-\rho_g}{\rho_{cr}}=\frac{B_{0l}+B_{0g}}{B_{0g}}-\frac{B_{0l}+B_{0g}}{\rho_{cr}B_{0g}}\rho_g, \tag{10a}$$

$$\frac{\rho_l-\rho_g}{\rho_{cr}}=-\frac{B_{0l}+B_{0g}}{B_{0l}}+\frac{B_{0l}+B_{0g}}{\rho_{cr}B_{0l}}\rho_l. \tag{10b}$$

Figure 4 shows density data for various substances in relative units $(\rho_1-\rho_g)/\rho_{cr}=f(\rho/\rho_{cr})$. For all substances, the experimental points fall on two branches that emerge from the point 1.0, and the tangents drawn to these branches at this point have an intercept 2 on the $(\rho_1-\rho_g)/\rho_{cr}$ axis, i.e., in the limit as $|\tau|\to 0$ and $\rho\to\rho_{cr}$ we have

$$(B_{0l}+B_{0g})/B_{0l}=(B_{0l}+B_{0g})/B_{0g}=2,$$

which is possible if $B_{0g}=B_{cr}$.

Thus, the equalities $B_1=B_g=B$ and $\beta_1=\beta_g=\beta$ hold true in the limit in the asymptotic liquid–gas CC equation for all the considered substances. This confirms the validity of the symmetric asymptotic scaling theory. The values of B closest to asymptotic are obtained from an analysis of Eq. (7).

We note that Fig. 4 contains also additional information. First, it demonstrates clearly the need for taking into account the nonasymptotic terms in Eqs. (1) and (2). Second, the fact that the deviations of the experimental curves from the symmetrical lines are equal in absolute value is evidence that the asymmetric corrections to the liquid and gas branches of the CC should also be equal. By the same token, the choice of the forms used for Eqs. (1) and (2) is additionally justified.

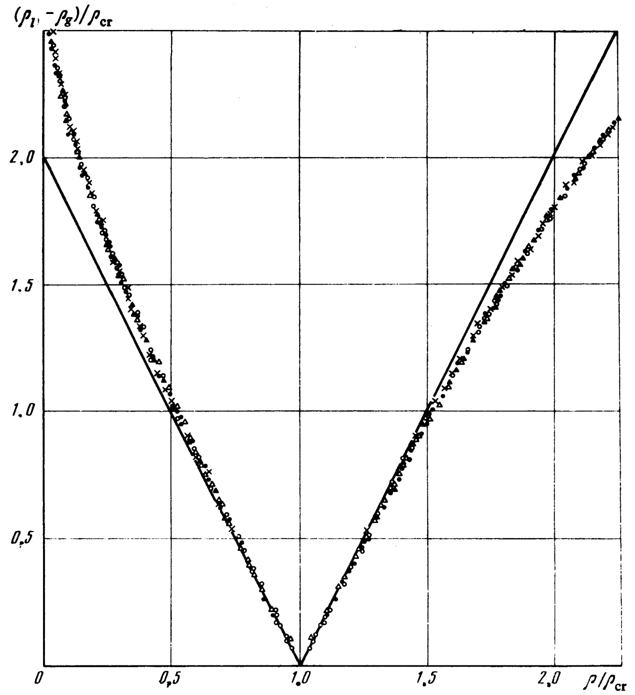

FIG. 4. Density data in terms of the reduced quantities $(\rho_1-\rho_g)/\rho_{cr}=f(\rho,\rho_{cr})$ for five substances: ○) heptane,[12] △) benzene,[33] ▲) CO$_2$,[34] ×) F-23,[16] and ●) Feron-113 (present results).

6. INVESTIGATION OF THE EXTENDED EXPANSIONS OF THE CC OF FREON-113

The determination of the succeeding (correction) terms in formulas (1) and (2) is a more complicated task, since these corrections are more strongly influenced by the measurement errors.

The first correction term for the CC is $B_1|\tau|^{\beta_1}$. The same term is simultaneously the leading term in formula (4) for the temperature dependence of the arithmetic mean of the densities—of the CC diameter. We can therefore attempt to determine β_1 and B_1 by using procedures similar to those employed to determine β_0 and B_0, i.e., retain in the right-hand side of (4) one term, and trace the temperature-dependent changes of the effective values of β_1 and B_1. We have reduced in this manner our experimental data for 20 temperature intervals in which the average temperature approached T_{cr} successively.

For the entire investigated temperature range $1.5\times10^{-4}<\tau<3.9\times10^{-4}$ we obtained the effective values $\beta_1=0.918\pm0.003$ and $B_1=0.886\pm0.004$ (at $\chi^2=6.4$). The large χ^2 of this calculation is evidence that the asymmetry for the entire temperature interval cannot be approximated by a single term, so that the obtained effective values of β_1 and B_1 are not true ones.

When the low-temperature points are excluded in succession (in steps of 2–5 points), one observes first a weak decrease of the effective β_1 and B_1, similar qualitatively to the temperature dependence of the effective values of the exponent and of the coefficient of the above-described leading term of the liquid branch of the CC. A decrease of χ^2 is observed in parallel. For intervals closer to T_{cr}, the errors in the calculation of β_1 and B_1 increase considerably, apparently as a result of the experimental errors, whose role increases with approach to the temperature region where the CC is practically completely described by its leading term.

This data reduction yielded the following limiting exponent and coefficient of the first correction term: $\beta_1 = 0.84 \pm 0.09$ and $B_1 = 0.71 \pm 0.08$. These results cannot be regarded as final, since the influences of the region close to critical, where the errors in the measurement of the CC diameter, and of the low-temperature region, where the influence of the term $B_3|\tau|^{\beta_3}$ should manifest itself, remain unexplained.

We determined β_3 and B_3 in two ways. The first was to shift to the left-hand side the term $B_1|\tau|^{\beta_1}$ with definite limiting values of the coefficient B_1 and of the exponent β_1, and use the calculated remainders to find the parameters β_3 and B_3. For the entire investigated temperature interval we then obtained $\beta_3 = 2.25 \pm 0.59$ and $B_3 = 0.37 \pm 0.13$. The large errors incurred in this method of finding β_3 and B_3 are perfectly natural, since the experimental errors are repeatedly summed in this case.

The other way was to use a four-parameter approximation of the experimental data in accord with (4), i.e., to find simultaneously all four parameters β_1, B_1, β_3, and B_3 obtained by the described computer program. The computer calculations were made for different temperature intervals. In accord with the best χ^2 we chose the following final values: $\beta_1 = 0.846 \pm 0.025$, $B_1 = 0.715 \pm 0.068$, $\beta_3 = 1.99 \pm 0.40$, and $B_3 = 0.398 \pm 0.035$. In this case $\chi^2 = 1$. We note that these values correspond to those of β_1, B_1, β_3, and B_3 obtained by the first method and given above. An analysis of the differences between the experimentally obtained values of the half-sum of the densities and those calculated from formula (4) with the indicated numerical values of the parameters are evidence that they agree with the experimental measurement errors in the entire investigated temperature interval.

In analogy with the analysis of the term $B_3|\tau|^{\beta_3}$, we analyzed the term $B_2|\tau|^{\beta_2}$ of formula (3). In this case the problem was simpler because the first term in the right-hand side of $B_0|\tau|^{\beta_0}$ was obtained with sufficient accuracy. Both ways (transfer of the term the left-hand side and simultaneous calculation of all four parameters of the right-hand side) yielded identical results: $\beta_2 = 1.36 \pm 0.12$, $B_2 = 0.311 \pm 0.021$, and $\chi^2 = 0.6$.

When the second procedure was used for temperature intervals close to critical, the values of β_0 and B_0 turned out to be the same as in the analysis of the behavior of the temperature dependence of the effective exponent and of the coefficient in accord with the single-term formula as τ tends to zero, but with smaller errors ($\beta_0 = 0.342 \pm 0.003$, $B_0 = 2.023 \pm 0.013$). Comparison shows that $\beta_0 < \beta_1 < \beta_2 < \beta_3$.

Thus, to describe the Freon-113 coexistence curve with allowance for its "diameter," we obtained the formula

$$\frac{\rho - 0.5665}{0.5665} = \pm(2{,}023 \pm 0{,}013)\,|\tau|^{0{,}342 \pm 0{,}003} + (0{,}715 \pm 0{,}068)\,|\tau|^{0{,}846 \pm 0{,}025} \pm (-0{,}311 \pm 0{,}021)\,|\tau|^{1{,}36 \pm 0{,}12} + (0{,}398 \pm 0{,}035)\,|\tau|^{1{,}99 \pm 0{,}40} \tag{11}$$

The agreement between this formula and the experimental data can be illustrated by Figs. 5a and 5b, which shows plots of the remainders—the differences between the experimental data and the successively calculated values of ρ from the single-, two-, three-, and four-term formulas for the liquid and gas branches of the CC. The only difference is that, owing to the negative value of B_2, the term $B_2|\tau|^{\beta_2}$ and $B_3|\tau|^{\beta_3}$ on the liquid branch cancel each other almost completely. The contribution of each of the terms for the liquid and gas branches of the CC is illustrated in Table II. The ratio of the percentage contributions of the different terms at any fixed temperature can be grounds for concluding that we have actually succeeded, by using the described reduction of the experimental data, to obtain

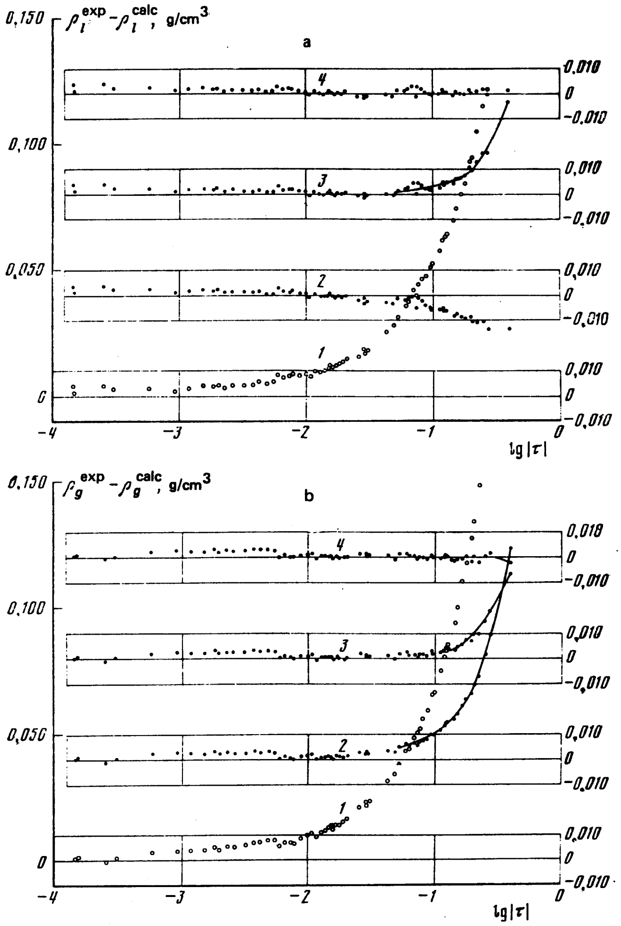

FIG. 5. Temperature dependence of the remainders calculated for the liquid (a) and gas (b) branches of the CC of Freon-113 using the formulas: 1) $\rho^{exp} - \rho^{calc} = \rho^{calc} - \rho_{cr}(1 \pm B_0|\tau|^{\beta_0})$, 2) $\rho^{exp} - \rho^{calc} = \rho^{exp} - \rho_{cr}(1 \pm B_0|\tau|^{\beta_0} + B_1|\tau|^{\beta_1})$, 3) $\rho^{exp} - \rho^{calc} = \rho^{exp} - \rho_{cr}(1 \pm B_0|\tau|^{\beta_0} + B_1|\tau|^{\beta_1} \pm B_2|\tau|^{\beta_2})$, 4) $\rho^{exp} - \rho^{calc} = \rho^{exp} - \rho_{cr}(1 \pm B_0|\tau|^{\beta_0} + B_2|\tau|^{\beta_2} + B_3|\tau|^{\beta_3}$, where $\beta_0 = 0.342$, $\beta_1 = 0.846$, $\beta_2 = 1.359$, $\beta_3 = 1.99$; $B_0 = 2.023$, $B_1 = 0.715$, $B_2 = -0.311$, and $B_2 = 0.398$.

TABLE II. Percentage contribution made to the functional relation ($\rho-\rho_{cr} = \pm B_0|\tau|^{\beta_0} + B_2|\tau|^{\beta_2} + B_3|\tau|^{\beta_3}$ for the liquid and gas branches of the CC of Freon-113.

	Number of experimental points				
	66	61	44	14	1
$\tau=(T-T_{cr})/T_{cr}$	$1.5\cdot10^{-4}$	$0.92\cdot10^{-3}$	$0.99\cdot10^{-2}$	$1.116\cdot10^{-1}$	0.3957
liquid branch of CC					
$y_l=[(\rho_l-\rho_{cr})/\rho_{cr}]^{calc}$	100%	100%	100%	100%	100%
$B_0\|\tau\|^{\beta_0}/y_l$	99,59%	98.98%	96.79%	90.43%	83,04%
$B_1\|\tau\|^{\beta_1}/y_l$	0.42%	1.03%	3.34%	10.59%	18.39%
$B_2\|\tau\|^{\beta_2}/y_l$	−0.00%	−0.01%	−0,14%	−1.50%	−4.97%
$B_3\|\tau\|^{\beta_3}/y_l$	0,00%	0.00%	0.01%	0.48%	3.54%
ρ_l^{exp}, g/cm³	0.6262	0.6737	0.8109	1.1641	1.5715
ρ_l^{exp}, g/cm³	0.6232	0.6725	0.8108	1,1652	1.5716
$(\rho_l^{exp}-\rho_l^{calc})/\rho_l^{exp}$	0.48%	0.18%	0.015%	0.09%	0.01%
gas branch of CC					
$y_g=[(\rho_g-\rho_{cr})/\rho_{cr}]^{calc}$	100%	100%	100%	100%	100%
$-B_0\|\tau\|^{\beta_0}/y_g$	100.42%	101.06%	103.74%	116.12%	147,93%
$B_1\|\tau\|^{\beta_1}/y_g$	−0,42%	−1.05%	−3.58%	−13.59%	−32,77%
$-B_2\|\tau\|^{\beta_2}/y_g$	−0.00%	−0.01%	−0.15%	−1,92%	−8.85%
$B_3\|\tau\|^{\beta_3}/y_g$	−0,00%	−0.00%	−0.01%	−0,61%	−6.31%
ρ_g^{exp}, g/cm³	0.5110	0.4653	0.3401	0.1004	0,0018
ρ_g^{calc}, g/cm³	0.5103	0.4627	0,3386	0.1003	0,0022
$(\rho_g^{exp}-\rho_g^{calc})/\rho_g^{exp}$	0.13%	−0.56%	0.4%	0.1%	−20%

the first four terms of the converging term that describes the CC in the entire region of the existence of the first-order liquid–vapor phase transition. The change of this ratio as the temperature approaches the critical value is evidence that the convergence improves as $\tau\to0$, that the role of the first term is increased, and that the symmetrical theory of critical phenomena is valid in the indicated limit.

Additional arguments favoring the validity of the obtained expression are the following. The region of convergence of the series should extend all the way to $\tau=-1$. When the formula is extrapolated to absolute zero temperature, where the gas density should also be zero, formula (2) leads to the equality

$$1+B_1+B_3+\ldots=B_0+B_2\ \ldots .$$

It follows from the assumption that the functional series converge that the numerical series in the left- and right-hand sides should also converge. We can therefore expect satisfaction of the approximate equalities

$$1+B_1\approx B_0+B_2,$$
$$1+B_1+B_3\approx B_0+B_2+B_4$$

and so forth. The obtained numerical values of the coefficients show that the first of the foregoing approximate equalities is well satisfied $[1+0.715\approx2.023+(-0.311)$ or $1.715\approx1.712]$.

7. DISCUSSION OF EXPERIMENTAL RESULTS

The foregoing analysis of the experimental data shows that the liquid and gas branches of the CC are well described in a large region near the critical point by the generalized formula $(\rho-\rho_{cr})/\rho_{cr}=\pm F(\tau)+f(\tau)$, where $F(\tau)$ and $f(\tau)$ are respectively the symmetrical and asymmetrical parts of the CC equation, and are the same for the coexisting liquid and vapor. The obtained data on Freon-113 disagree therefore with all the theories in which differences are assumed either between the coefficients or between the exponents of the formulas for the liquid and gas branches.[5]

When the critical point is approached, the densities of the coexisting liquid and vapor have an asymptotically symmetrical power-law dependence on the temperature. The obtained value $\beta_0=0.342\pm0.003$ agrees well with the results of the latest experimental studies of liquid–gas critical phenomena,[24] as well as with the results of renormalization-group calculations and calculations by the ε-expansion method accurate to quadratic terms. The coefficient of the leading term $B_0=2.023\pm0.013$ is close to the corresponding values determined for other substances,[11-24] but the quantitative differences exceed the errors indicated by the authors. It can be assumed that the coefficient B_0, as well as incidentally all other coefficients, is an individual characteristic of the substance.

The limiting symmetrical behavior of the CC still does not mean that the half-sum of the densities (the CC diameter) depends linearly on the temperature or is *a fortiori* constant even near the critical point. The obtained two-term temperature dependence of the CC diameter has a leading term with an exponent $\beta_1=0.846\pm0.025$. This value, with the error taken into account, is close to the result of those investigations in which the values of β_1 were not fixed beforehand. For example, values $\beta_1=0.88\pm0.08$ and $\beta_1=0.866\pm0.026$ are cited in Refs. 22 and 23, respectively. In Ref. 24 was used the expression $\beta_1=1-\alpha$ determined by the method of algebra of fluctuating quantities, together with the value $\alpha=0.11$ obtained from heat-capacity experiments. The value β_1 calculated in this manner was fixed in the course of the subsequent reduction of the experimental data, and this undoubtedly affected the coefficient B_1 and the following terms of the expansion. However, this shift is apparently not large, since the value of β_1 obtained by us directly from experiment, with allowance for the experimental errors, is close to $1-\alpha$. The patent deviation of β_1 from unity is evidence that the CC diameter is singular at the critical point.

We know of only one experimental study[18] in which β_2 was estimated to be of the order of 1.3. A study[23] of the mixing CC of a polystyrene–cyclohexane system using a four-parameter approximation of the concentration difference yielded a value of β_2 slightly higher than unity. Both our result $\beta_2=1.36\pm0.12$ and the aforementioned data by others differ very greatly from the estimates based on the renormalization-group approach, which yielded $\beta_2=\beta_0+\Delta$ with $\Delta=0.5$ (Ref. 6) and $\Delta=0.45$ (Ref. 10).

We found no published report of an experimental determination of β_3. In the reduction of the experimental data on the CC the corresponding term of the expansion was either disregarded completely or was calculated and fixed by choosing the value of β_3 in accord with some theoretical considerations.[21,22,24]

It is useful to compare our results with the theories that describe the CC in the form of series, and predict an interrelation between the exponents.[4,5,8] By expanding in powers of the thermodynamic variables, Cooper found an equation of state that led to a coexistence curve in the form of a series with exponents β_0, $2\beta_0$, $3\beta_0, \ldots$, which patently contradict our experimental data. In the later paper[5] a series $\beta_0, \beta_0+1/\varepsilon', \beta_0+2/\varepsilon', \ldots$ was proposed for the exponents, with ε', a certain new parameter of the generalized theory of parametric scaling. This theory can be reconciled with our data if we assume that $1/\varepsilon' = 0.5$, a value close to the conclusions of Ref. 21.

An outwardly similar result was obtained by Chalyi.[8] By expanding in the reciprocal of the correlation radius he obtained an equation of state from which follows a polynomial equation for the CC with the exponent series β_0, $\beta_0+\nu, \beta_0+2\nu$, etc. In accord with the sense of the derivation, ν is the critical exponent of the temperature dependence of the correlation radius. The exponent ν is assigned a value 0.5 in the self-consistent-field theory, 0.638 in the three-dimensional Ising model, and 0.626 in the ε-expansion method (accurate to terms ε^2). On the basis of our results, the value of this critical exponent in the description of the CC should be assumed close to the classical $\nu = 0.5$, which is not understandable.

8. CONCLUSION

The experimental investigations of the CC of Freon-113 in a wide range of temperature, including the close vicinity of the critical point, and the statistical computer reduction of the results, show that the coexistence curve can be satisfactorily described by a formula with a minimum of four terms. In the choice of the numerical values of the coefficients and of the exponents of the corresponding expression, an important role is played by the establishment of the values of the critical parameters within the limits of their experimental error. A correct determination of these parameters provides an experimental confirmation of the theory of zero-order symmetric scaling.

A comparison of the experimentally obtained symmetrical and asymmetrical correction terms with the results of the theories developed to date offers evidence that none of the existing theories is as yet adequate for a quantitative description of a large vicinity of the critical point. Nonetheless the nonanalytic enlarged expansions obtained by now are in good qualitative agreement with the experimental data in a wide range of state parameters. This gives grounds for hoping to obtain in the nearest future, by taking the fluctuating quantities into account, a quantitative state equation that covers a large region of the existence of the liquid and gas and of their mutual phase transitions. Even now it is at least possible to regard the entire region of the liquid–gas phase transition as the vicinity of the critical point.

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Effect of electron-electron collisions on the energy distribution of excess quasiparticles in superconductors

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A solution is obtained of the kinetic equation for the distribution function of the excess quasiparticles produced by a broad source, with account taken of the electron-electron collisions. It is shown that these collisions do not alter qualitatively the form of the quasiparticle distribution function if the electron-electron interaction constant is not zero.

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INTRODUCTION

It can be regarded as established that many properties of nonequilibrium superconductors with an excess of quasiparticles are determined by the form of the quasiparticle distribution function (QDF), particularly by the character of the dependence of the order parameter Δ on the temperature and on the strength β of the quasiparticle source, by the sign of the current that describes the linear response to the magnetic field, by the stability of the states to inhomogeneous perturbations, and by others. The foregoing effects are exceedingly sensitive to the energy distribution of the nonequilibrium quasiparticles produced by the source (optical pumping or tunnel injection). In fact even small deviations of the QDF from the equilibrium distribution

$$n_T=(e^{\varepsilon/T}+1)^{-1}$$

can radically alter the picture and lead to ambiguous dependences of Δ on T and β, to the appearance of instabilities of different types, and to reversal of the sign of the current in the magnetic field. For a correct description it is therefore necessary to find the QDF from the corresponding kinetic equations obtained by Eliashberg.[1]

For a broad source, such solutions were obtained earlier[2] near the phase transition region, where $\Delta/\Delta_0 \ll 1$(Δ_0 is the order parameter in the absence of pumping), and in the entire interval of Δ/Δ_0.[3] It was shown that $n(\xi)$ is a monotonically decreasing function ($\xi=p^2/2m-E_F$, E_F is the Fermi energy), does not exceed $\frac{1}{2}$, and is localized in an energy interval $\xi\sim\Delta_0$. If $n(\xi)$ is compared with n_T, then a characteristic property is the "superheat" of the energy distribution of the nonequilibrium quasiparticles,[1)] i.e., the decrease of the number of quasiparticles near small ξ, particularly at $\xi=0$:

$$n(\xi=0)<n_T(\xi=0). \tag{1}$$

This decrease is due to the increase of the recombination rate of the quasiparticles at small ξ because of the coherent factors in the kinetic equation, which take into account the coherent character of the interaction of the quasiparticles with the phonons.

Coherent factors play a major role in the considered phenomena, so that it is convenient to separate their contribution to the QDF by changing over to the form[2]

$$n(\xi)=n_0+n_1,\quad \varepsilon=(\xi^2+\Delta^2)^{1/2}, \tag{2}$$

where n_0 satisfies the kinetic equation with zero coherent factors and n_1 is the correction necessitated by the coherent factors. It has been shown[3,6] that the function n_0 reaches a maximum equal to $\frac{1}{2}$ at $\xi=0$:

$$n_0(0)=1/2, \tag{3}$$

after which it decreases monotonically. In the interval $0<\xi<\bar{\xi}$, where $\bar{\xi}/\Delta_0\sim4$, the function n_0 is close to the thermal one, after which it falls off more slowly than n_T.

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