Scaling theory and the equation of state of argon in a wide region around the critical point

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(Submitted August 7, 1973)
Zh. Eksp. Teor. Fiz. **66**, 742–757 (February 1974)

It is shown, on the basis of an analysis of earlier and newly obtained experimental data on the thermodynamic properties of argon, that a scaling equation of state can be used as a zeroth-order approximation to describe a gas and liquid in a wide interval of variation of the state parameters around the critical point: $-0.8 \lesssim \Delta p = (p - p_c)/p_c \lesssim 0.4$, $t = (T - T_c)/T_c \lesssim 0.5$. It is shown that the "linear model" of the scaling equation of state gives a correct description of the critical region of argon within an accuracy of 1%. The universality of the "linear-model" coefficients are discussed. It is shown experimentally that the corrections to the asymptotic ($t \leqslant 1$) behavior of the specific heat in the region $t \leqslant 0.3$ are nonanalytic and may be related to the subsequent approximations of scaling theory.

1. INTRODUCTION

At the present time the success of scaling theory[1,2] in describing the anomalous behavior of thermodynamic quantities near the critical point of a liquid is generally recognized. Of course, certain unclear points and disagreements between theory and experiment still exist and are subject to intensive discussion (see[3]). But there is no doubt that the most significant features of critical phenomena have been grasped correctly. Although the theory[1,2] claims validity only as an asymptotic ($T \to T_c$, $\rho \to \rho_c$) description of the critical region, and in practice the scaling equation of state is sufficiently accurate only within a range of a few percent around T_c and ρ_c[4-8], there are experimental indications that this interval can be extended considerably[9,10]. It has therefore been suggested[10] that scaling theory can serve as a basis for a new approach to the physics of the liquid state.

In the present work, on the basis of an analysis of the earlier and newly obtained experimental data on the thermodynamic properties of argon, we demonstrate the possibility of using the scaling equation of state as a zeroth-order approximation for the description of a liquid and dense-gas over a wide range of densities and temperatures:

$$-0.8 \leqslant \Delta\rho = \frac{\rho - \rho_c}{\rho_c} \leqslant 0.4, \quad t = \frac{T - T_c}{T_c} \leqslant 0.5$$

in the one-phase region.

It is well known that the thermodynamic quantities of liquids and dense gases, unlike those of solids and rarefied gases, cannot be calculated in general form, since in the absence of a small parameter the specific laws governing the interactions between the particles play the predominant role[11,12]. The situation is different near the critical point. Here the thermodynamic quantities are determined by growing fluctuations that are universal in character[1,2,13] and, equally importantly, provide the primary contribution over practically the entire region $t < 1$ and $|\Delta\rho| < 1$. On this experimental fact is based the proposed approach: to regard the individual properties of liquids in this region as corrections to the universal zeroth-order approximation, the critical state.

We have confined our analysis of the experimental data to the range of t and $\Delta\rho$ in which the corrections to the zeroth-order approximation are small. We shall show also that at $\rho < \rho_c$ this range merges with the region where the virial expansion is valid (see Fig. 1). As for a dense liquid, we can expect the existence of another zeroth-order approximation, since in the vicinity of the crystallization line the thermodynamic quantities again display some common features[12,17].

2. EQUATION OF STATE IN THE ZEROTH-ORDER APPROXIMATION

The question naturally arises: what specific form of the equation of state should be taken as the zeroth-order approximation, and to what extent is it universal? Widom[18] has suggested the following equation of state for a liquid near the critical point:

$$\Delta\mu = \Delta\rho\,|\Delta\rho|^{\delta-1} h(x), \tag{1}$$

from which the expression for the specific heat follows immediately:

$$\frac{\rho C_v}{T} = \frac{MP_c}{T_c^2}\left[\,|\Delta\rho|^{-\alpha/\beta} f(x) - \mu''(\rho_c, T)\Delta\rho + B(T)\right]. \tag{2}$$

In Eqs. (1) and (2) we use

$$\Delta\mu = \frac{1}{P_c V_c}[\mu(\rho, T) - \mu(\rho_c, T)], \quad \mu''(\rho_c, T) = \frac{T_c^2}{P_c V_c}\left(\frac{\partial^2\mu}{\partial T^2}\right)\Big|_{\rho=\rho_c},$$
$$B(T) = \psi(T) - \mu''(\rho_c, T),$$

$\mu(\rho, T)$ is the chemical potential, $h(x) = h(t/|\Delta\rho|^{1/\beta})$ and $f(x) = f(t/|\Delta\rho|^{1/\beta})$ are functions with known asymptotic forms[1,2], $\mu(\rho_c, T)$ and $\psi(T)$ are analytic

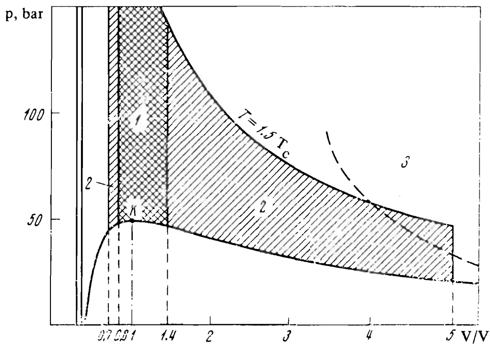

FIG. 1. P-V diagram of Ar. Area 1 corresponds to the region of validity of the "zeroth-order approximation" given by Eqs. (1) and (2), and area 2 to the introduction of the first correction ($\sim\Delta\rho^2$) to Eq. (2). The dashed line is the tentative boundary of the region 3 in which the virial equation of state, with second and third virial coefficients [14-16], is valid.

functions of the temperature, and M is the molecular weight.

A purely empirical choice of the function h(x) was suggested in[4], where the available experimental data for CO_2, Xe, O_2, He^4, and He^3 were analyzed. The analysis in[4] (mainly P-V-T data) indicated a critical exponent $\alpha \approx 0.04$ for the specific heat in Xe, CO_2, and He^4. This does not agree with the results $\alpha = 0.10$ to 0.13 of direct measurements of the specific heat in the given substances[19,20]. For He^3 (the reference of[4]) a systematic divergence (~10%) between the experimental data on the specific heat and the calculated curve was observed[7].

The parametric representation proposed by Josephson and Schofield[21] is both simple and physically clear. A special case of this representation is the so-called "linear model" (LM) of the equation of state[22], which is obtained by eliminating the variable r that characterizes the "distance" from the critical point and the "angular" variable θ from the system of equations

$$\Delta\mu=ar^{\beta\delta}\theta(1-\theta^2),\quad t=r(1-b^2\theta^2),\quad \Delta\rho=kr^\beta\theta, \tag{3}$$

where $b^2 = (\gamma - 2\beta)/\gamma(1 - 2\beta)$, and γ, β, and δ are the respective critical exponents of the compressibility, the coexistence curve, and the critical isotherm[1,2].

Migdal[23] obtained an equation of state by assuming analyticity of the isocline:

$$\zeta=\varphi(\eta)=\eta+\varphi_3\eta^3+\varphi_5\eta^5+\dots, \tag{4}$$

where

$$\zeta=\Delta\mu\left[\frac{P_cV_c^2}{M}\left(\frac{\partial\rho}{\partial\mu}\right)_T\right]^{(\beta+\gamma)/\gamma},\quad \eta=\Delta\rho\left[\frac{P_cV_c^2}{M}\left(\frac{\partial\rho}{\partial\mu}\right)_T\right]^{\beta/\gamma}.$$

He showed that Eq. (4), using only the terms in η and η^3, can lead by a change of variables to an LM with the additional requirement $\tilde{\epsilon} = \beta + \gamma - 3/2 = 0$. Inclusion of the terms $\sim\eta^5$ leads to corrections in $\tilde{\epsilon}$ to the LM, but this gives rise to a new condition on the relation between β and γ.

Thus the relationship between the LM and the Migdal equation remains not entirely clear. We have carried out the reverse analysis, constructing the isocline equation from the LM:

$$\zeta=k\left(\frac{k}{a}\right)^{\beta/\gamma}\theta(1-\theta^2)[\Psi(\theta)]^{(\beta+\gamma)/\gamma}, \tag{5}$$

$$\eta=k\left(\frac{k}{a}\right)^{\beta/\gamma}\theta[\Psi(\theta)]^{\beta/\gamma}, \tag{6}$$

where

$$\Psi(\theta)=\left(1+\frac{2\tilde{\varepsilon}}{1-2\beta}\theta^2\right)^{-1}.$$

By eliminating θ from Eqs. (4) and (5) and noting that $\tilde{\epsilon} \ll 1$, we obtain the complete series $\zeta(\eta)$ with the coefficients

$$\varphi_3=-\frac{1}{k^2}\left(\frac{a}{k}\right)^{2\beta/\gamma}\left[1+\frac{2\tilde{\varepsilon}}{1-2\beta}\right], \tag{7}$$

$$\varphi_5=\frac{1}{k^4}\left(\frac{a}{k}\right)^{4\beta/\gamma}\frac{2\tilde{\varepsilon}}{1-2\beta}\left(1+\frac{3+2\tilde{\varepsilon}}{1-2\beta}\right)\left(1-\frac{2\beta}{\gamma}\right), \tag{8}$$

and so on.

The ratio φ_5/φ_3^2 differs from the corresponding result of Migdal in the second order in $\tilde{\epsilon}$, which corresponds to the subsequent terms of the $\zeta(\eta)$ series (from Eqs. (5) and (6) we have $\varphi_7 \sim \tilde{\epsilon}^2$), which were omitted[23] in deriving the expression for φ_5/φ_3^2.

We see thus from the above simple comparison of the LM and the Migdal equation that the difference between them is insignificant at the current experimental accuracy; it appears only in the second order in $\tilde{\epsilon} = \beta + \gamma - 3/2 \approx 0.06$.

This conclusion is also confirmed by the results of Brézin, Wallace, and Wilson[24] and Avdeeva and Migdal[25], who obtained both the isocline equation (4) and the LM equation (3) using the Wilson method[26] in the same approximations. This does not mean, of course, that the LM is perfect. Although many experiments agree with the LM within a few percent[5,7,8,22], its adequacy to describe the influence of the gravitational effect on the specific heat remains unclear[27]. In this case either the predictions of the LM are wrong, or the interpretation proposed in[27] for the calorimetric experiment in a gravitational field must be reexamined. In any case, the LM can at present be regarded both as sufficiently well justified and as convenient for the comparison of the equation of state near the critical point with experiment, and we shall base the following analysis on it.

Let us write down the expressions arising from the LM for the homogeneous chemical-potential and the specific-heat functions that are used below:

$$h(x)=a\theta(1-\theta^2)(k|\theta|)^{-\delta}, \tag{9}$$

$$f(x)=\frac{ak}{2\alpha b^2}\gamma(\gamma-1)(k|\theta|)^{-\alpha/\beta}, \tag{10}$$

$$x=t|\Delta\rho|^{-1/\beta}=(1-b^2\theta^2)(k|\theta|)^{-1/\beta}. \tag{11}$$

If we now use Eq. (11) to eliminate θ from Eqs. (9) and (10), we obtain for h(x) and f(x) expressions that represent products of universal functions of the argument $k^{1/\beta}x$ and factors that depend on combinations of a and k, in agreement with the condition of scaling invariance (see[25]).

To compare Eqs. (9) and (10) with experiment we must determine any two of the four exponents α, β, γ, and δ, which are connected by two theoretical scaling relations[1,2]:

$$\alpha+2\beta+\gamma=2, \tag{12a}$$

$$\beta(\delta-1)=\gamma, \tag{12b}$$

and the two coefficients a and k. Of these, k can be determined from the measured behavior of the density of the coexistent phases, according to Eq. (11) at $|\theta| = 1$ ($\Delta\rho = \pm(|t|/x_0)^\beta$, $k = [(b^2 - 1)/x_0]^\beta$). Then a can be found, for instance, from the value of the coefficient $A^+(t > 0)$ in the singular part of the specific heat

$$C_V/T=A^\pm t^{-\alpha^\pm}+B_0^\pm, \tag{13}$$

where, in accordance with Eq. (3),

$$\frac{T_c^2}{P_cV_c}A^+=\frac{ak}{2\alpha b^2}\gamma(\gamma-1).$$

In its phenomenological form[1,2], scaling theory does not require that the critical indices, and even less the coefficients, be universal. On the other hand, such universality is desirable in order for the critical state to be used as a "zeroth-order approximation" to describe liquids and dense gases just as effectively as the equation of state of an ideal gas is used to describe rarefied gases.

An analysis of the experimental data shows that the scatter in the values of the critical exponents obtained for various substances (with the possible exception of quantum liquids) does not exceed the experimental scatter of the same quantity measured in the same substance by different methods and in different laboratories. The most probable (in our opinion) values of the critical exponents for simple liquids are presented in Table I (Chu[28] gives the same estimates for β and ν). It is apparent from Table I that the exponents in liquids are very close to the results of numerical calculations of the three-dimensional lattice gas[29] and calculations by the ϵ-expansion method[26] ($\epsilon = 4 - d$, where d is the dimensionality of the space)[1)]. The relations between the exponents are satisfied within the limits of experimental error with some margin, in that the relation containing the dimensionality $d = 3$ is better satisfied for liquids than for the results of the numerical calculations in the lattice-gas model.

Since the ratio of the coefficients A^-/A^+ in the LM, like the parameter b (see Eq. (3)), depends only on the critical exponents, it also must be universal (to the extent that the critical exponents are universal):

$$\frac{A^-}{A^+}=4\left(\frac{\beta}{\gamma}\right)^2\left[\frac{\gamma(1-2\beta)}{2\beta(\gamma-1)}\right]^{\gamma+2\beta}. \tag{14}$$

There is also some reason to hope for a certain amount of universality in the coefficients a and k themselves. The quantity $x_0^{-\beta} \sim k$ is the same for different substances within ~10% (again with the exception of the quantum liquids), and the differences are due to the choice of different values for β. Evidently we can state that x_0, and therefore k, are universal within the accuracy of the law of corresponding states.

There are considerations[30] from which we can estimate the degree of non-universality of a. We write the free energy near the critical point in the form

$$F=F_0V/r_c^3, \tag{15}$$

where the correlation radius is

$$r_c=r_0t^{-\nu}R(x/x_0). \tag{16}$$

It is assumed[30] that $R(x/x_0)$ is a universal function. This assumption is equivalent to the condition of scaling invariance (see[25]). It follows from Eq. (15) that the non-universal part of the coefficients depends on the parameter F_0V_c/r_0^3; for example, $A^+ = F_0(2 - \alpha) \times (1 - \alpha)\cdot(V_c/r_0^3)T_c^{-2}$. Analysis of the experimental data (see Table II) shows that F_0 is a universal constant for Ar, Xe, and CO_2 with an accuracy no worse than 5%, and differs from F_0 in a lattice gas by ~15%.

TABLE I. Probable critical exponents in simple liquids and in the lattice-gas model

	α	β	γ	ν	$\alpha+2\beta+\gamma-2$	$2-\alpha-d\nu$
Liquids	0.12±0,02	0,34±0.02	1,23±0,02	0,63±0.02	0,03±0,08	0,01±0,06
	Numerical methods					
Three-dimensional lattice gas	0,125	0,312 (5)	1,250	0,638	0	0,04
	ϵ-expansion (includes term $\sim\epsilon^2$)					
	0,077	0,339 (5)	1,244	0,634	0	0,02

TABLE II. Relations between coefficients of the equation of state near the critical point and the microscopic parameters of liquids

	$x_0^{-\beta}$ ($\sim k$)	r_0, Å	V_C/r_0^3	$\mathscr{A}^+r_0^3 V_C$	σ, Å	$\sigma/2r_0$
Ar	1.67	1.7 [31]	25,4	0.15 [10]	3,40 [14, 16]	1.0
Xe	1.70	2,1 [32]	21.6	0.16 [20]	4.22 [15] 4.10 [16]	1.0 0.98
CO_2	1,87	1.6 [33]	38,3	0.15 [20]	3.27 [16]	1.0
TLG (numerical methods)				0.133 [30]		1,0

Note. The following notation is used: TLG is the three-dimensional lattice gas; $\mathscr{A}^+ \equiv A^+T_c^2/k_B$. The experimental values of r_0 and A^+ are computed with $\nu = 0.625$ and $\alpha = 2-3\nu = 0.125$; for fixed α and ν, the error in r_0 and A^+ does not exceed 2–3%. The values of x_0 are given for $\beta = 0.33$.

Thus the basic non-universal parameter that determines the equation of state near the critical point is the ratio V_c/r_0^3. However, it is worth noting that twice the direct correlation radius r_0 proves to be almost exactly equal to the parameter σ—the so-called collision diameter—in the Lennard-Jones potential (spherical molecules) for Ar and Xe, and in the Kihara potential (cylindrospherical molecules) for CO_2. It is therefore quite possible that, at least for simple liquids, there exists a universal combination of r_0 and σ.

For a further analysis we need the parameters of the zeroth-order approximation. The following values were obtained in[10] for argon in the asymptotic, and at the same time methodologically reliable, interval $t = 10^{-2}$ to 10^{-4}: $\alpha^+ = 0.11 \pm 0.02$, $\beta = 0.34 \pm 0.02$, $x_0 = 0.21 \pm 0.01$, $A^+ = 0.270$ J/mole-deg², $B_0^+ = -0.243$ J/mole-deg², and $A^-/A^+ = 1.92$ (for $\alpha = 0.11$). The values chosen for the LM parameters are given below:

$$T_c=150.66(4)\ °\mathrm{K};\quad \rho_c=0.531(5)\ \mathrm{g/cm^3};\quad P_c=48.5\ \mathrm{bar};\quad \alpha=0.11;\quad \beta=0.33;\quad \gamma=1.23,\quad k=1.20;\quad a=15.0;\quad A^-/A^+=1.95. \tag{17}$$

The value of γ was calculated from Eq. (12a) and agrees with the directly measured[31] value $\gamma = 1.20 \pm 0.05$. The value $\beta = 0.33$ appears to us to be preferable to $\beta = 0.34$, since the reduction of this value by 0.01 (within the limits of experimental error) sharply improves the agreement of the value of A^-/A^+ calculated from Eq. (13) with experiment.

As a rule, the coefficient ratio A^-/A^+ can be determined experimentally with greater accuracy than the critical exponents. The dependence of A^-/A^+ on β and γ can be represented (Eq. (13)) by a graph in which the axes are A^-/A^+ and β, and on which a network of lines of constant α and γ is plotted (Fig. 2). It is a property of the graph that each point of its plane corresponds to three critical exponents related by Eq. (12a). The sensitivity of the ratio A^-/A^+ to the values of β and γ is clearly apparent. The universality of A^-/A^+ is a necessary condition for the universality of the exponents α, β, and γ, and can be used as a criterion for the self-consistency of the experimental data. As may be seen

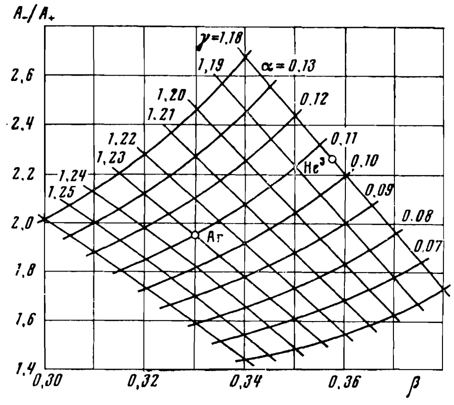

FIG. 2. Ratio of the specific heat coefficients on the critical isochor above and below T_C as a function of the critical exponents, from Eq. (14).

from Fig. 2, self-consistent results are obtained only for argon[10] and He^3[7], while for CO_2, for instance, direct measurements[20] give $\alpha = 0.125$ and $A^-/A^+ = 1.88$, and the values $\beta = 0.35$ and $\gamma = 1.26$ cited in[4] lead to $A^-/A^+ = 1.3$ (another variant, using the same value of β and $\alpha = 0.125$[20], gives $A^-/A^+ = 2.6$).

3. CORRECTIONS TO THE ASYMPTOTIC LAWS

As the system recedes from the critical point, corrections to the asymptotic laws must be taken into account. The nature and form of these corrections can differ. Let us first consider the corrections that arise even in the "ideal" lattice-gas system. For this model the function $\mu(\rho_c, T)$ in the asymptotic laws (1) and (2) is linear, so that $\mu''(\rho_c, T) = 0$ and complete symmetry exists with respect to the critical isochor.

Wegner[34] obtained nonanalytic corrections to the "ideal" system by the ϵ-expansion method[26]. Since these corrections are related to the subsequent approximations of scaling theory, they are universal. A real liquid lacks the total symmetry of a lattice gas. Even the Widom equation (1), which is symmetric with respect to the critical isochor, leads to some asymmetry in the specific heat (2) if $\mu''(\rho_c, T) \neq 0$.

Fisher[35] suggested a general approach for describing real systems in the language of "ideal" systems by means of a special transformation of the thermodynamic variables2) (see also[3]). Pokrovskiĭ[38] showed that for the transition from a lattice gas to a real liquid this transformation is linear. One consequence of this is the "singular diameter" of the coexistence curve. The following are the formulas for the corrections to the asymptotic laws, which correspond to the next order of approximation in scaling theory[34] and to the inclusion of asymmetry in real liquids[38]:

$$|\Delta\rho| - (|t|/x_0)^\beta = \begin{cases} \sim |t|^{\beta+\Delta} & [^{34}] \\ \sim |t|^{1-\alpha} & [^{38}] \end{cases}, \quad \Delta\mu|_{\rho=\rho_c} = \begin{cases} 0 & [^{34}] \\ \sim t & [^{38}] \end{cases},$$

$$\left[\frac{C_V}{T} - (A^+ t^{-\alpha} + B_0)\right]_{\rho=\rho_c} = \begin{cases} \sim t^{-\alpha+\Delta} & [^{34}] \\ \sim t^{-\alpha+2(1-\alpha-\beta)} & [^{38}] \end{cases},$$

$$\left[\left(\frac{\partial\rho}{\partial\mu}\right)_T - \Gamma t^{-\gamma}\right]_{\rho=\rho_c} = \begin{cases} \sim t^{-\gamma+\Delta} & [^{34}] \\ \sim t^{-\alpha} & [^{38}] \end{cases}.$$

To first order in ϵ we have $\Delta = 1/2$.

Green, Cooper, and Levelt-Sengers[39] have proposed a special parametric equation of state for liquids that also gives rise to a "singular diameter." The corrections to the other quantities in[38] and[39] are different. For instance, the specific-heat correction term obtained by Pokrovskiĭ[38], which vanishes on going to "isomorphic" variables, corresponds to the second-order correction in[39]. However, it is easy to show3) that these corrections[39] do not satisfy the ϵ-expansion[26] and thus cannot be regarded as the next order of approximation in scaling theory.

By taking into account the specific properties of the liquids[38] we obtain nonsymmetric, nonanalytic corrections to the asymptotic temperature dependence of the liquid and gas densities ρ_l and ρ_g on the coexistence curve. These corrections cancel out when the temperature dependence of $\rho_l - \rho_g$ is analyzed. However, there still remain some symmetric corrections that appear even in an "ideal" system. These corrections may possibly lead to systematic overestimates of the experimental values of $\beta \approx 0.34$ to 0.36 compared to the results obtained by numerical methods for the three-dimensional lattice gas.

Unfortunately, the accuracy of the currently available experimental data is not sufficient to confirm the presence or absence of a "singular diameter" (see, e.g.,[40]) or the possible singularity of the third derivative of the chemical potential with respect to temperature[39]. A study of the critical isotherm of He^3 has shown[41] that the correction terms in the chemical potential can be described with nearly identical accuracy either by a nonanalytic function $\sim|\Delta\rho|^{2\delta-1/\beta}$, for example, or by an analytic term $\sim\Delta\rho^6$. It is natural also to expect analytic corrections to the specific heat and the chemical potential on the isochore and to the density on the coexistence curve.

4. TESTS OF THE HOMOGENEITY FUNCTIONS OF THE THERMODYNAMIC FUNCTIONS OF ARGON IN A WIDE REGION AROUND THE CRITICAL POINT

Table III shows experimental values of the specific heat of argon on four isochors for $\rho < \rho_c$. The experimental procedure was explained in detail in[10]. We have also used values of C_V calculated[15] from P-V-T data. These values on the critical isochore agree with the results of our direct measurements to within ~25%.

Figure 3 shows the function $f(x)$ calculated from Eq. (2) using constants determined from experiments[10,15] ($B(T_c) = -15.5$, $\mu''(\rho_c, T_c) = -7 \pm 1$) in the asymptotic limit $T \to T_c$, i.e., the temperature dependence of $\mu''(\rho_c, T)$ and $B(T)$ was not taken into account. The homogeneous function $f(x)$ on the near-critical isochors of He^3 was constructed in the same approximation[7]. The continuous line in Fig. 3 corresponds to Eq. (10) with the parameters (17). Deviations from the zeroth-order approximation are observed only for points lying more than 10% distant from T_c and ρ_c; in all cases they are small ($\lesssim$10–20%) and appear to be systematic. We can partially reduce these deviations, even within the limits of the zeroth-order approximation, since the complete temperature dependence of the chemical potential on the critical isochor must be taken into account in Eqs. (1) and (2). The temperature dependence of $\mu(\rho_c, T)$ and $B(T)$ was determined by graphical interpolation of $\rho C_V/T$ and $\mu(\rho, T)$ on the critical isochor (see Fig. 4).

By taking these dependences into account we can widen the interval of homogeneity of the experimental

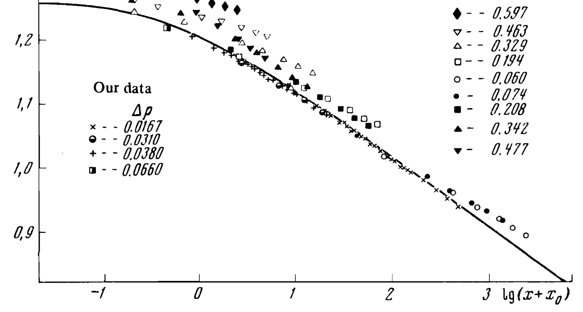

FIG. 3. Scaling function of the specific heat from Eq. (2) in the approximation $\mu''(\rho_c, T)$ = const and B(T) = const. The solid line is plotted from the LM equation (10) with the parameters (17).

TABLE III. Specific heat of argon (C_V in J/mole deg) at noncritical densities

T_1, °K	T_2, °K	C_V	T_1, °K	T_2, °K	C_V
$\rho=0.522(6)$ g/cm^3			$\rho=0.515$ g/cm^3		
150.6666	150.6733	87.71	150.6672	150.6828	73.20
150.6672	150.6745	83.70	150.6825	150.6996	64.40
150.6678	150.6764	82.13	150.6992	150.7249	59.53
150.6682	150.6812	80.00	150.7245	150.7581	55.38
150.6734	150.6807	77.69			
150.6746	150.6832	74.00	$\rho=0.511(3)$ g/cm^3		
150.6773	150.6868	71.82			
150.6780	150.6977	69,40	150.6659	150.6734	75.90
150.6791	150.6949	70.33	150.6674	150.6781	74,75
150.6808	150.6897	72.5	150.6697	150.6829	68.95
150.6833	150.6924	69.50	150.6723	150.6801	70.75
150.6879	150.6880	66.43	150.6756	150.6840	68.90
150.6900	150.7017	66.6	150.6763	150.6970	66.65
150.6940	150.7110	63.56	150.6774	150.7014	65.74
150.6992	150.7123	63.20	150.6781	150.6896	67.80
150.7019	150.7217	61.40	150.6784	150.6866	68.30
150.7077	150.7298	59.30	150.6819	150.6931	67.20
150.7100	150.7324	58.58	150.6892	150.7012	64.00
150.7135	150.7414	57.26	150.6920	150.7034	62.98
150.7312	150.7546	55.10	150.6952	150.7084	61.50
150.7333	150.7561	56.56	150.6990	150.7146	59.50
150.7428	150.7719	54.22	150.7062	150.7278	59.04
150 7528	150.7764	54.10	150.7141	150.7347	56.74
150.7733	150.8143	50.94	150.7234	150.7473	56,95
150.8164	150.8623	49.0	150.7338	150.7619	54 10
150.8638	150.9216	45,43	150.7612	150.7972	51,20
150.9232	150.9962	43.45	150.7963	150.8434	48.30
			$\rho=0.496(4)$ g/cm^3		
			150.6657	150.6828	60.90

Note. T_1 and T_2 are the starting and ending temperatures of the calorimetric experiment. The temperature are given in the natural thermometer scale; in this case $T_C = 150.6645$ [10].

values of f(x) to $t \approx 0.5$ for $-0.3 \lesssim \Delta\rho \lesssim 0.2$ (Fig. 5). Figure 6 shows the function h(x) for the chemical potential calculated from Eq. (1) (the solid line corresponds to Eq. (10)). We should stress that the experimental values of h(x) in Figs. 6 and 5 were constructed using the same approximations. The intervals of $\Delta\rho$ and t in which the experimental data satisfy the homogeneity condition are the same as those for the specific heat (see Fig. 1).

The interval of homogeneity cannot be expanded further within the limits of the zeroth-order approximation. Let us consider the effect of including the next terms (of order $\sim\Delta\rho^2$) in Eq. (2) for the specific heat. We shall use the expression $\Delta\rho^2(a_0 + a_1 t)$ to approximate the deviations of the experimental values from the homogeneous function. The values $a_0 = -5.5$ and $a_1 = 7.7$ for the coefficients were obtained by minimizing the errors, with the additional condition that the alterations of the experimental values due to the introduction of the corrections should not exceed the experimental error. This condition was satisfied by the isochors in the range $-0.73 \le \Delta\rho \le 0.34$ (Fig. 7). By introducing the corrections of the next order in $\Delta\rho$ we can easily widen even further the region in which the proposed method can be used to describe the thermodynamic properties of argon. This method is evidently quite effective for our practical purposes. However, the presence of absence of nonanalytic terms in the corrections (see Sec. 3) is of fundamental significance. The insufficient accuracy and large temperature spacing of the experimental data[15] prevent any definite answer to this question, although some deviations from smooth behavior can be noted in the difference between the experimental values of the specific heat and the values that correspond to the asymptotic law near T_C on the near-critical isochors (Fig. 4).

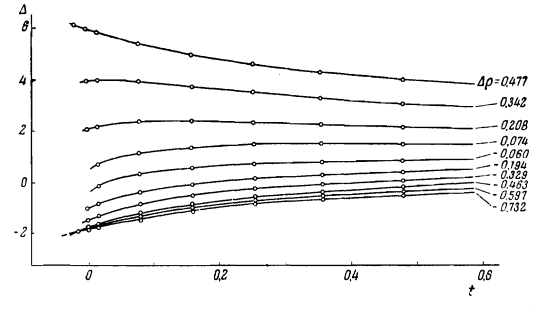

FIG. 4. Deviations of the experimental specific heat $\Delta = \rho C_V/T - (\Delta\rho^{-\alpha/\beta} f(x) + B)$ from the values given by Eq. (2) (in dimensionless units) in the approximation $\mu''(\rho_C, T) = 0$, B(T) = const.

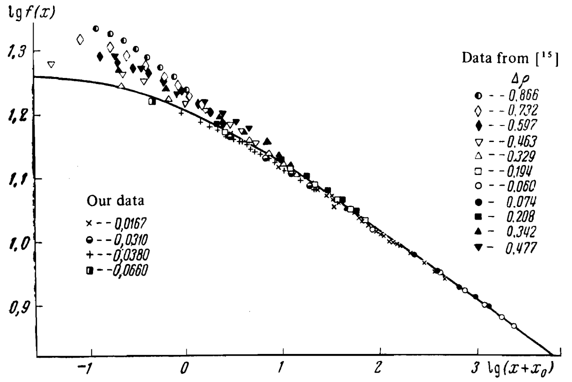

FIG. 5. Scaling function of the specific heat in the "zeroth-order approximation" from Eq. (2), with the temperature dependence of B(T) and $\mu''(\rho_C, T)$ taken into account. The solid line is the same as in Fig. 3.

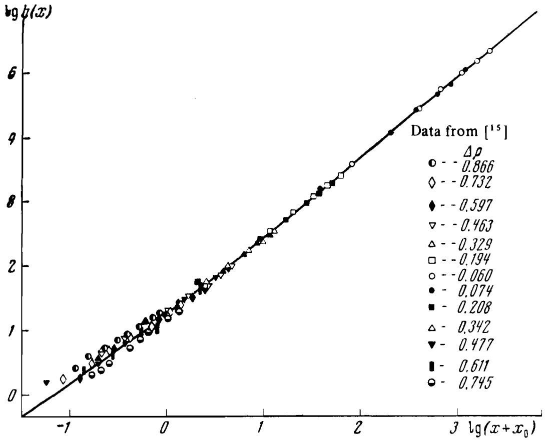

FIG. 6. Scaling function of the chemical potential in the "zeroth-order approximation" from Eq. (1). The solid line is plotted from the LM equation (9) with the parameters (17).

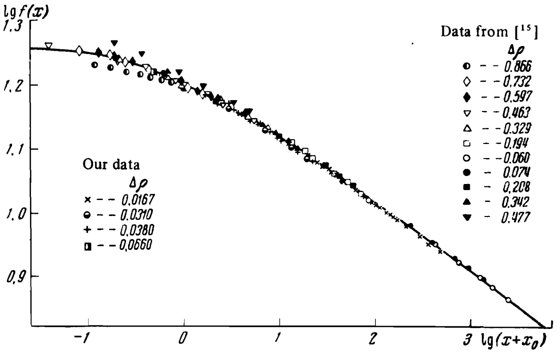

FIG. 7. Scaling function of the specific heat with corrections $\sim\Delta\rho^2$.

5. SPECIFIC HEAT OF ARGON ON THE CRITICAL ISOCHOR OVER A WIDE RANGE OF TEMPERATURES

To determine more accurately the functional dependence of the asymptotic correction terms, we carried out additional measurements of the isochoric specific heat at $\rho = \rho_c$ in the one-phase region, up to $T = 1.8T_c$. The measurements were performed in an improved calorimeter (compared with that used in earlier work[10]) that had been tested at pressures up to 400 bar. The specific heat of the empty calorimeter was ~60 J/deg. The mean error in the measurement of C_V was ~0.3%. A detailed description of the construction of the improved calorimetric apparatus and the measurement procedure has been given elsewhere[42]. The results are shown in Table IV and Fig. 8. The solid line corresponds to the asymptotic law (13). The deviations of the experimental values of C_V from the asymptotic behavior are shown in Fig. 9; in the range $t \lesssim 0.3$ they are described by the expression

$$C_v/T-(A^+t^{-\alpha}+B_0)=(A^+A_1)t^{\alpha_1}, \tag{18}$$

where $(A^+A_1) = 0.035$ J/mole-deg^2, $A_1 = 0.13$, and $\alpha_1 = 0.5 \pm 0.1$. This value of α_1 is close to the theoretical estimate $\alpha_1 \approx 0.4$[34].

Brown and Meyer[7], who approximated a similar correction by expression (18) with $\alpha_1 = 1 - 2\alpha - \beta = 0.44$ (the value predicted in[39]), found $A_1 = 0.11$ for He^3. For argon, $A_1 = 0.13$. When the same value of α_1 is used in both results, the two values of A_1 agree within 5%. This may indicate that the nonanalytic corrections to the asymptotic law are universal. The fact that the form of the corrections obtained experimentally corresponds to estimates of the next-order approximations in scaling theory indicates that self-consistent field theory is inapplicable to liquids, at least for Ar and He, when $t < 1$. Earlier analyses of the behavior of C_V for $t \lesssim 1$ indicated that the experimental data for many substances were compatible with fluctuation corrections of the self-consistent field[10,17]. However, the new and more accurate data for argon presented here lead rather to nonanalytic corrections of the form implied by the results of Wegner[34].

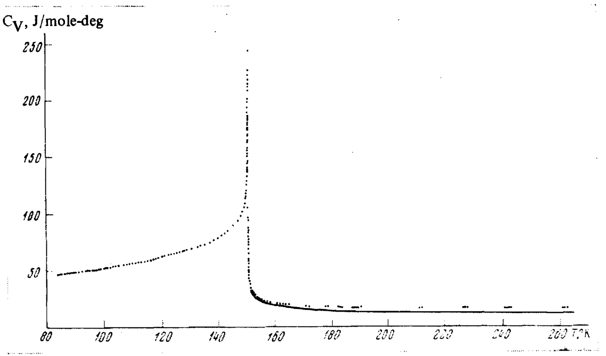

FIG. 8. Temperature dependence of the specific heat C_V on the critical isochore over a wide temperature interval. The solid line corresponds to the asymptotic law (13).

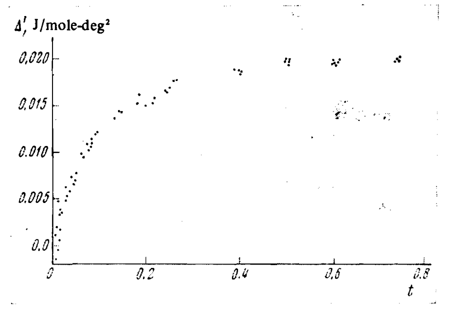

FIG. 9. Difference $\Delta' = C_V^{\exp}/T-(At^{-\alpha} + B)$ between the experimental specific heat C_V of Ar on the critical isochore at $T > T_c$ and the values given by the asymptotic law (13).

TABLE IV. Specific heat of argon (C_V in J/mole deg) at the critical density over a wide temperature interval

T_1, °K	T_2, °K	C_V	T_1, °K	T_2, °K	C_V
152.4267	152.5822	29.5	178.3729	178.9297	17.5
152.5780	152.8339	29.9	182.0052	182.5988	17.0
152.9448	153.6762	27.2	182.9052	183.4234	16.8
153.6716	153.8925	26.4	183.4054	183.9261	16.8
154.1071	154.3290	26.0	187.1031	187.6142	16.6
154.3250	154.5478	25.5	187.6101	188.1208	16.5
154.5440	154.7675	25.3	188.1182	188.6302	16.5
154.7640	154.9730	25.1	189.3586	190.1878	16.6
154.9686	155.7559	24.6	190.1856	190.6810	16.6
155.7513	156.3046	23.8	210.2350	210.7027	15.6
156.3004	156.8557	23.3	210.7004	211.1677	15.6
156.8519	157.3737	23.0	211.1624	211.6290	15.6
157.3688	157.8918	22.5	211.5901	212.0567	15.6
157.8886	158.4131	22.1	225.1500	225.5801	15.5
158.4099	158.9355	21.8	225.5871	226.0167	15.4
160.5044	161.0330	20.8	225.5836	226.0439	15.4
161.0307	161.5595	20.7	226.0449	226.5054	15.3
161.5576	162.0873	20.5	226.5059	226.9661	15.3
162.0854	162.6156	20.3	226.9669	227.4269	15.3
162.6139	163.1444	20.1	240.3403	240.7716	14.9
163.1411	163.6721	20.0	240.7707	241.2012	15.0
163.6686	164.1998	19.8	241.6479	242.0792	14.9
164.1979	164.7290	19.7	242.0919	242.5228	15.0
164.7275	165.2586	19.6	242.5249	242.9554	15.0
170.7161	171.2471	18.4	261.0676	261.4929	14.6
171.2464	171.7770	18.3	261.4894	261.9146	14.6
171.7767	172.3073	18.2	261.9143	262.3409	14.6
171.7750	178.3699	17.3	262.3328	262.7578	14.6

6. CONCLUSIONS

An analysis of the thermodynamic properties of argon shows that, in a wide range of variation of the state parameters, the primary contribution comes from terms whose behavior is to a great extent universal for all liquids. This means that in the given region the fluctuations of the order parameter (density) are large, and the correlation radius exceeds the effective range of the intermolecular forces. The existence of such a wide universality range is evidently related physically to the short-range forces in simple liquids ($\sigma/2r_0 \approx 1$) and to the resulting absence of a region in which the self-consistent field theory is applicable.

We have not attempted here to construct a single equation of state for argon from the ideal gas to the crystallization line. Nevertheless it appears probable that the proposed approach (using the critical state as a zeroth-order approximation) can be employed to obtain such a single equation of state, at least for the gaseous phase. In fact, an expression in the form of a virial equation of state can be obtained by expanding the nonanalytic functions of scaling theory in powers of ρ/ρ_c in the vicinity of the nonsingular zero-density point.

We wish to thank E. E. Gorodetskiĭ, Yu. F. Kiyachenko, A. I. Larkin, A. A. Migdal, and V. L. Pokrovskiĭ for useful discussions of this work, and T. N. Pavlikova for help in processing the experimental data.

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[1] Unfortunately, it is difficult at present to estimate the true accuracy of these methods.

[2] This approach was used successfully to describe the behavior of solutions near the critical point in the language of one-component liquids [36,37] (the isomorphism hypothesis).

[3] This fact was pointed out by A. A. Migdal.

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Translated by R. Rutherford III
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