Thermodynamic properties over a wide vicinity of the critical point

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A theoretical study is made of the behavior of thermodynamic properties over a wide vicinity of the critical point of a liquid–gas transition. Based on the renormalization group method and the first order ε-expansion, simple crossover expressions explicitly containing the Ginzburg parameter are derived for the susceptibility, correlation length, specific heat, and order parameter, both above and below the transition temperature. The question of the universality of the complex R_{cr} composed of the critical amplitudes and critical exponents determining the asymptotic specific heat behavior is discussed. A phenomenological model based on the results is found to be in good agreement with experiment.

1. INTRODUCTION

The theory of second-order phase transitions was largely completed by the 1970's. There are two major regions to be distinguished in the vicinity of a second-order phase transition. Far enough from the critical point one may neglect order-parameter fluctuations and apply the Landau theory[1] to describe the behavior of the observables of the system. In terms of the temperature, this region is determined from the so-called Ginzburg criterion[2] conventionally written as

$$Gi \ll |\tau| \ll 1, \tag{1.1}$$

where Gi is the dimensionless Ginzburg parameter and $\tau = T - T_c/T_c$ is the dimensionless deviation of the temperature T from its critical value T_c.

Close to the phase transition, the singular parts of the susceptibility χ, correlation length r_c, specific heat C, and order parameter φ vary as powers of the dimensionless temperature τ

$$\begin{aligned} &\chi^{\pm} = \Gamma^{\pm}|\tau|^{-\gamma} + \chi_{bg}, \quad r_c^{\pm} = r_0^{\pm}|\tau|^{-\nu} + r_{bg}, \\ &C^{\pm} = A^{\pm}|\tau|^{-\alpha} + C_{bg}, \quad \varphi^{-} = \varphi = B|\tau|^{\beta}. \end{aligned} \tag{1.2}$$

Here χ_{bg}, r_{bg}, and C_{bg} are the regular parts of the respective thermodynamic properties, and the superscripts "+" and "−" refer to the regions above ($\tau \geqslant 0$) and below ($\tau < 0$) the transition. The corresponding exponents are known as *critical exponents*, and the coefficients of the power function τ as *critical amplitudes*. The mean-field theory values of the critical exponents are

$$\gamma = 1 \text{ (Curie–Weiss law)}, \quad \nu = \tfrac{1}{2}, \quad \alpha = 0, \quad \beta = \tfrac{1}{2}. \tag{1.3}$$

Asymptotically close to the second-order phase transition, the experimental critical exponents disagree with their mean-field values. The behavior of the system in this region is controlled by anomalous order-parameter fluctuations, and according to fluctuation (or scaling) theory[2–5] the critical exponents depend on the spatial dimensionality d and on the number n of order parameter components. Statistical systems having identical d, n pairs belong to the same universality class. Liquids in the vicinity of the critical point of the liquid–gas transition and solutions near the separation point belong to the universality class of the three-dimensional Ising model[6] ($d=3$, $n=1$). The theoretical critical exponents for this class are[7,8]

$$\gamma \approx 1.24, \quad \nu \approx 0.63, \quad \alpha \approx 0.11, \quad \beta \approx 0.325. \tag{1.4}$$

Although the experimental values of the exponents agree well with theory, it should be noted that the asymptotic behavior of the form (1.2) with critical exponents (1.4) is actually observed in an extremely narrow region ($\tau \leqslant 10^{-3}$, see Ref. 9). If the Ginzburg parameter is sufficiently small ($Gi \ll 1$), then at temperatures away from the critical point we enter the intermediate (or crossover) region which in the limit $Gi \ll |\tau| \ll 1$ goes over to the mean-field region with critical values given by (1.3).

Because thermodynamic-property expressions valid in the crossover region enable a much wider range of experimental data to be described, their derivation is a problem of great practical importance and has been the subject of many studies. Some of the authors develop phenomenological approaches based on *a priori* knowledge of the critical exponents,[10] but it is the combination of the renormalization group method and the ε-expansion ($\varepsilon = 4 - d$) (see Refs. 2–5) which seems to be the most consistent approach theoretically. Among the first works of this type were Refs. 11 and 12 using the RG method and the ε-expansion in the transition region. Further development along this line is presented in Refs. 13 and 14, of which the latter gives third-order-ε expressions for crossover thermodynamic properties. Bagnuls and Bervillier,[15,16] following the numerical solution of RG equations for real ($d=3$) space, were able to construct analytical approximations for the thermodynamic properties of the system over a wide vicinity of the critical point. In their later paper[17] the same authors suggest a new universal complex R_{cr} consisting of the amplitudes and critical exponents for the specific heat in the asymptotic region.

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However, the problem of the crossover behavior cannot yet be considered closed. First, the fact that the above results do not contain the Ginzburg parameter explicitly complicates data analysis and prevents writing the crossover functions in a simple analytical form. Second, there remains the problem of the amplitude complex R_{cr} whose universality is questioned in Ref. 18.

The present work performs a one-loop crossover behavior analysis and yields susceptibility, correlation-length, specific-heat, and order-parameter expressions explicitly containing the Ginzburg parameter. We discuss the degree of universality of our results and separate the nonuniversal parameters of each of the thermodynamic properties. We also discuss the role of the cutoff parameter and the universality of the complex R_{cr}. In the final section we present a phenomenological generalization of the results obtained and give an interpretation of the experimental specific-heat data for CO_2 and Ar in the critical region.

2. DISORDERED PHASE

We consider here the behavior of a liquid–gas system on the critical isochore. If the temperature T is below T_c, then the thermodynamic potential as a function of the density ρ has two minima, one for the liquid and the other for the gaseous phase. For $T>T_c$, there is only one minimum located at $\rho=\rho_c$. The Landau Hamiltonian for this situation is[1,2]

$$H=\frac{1}{V}\int[a\varphi^2+c(\nabla\varphi)^2+u\varphi^4]dV, \tag{2.1}$$

where V is the volume of the system, $\varphi=(\rho-\rho_c)/\rho_c$ the order parameter, and a, c, and u are the coefficients in the Landau expansion. The coefficients c and u must be positive [otherwise we must retain higher order terms in the expansion (2.1)], and a vanishes at the critical point

$$a=\alpha_0\tau, \tag{2.2}$$

where α_0 is a constant.

For $a>0$ the mean value of the field φ is zero

$$\langle\varphi\rangle\equiv\int D\varphi e^{-H/kT}\varphi=0.$$

If $a<0$, a nonzero condensate of the field φ appears, i.e., $\langle\varphi\rangle\neq 0$ (we use angular brackets to denote averaging over the Gibbs distribution).

It is now convenient to change to the momentum representation in the Landau Hamiltonian (2.1). Let us write the field φ in terms of its Fourier expansion

$$\varphi(\mathbf{r})=\int\varphi_q e^{i\mathbf{qr}}\frac{d^dq}{(2\pi)^d}.$$

(Here and hereafter the space dimensionality d is arbitrary.) Substituting this in (2.1) we find

$$H=\int_{|\mathbf{q}|<\Lambda_0}\frac{d^dq}{(2\pi)^d}(a+cq^2)\varphi_q\varphi_{-q}+\int_{|\mathbf{q}_i|<\Lambda_0}\frac{d^dq_1d^dq_2d^dq_3}{(2\pi)^{3d}}u\varphi_{q_1}\varphi_{q_2}\varphi_{q_3}\varphi_{-q_1-q_2-q_3}. \tag{2.3}$$

The initial expression (2.1) determines the energy corresponding to the given distribution of the field φ and is only meaningful if the spatial scale for φ is large compared to the molecular dimension r_m. Accordingly, we must impose the condition $|\mathbf{q}|\ll r_m^{-1}$ on the region of integration over the wave vector $\mathbf{q}$ in (2.3). We therefore introduce a cutoff parameter $\Lambda_0\ll r_m^{-1}$ and integrate in the region $|\mathbf{q}|<\Lambda_0$.

In the mean-field theory the order parameter φ is everywhere replaced by its mean value. Equation (2.3) then retains only one Fourier component with $q=0$ of φ, and all thermodynamic properties are directly expressible in terms of the bare values of a, c, and u ($a=a_0$, $c=c_0$, $u=u_0$).

The domain of validity of mean-field theory is readily estimated by calculating the first fluctuation correction to a and comparing the correction with the bare (i.e., mean field) value a_0. Landau theory is valid if the correction is relatively small compared with $a=a_0$, meaning

$$\tau\gg Gi=\frac{9}{64\pi^2}k^2T_c^2\frac{u_0^2}{\alpha_0c_0^3}. \tag{2.4}$$

This is the Ginzburg criterion[2] (designated Gi) for the validity of Landau theory. Comparing the fluctuation correction with the mean-field value for other thermodynamic properties (specific heat, for example) will also yield the Ginzburg criterion—but with a different numerical factor in the right-hand side of (2.4).

On approaching the second-order phase transition, the coefficient a in (2.1) decreases, with a consequence that the energy for producing the long-wavelength fluctuation of the field φ tends to zero. Very close to the continuous phase transition, a large number of coupled long-wavelength order-parameter fluctuations form, and the behavior of the system in this vicinity is described in terms of the RG method and the ε-expansion.

The present study uses the RG method in the Wilson formulation as discussed in Ref. 3. The method proceeds by first dividing the total domain of integration over $|\mathbf{q}|$ ($0<|\mathbf{q}|<\Lambda_0$) into regions of "fast" ($\Lambda<|\mathbf{q}|<\Lambda_0$) and "slow" ($0<|\mathbf{q}|<\Lambda$) fields φ_q and then integrating over the former. Repeated application of this procedure yields fluctuation corrections to various quantities (the magnitude of the correction remaining relatively small at each step), and the Landau Hamiltonian H, Eq. (2.3), is replaced by a sequence of smoothed Hamiltonians H_Λ, with coefficients a_Λ and u_Λ dependent on the current cutoff parameter Λ.

We consider the disordered phase first. In the one-loop approximation the corrections to a, u, and c are given by the two diagrams shown in Fig. 1. It is readily seen that diagram 1a does not contain any dependence on the exter-

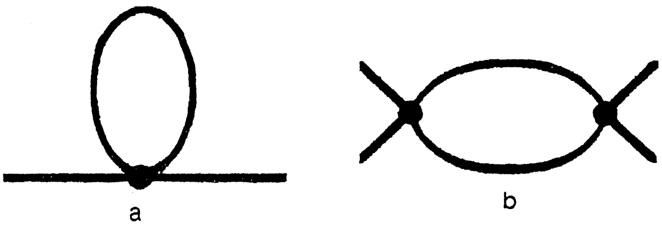

FIG. 1. Diagrams for the one-loop corrections to the coefficients a (a) and u (b) in the Hamiltonian (2.3).

nal wave vector and hence the coefficient c remains nonrenormalized in this approximation. The correction to a as given by the diagram of Fig. 1a has an ultraviolet singularity which has nothing to do with the proximity to the critical point and must therefore be eliminated; this can be done by differentiating with respect to T. In this case we have the following differential equations to determine the changes in $\alpha_\Lambda = da_\Lambda/dT$ and u_Λ due to renormalization in a space with dimensionality $d=4-\varepsilon$:

$$\frac{d\alpha_\Lambda}{d\Lambda} = Au_\Lambda\alpha_\Lambda\frac{\Lambda^{3-\varepsilon}}{(a_\Lambda+c_0\Lambda^2)^2}, \qquad \frac{du_\Lambda}{d\Lambda} = 3Au_\Lambda^2\frac{\Lambda^{3-\varepsilon}}{(a_\Lambda+c_0\Lambda^2)^2}. \tag{2.5}$$

Here $A=3kTS_d/(2\pi)^d$, where S_d is the surface area of the unit sphere in d dimensions. In the present study we do not apply the inverse scaling transformation[2,3,5]

$$r_\Lambda \equiv a_\Lambda\Lambda^{-2}, \quad b_\Lambda \equiv u_\Lambda\Lambda^{-\varepsilon}, \tag{2.6}$$

which would reduce (2.5) to autonomous form.[2] The solution of the system (2.5) with initial conditions $a_{\Lambda=\Lambda_0} = a_0$ and $u_{\Lambda=\Lambda_0} = u_0$ is

$$\alpha_\Lambda = \alpha_0[1+3Au_0L(\Lambda,\Lambda_0;a_q)]^{-1/3}, \qquad u_\Lambda = u_0[1+3Au_0L(\Lambda,\Lambda_0;a_q)]^{-1}, \tag{2.7}$$

where

$$L(\Lambda,\Lambda_0;a_q) \equiv \int_\Lambda^{\Lambda_0}\frac{q^{3-\varepsilon}dq}{(a_q+c_0q^2)^2}.$$

Differential equations (2.5) and their solutions (2.7) are usually employed for determining the values of the critical exponents in the asymptotic critical region. In the region $1 \gg \tau \gg Gi$ the thermodynamic theory of fluctuations is valid. The description of the intermediate region raises the problem of matching the renormalized quantities a_Λ and u_Λ to the known Landau-theory expressions. The matching condition chosen in Refs. 11–14 is equivalent to replacing the integral $L(\Lambda,\Lambda_0;a_q)$ in (2.7) by $L(\Lambda = \sqrt{a_\Lambda/c_0} = r_c^{-1},\Lambda_0;0)$. In the present work, fluctuation- and mean-field-theory results are matched by replacing the integral $L(\Lambda,\Lambda_0;a_q)$ by $L(\Lambda,\Lambda_0;a_\Lambda)$. As a consequence of this, the final results contain the amplitudes of the first fluctuation corrections to the mean-field values.

Substitution of the matching condition into (2.7) gives the following expressions for the renormalized coefficients of the Hamiltonian ($a_R \equiv a_{\Lambda=0}$ and $u_R \equiv u_{\Lambda=0}$):

$$a_R = a_0Y_+^{-1/3}\left(1+\frac{\varepsilon}{2}Y_+^{-1}\left(\frac{a_R}{\alpha_0 Gi}\right)^{-\varepsilon/2}\right)^{-1}, \qquad u_R = u_0Y_+^{-1}. \tag{2.8}$$

Here

$$Y_+ = 1+3\left(\frac{a_R}{\alpha_0 Gi}\right)^{-\varepsilon/2} - 3g_0,$$

$$g_0 = \left(1+\frac{\varepsilon}{2}\right)\frac{\sin(\pi\varepsilon/2)}{\pi\varepsilon/2}\left(\frac{Gi}{(r_0\Lambda_0)^2}\right)^{\varepsilon/2},$$

where $r_0=(c_0/\alpha_0)^{1/2}$ is the bare correlation radius amplitude. The parameter Gi in (2.8) is defined by

$$Gi = \left(\frac{1}{2}\left(1-\frac{\varepsilon}{2}\right)\frac{\pi}{\sin(\pi\varepsilon/2)}\frac{Au_0}{c_0^{2-\varepsilon/2}\alpha_0^{\varepsilon/2}}\right)^{2/\varepsilon} \tag{2.9}$$

The standard notation Gi is here applicable because at $\varepsilon=1$ this parameter is identical to the Ginzburg parameter defined in (2.4).

Equations (2.8) lead to a criterion for the validity of mean field theory to be obtained. The coefficient a_R assumes its mean-field value a_0 when

$$\tau \gg \frac{Gi}{(1+g_0)^{2/\varepsilon}}. \tag{2.10}$$

In contrast to the Ginzburg criterion (2.4), Eq. (2.10) contains a dependence on $g_0 \sim \Lambda_0^{-\varepsilon}$. It is readily seen that in three dimensions (2.10) is identical to (2.4) in the limit as $\Lambda_0 \to \infty$. It should also be noted that for ε positive, the autonomous equation for the quantity b_Λ defined by (2.6) has a nontrivial fixed point b^* (see Refs. 2–5). The ratio $b_{\Lambda=\Lambda_0}/b^*$ agrees within a factor with the quantity $Gi^{\varepsilon/2}$.

Using Eqs. (2.8), the thermodynamic properties of the disordered system can be derived. We first discuss the susceptibility. From general principles, the susceptibility of system in the disordered phase is[2]

$$\chi_+^{-1} = 2a_R. \tag{2.11}$$

From (2.8) we can obtain

$$\tilde{\chi}_+^{-1} = \tau X_+^{-1/3}\left(1+\frac{\varepsilon}{6}X_+^{-1}\left(\frac{\tilde{\chi}^{-1}}{Gi}\right)^{-\varepsilon/2}\right)^{-1}, \qquad X_+ = 1+3\left(\frac{\tilde{\chi}_+^{-1}}{Gi}\right)^{-\varepsilon/2} - 3g_0, \tag{2.12}$$

where $\tilde{\chi}_+^{-1} = \chi_+^{-1}/2\alpha_0$. Eqs. (1.2) and (2.12) show that the crossover susceptibility χ_+ contains four nonuniversal parameters, namely, χ_{bg}^+, $\chi_0^{-1}=2\alpha_0$, Gi, and g_0.

Above the phase transition ($T>T_c$), the one-loop approximation gives for the correlation radius

$$r_c^+ = \sqrt{\frac{c_0}{a_R}}. \tag{2.13}$$

Going to higher orders requires the renormalization of c.

We now proceed to derive the crossover specific-heat expression. The singular part of the free energy is given by the standard relation

$$F=-kT\ln\left(\int D\varphi e^{-H/kT}\right). \tag{2.14}$$

The specific heat is obtained from (2.14) by taking the second derivative with respect to T and keeping the terms most singular in the limit $\tau\to 0$. This gives

$$C^{+}=C_{bg}^{+}-B_{\rm cr}+B_{\rm cr}\left(1+3\left(\frac{\tilde{\chi}_{+}^{-1}}{Gi}\right)^{-\varepsilon/2}-3g_0\right)^{1/3}. \tag{2.15}$$

The (nonuniversal) constant $B_{\rm cr}=\alpha_0^2/6u_0T_c$ in the singular part renormalizes the regular part in the fluctuation region. In analogy with the susceptibility case, here again there are four nonuniversal parameters (C_{bg}^{+}, $B_{\rm cr}$, Gi, and g_0) in the crossover specific-heat expression (2.15). We postpone the discussion of the above results to Sec. 4 and turn now to consider the ordered phase.

3. ORDERED PHASE

Analysis of the ordered system parallels quite closely that performed in the preceding section for the disordered case, so we shall focus on the major distinguishing features of the ordered phase behavior. Below the phase transition ($T<T_c$) the quantity $\langle\varphi\rangle$ (the mean value of the order parameter φ) becomes nonzero. It is convenient to set in the Hamiltonian H $\varphi=\langle\varphi\rangle+\psi$, where $\langle\psi\rangle=0$. The equation of state in zero external field then becomes

$$\left\langle\frac{\delta H}{\delta\psi}\right\rangle=h=0. \tag{3.1}$$

Evaluating the derivative and averaging we find

$$\varkappa_R\langle\varphi\rangle-4u_R\langle\varphi\rangle^3=h=0. \tag{3.2}$$

The quantities $\varkappa_R=a_R+6u_R\langle\varphi\rangle^2$ and u_R in (3.2) are the renormalized coefficients of the Hamiltonian H in the ordered phase.

The differential equations for the renormalization of $\varkappa_\Lambda$ and u_Λ are identical to Eqs. (2.5) for a_Λ and u_Λ [the corresponding Feynman diagrams are of the same form (see Fig. 1) as in the disordered phase, and in the ordered-phase correlation function $\langle\varphi\varphi\rangle$ the quantity a is replaced by $\varkappa$]. The system of differential equations for $\varkappa_\Lambda$ and u_Λ has a solution of the same form as (2.7), but with a_Λ replaced by $\varkappa_\Lambda$. The dependence of the renormalized quantities $\varkappa_{\Lambda=0}\equiv\varkappa_R$ and $u_{\Lambda=0}\equiv u_R$ on their respective bare values $\varkappa_{\Lambda=\Lambda_0}\equiv\varkappa_0 = -2\alpha_0\tau$ and $u_{\Lambda=\Lambda_0}\equiv u_0$ are given by (2.8) with a replaced by $\varkappa$.

We consider next the behavior of the thermodynamic properties in the low-temperature phase ($T<T_c$). In the one-loop approximation the correlation length is given by

$$r_c^{-}=\sqrt{\frac{c}{\varkappa_R}}. \tag{3.3}$$

The order parameter $\langle\varphi\rangle$ can be calculated from the equation of state (3.2):

$$\langle\varphi\rangle^2=\frac{\varkappa_R}{4u_R}. \tag{3.4}$$

The correlation length r_c^{-} and the order parameter $\langle\varphi\rangle$ can be written explicitly by substituting the renormalized $\varkappa_R$ and u_R into Eqs. (3.3) and (3.4).

The ordered-phase susceptibility is most conveniently calculated by directly using the definition

$$\chi_{-}=\left(\frac{\partial\langle\varphi\rangle}{\partial h}\right)_T. \tag{3.5}$$

Taking into account the equation of state (3.2) we obtain

$$\tilde{\chi}_{-}^{-1}=\tilde{\varkappa}\left(1+\frac{3\varepsilon}{2}Y_{-}^{-1}\left(\frac{\tilde{\varkappa}}{Gi}\right)^{-\varepsilon/2}\right),$$
$$\tilde{\varkappa}=2|\tau|Y_{-}^{-1/3}\left(1+\frac{\varepsilon}{2}Y_{-}^{-1}\left(\frac{\tilde{\varkappa}}{Gi}\right)^{-\varepsilon/2}\right)^{-1}, \tag{3.6}$$
$$Y_{-}=1+3\left(\frac{\tilde{\varkappa}}{Gi}\right)^{-\varepsilon/2}-3g_0.$$

Here $\tilde{\varkappa}=\varkappa_R/\alpha_0$ and the rest of notation is the same as before.

In a way similar to that employed in the preceding section, the specific heat can be obtained by taking the second T-derivative of the ordered-phase free energy. Accurate to $O(\varepsilon)$, we get

$$C_0^{-}=C_{bg}^{-}-4B_{\rm cr}+4B_{\rm cr}Y_{-}^{1/3}\left[1-\frac{21}{16}\varepsilon Y_{-}^{-1}\left(\frac{\tilde{\varkappa}}{Gi}\right)^{-\varepsilon/2}\right]. \tag{3.7}$$

The correlation length (3.3), order parameter (3.4), susceptibility (3.6), and specific heat (3.7) describe the behavior of the thermodynamic system in the crossover region below the phase transition. We now turn to discuss the results.

4. DISCUSSION

For limiting cases of interest, the thermodynamic properties we have derived in Secs. 2 and 3 duplicate the corresponding results known from fluctuation and mean-field theories. Consider first the domain of validity of the latter, $Gi\ll\tau\ll 1$. In this region Eq. (2.8) for the renormalized coefficient a_R may be written as

$$a_R\approx a_0\left[1-\left(\frac{\tau}{Gi}\right)^{-\varepsilon/2}\right], \tag{4.1}$$

where we have retained the first fluctuation correction and neglected the constant $g_0\sim(1/Gi)^{-\varepsilon/2}$. Using (4.1) for $\varepsilon=1$ it is straightforward to retrieve the familiar expressions for first-order-corrected thermodynamic properties in the region $Gi\ll\tau\ll 1$. In particular, the heat capacity follows from (2.15) and (4.1) as

$$C=C_0-\frac{1}{16\pi}k\left(\frac{\alpha_0}{c_0}\right)^{3/2}\tau^{-1/2}, \tag{4.2}$$

which agrees with the first-order perturbation result due to Levanyuk.[19]

Next, consider the asymptotic vicinity of the phase transition. Equation (2.8) yields the following condition on the range of temperatures for which the fluctuation correction to a_R is large compared to its mean field value:

$$\tau \ll Gi\left(\frac{3}{1-3g_0}\right)^{2/\varepsilon} \sim Gi. \qquad (4.3)$$

In this region expression (2.8) for a_R can be represented by the Wegner[5,20] asymptotic expansion

$$a_R \approx 3^{-1/3}\left(1-\frac{\varepsilon}{6}\right)\alpha_0 Gi^{-\varepsilon/6}\tau^{1+\varepsilon/6}$$
$$\times\left[1-\frac{1}{9}\left(1-\frac{\varepsilon}{3}\right)(1-3g_0)\left(\frac{\tau}{Gi}\right)^{\varepsilon/2}+\ldots\right]. \qquad (4.4)$$

Note that apart from the leading term, Eq. (4.4) also retains the first correction term of the Wegner expansion, the one proportional to $(\tau/Gi)^{\varepsilon/2}$.

The treatment of the ordered phase in the fluctuation and mean field regimes is similar but with a_R replaced by $\varkappa_R = a_R + 6u_R\langle\varphi\rangle^2$. Using (4.4) for a_R in the disordered phase and an analogous expression for $\varkappa_R$ in the ordered, it is a simple matter to reproduce the standard fluctuation-theory results for the susceptibility, correlation length, heat capacity, and order parameter, both above and below the transition. In particular, the asymptotic critical behavior of the heat capacity can be written as

$$C^{\pm} = C_{bg} - B_{cr}^{\pm} + A^{\pm}\tau^{-\alpha}(1 + a_c^{\pm}\tau^{\Delta}), \qquad (4.5)$$

where $\alpha = \frac{\varepsilon}{6} + O(\varepsilon^2)$, $\Delta = \frac{\varepsilon}{2} + O(\varepsilon^2)$ (theoretical value $\Delta = 0.51$, Refs. 7 and 14). Here a_c is the Wegner correction amplitude. It is easy to retrieve the entire set of the universal amplitude ratios of leading asymptotic to correction terms.[7,14] It should be noted, however, that in our approximation the ratios of the Wegner-corrections are only correct to zeroth order in ε, and we should go over to the two-loop approximation to obtain corrections $\sim O(\varepsilon)$ (see Refs. 14 and 21). The same is true for the ratio of the asymptotic amplitudes of the heat capacity, A^+ above to A^-, below the critical point.

Reference 17 states that the following combination of heat-capacity amplitudes is universal in the fluctuation region:

$$R_{cr}^{+} = \frac{A^{+}|a^{+}|^{\alpha/\Delta}}{B_{cr}}. \qquad (4.6)$$

Substituting the amplitudes, this complex becomes

$$R_{cr}^{+} = \left(\frac{1}{3}\right)^{1/3}(1-3g_0)^{1/3}[1+O(\varepsilon)], \qquad (4.7)$$

which is exactly the result of Ref. 18. Since g_0 is not universal, neither is the amplitude combination (4.6). The conclusion to the contrary reached in Ref. 17 is a consequence of the assumption $\Lambda_0 = \infty$. In this case $g_0 = 0$, and the universal nature of the combination (4.6) in the one-loop approximation is obvious. From (2.8), using the natural estimate $\Lambda_0 \sim r_0^{-1}$, we have for $\varepsilon = 1$

$$g_0 \sim \frac{3}{\pi} Gi^{1/2}. \qquad (4.8)$$

If $Gi \ll 1$, Eqs. (4.7) and (4.8) imply that the magnitude of the amplitude combination R_{cr} is very nearly universal.

5. PHENOMENOLOGY

The above first-order-ε expressions for susceptibility, correlation length, specific heat, and order parameter involve *approximate* values of the critical exponents and hence cannot be applied to data analysis directly: such an analysis requires formulas with *correct* critical exponents. The crossover formulas of Ref. 14 are derived to third order in ε, but they again involve approximate critical parameters and are therefore unsuitable for data analysis; besides, they are extremely unwieldy. In order to be able to analyze the experimental data, one has somehow to resort to their phenomenological generalization. This approach has been adopted in Refs. 22 and 23 but, although the formulas therein do allow data analysis, they are again unwieldy and admit of no clear interpretation of the fitting parameters involved.

In the present work we suggest a phenomenological generalization based on first-order ε-approximation. The susceptibility and specific heat will be modeled, in this approximation, but with ε-dependent parameters replaced by unknown constants. Equations (2.12) and (2.15) then become

$$x = tZ^{\lambda_1}\left(1+\omega\frac{Z-1+g_0}{Z}\right)^{-1},$$
$$\tilde{C} = \tilde{C}_{bg} - 1 + Z^{\lambda_2}, \qquad (5.1)$$
$$Z = 1 + Z^{\lambda_3}x^{\lambda_4} - g_0,$$

where

$$x = \frac{\chi^{-1}}{\chi_0^{-1}Gi}, \quad \tilde{C} = \frac{C}{B_{cr}}, \quad t = \frac{\tau}{Gi},$$

χ_0 is the mean-field-theory susceptibility amplitude, and g_0 is a nonuniversal constant dependent on the cutoff parameter Λ_0. In deriving Eqs. (5.1) we have taken into account the renormalization of the coefficient c in front of the gradient term in the Landau Hamiltonian (2.1). The parameters λ_1, λ_2, λ_3, and λ_4 can be obtained by comparing Eqs. (5.1) with the known asymptotic behavior of the thermodynamic properties. This gives

$$\lambda_1 = \frac{(1-\gamma)}{\Delta}, \quad \lambda_2 = \frac{\alpha}{\Delta},$$
$$\lambda_3 = -\frac{\gamma}{\Delta}\eta\nu\frac{2-\Delta/\gamma}{\gamma+\eta\nu}, \quad \lambda_4 = -\frac{\Delta+2\eta\nu}{\gamma+\eta\nu}, \qquad (5.2)$$

where $\eta = 0.03$ (see Refs. 7 and 8) is the critical exponent of the anomalous dimensionality of the correlation function. The constant ω in (5.1) determines the amplitude

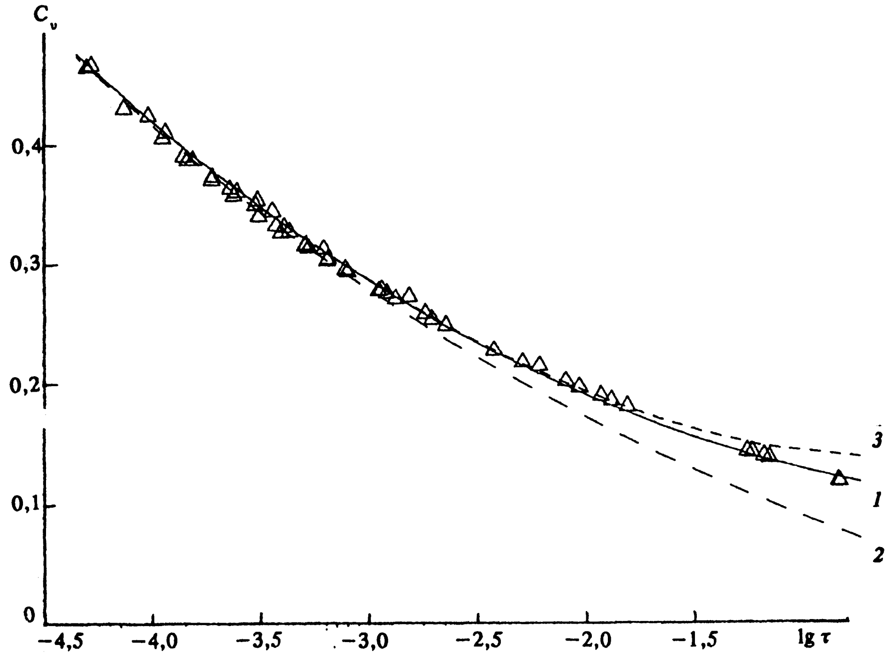

FIG. 2. Isochore heat capacity C versus $\log(\tau)$: Δ—CO_2 (Ref. 24), curve *1*—Eq. (5.1), curve *2*—asymptotic behavior ($C \propto \tau^{-\alpha}$), curve *3*—asymptotic behavior including the leading Wegner expansion term $[C \propto \tau^{-\alpha}(1 + a_c \tau^{\Delta})]$.

ratios for the first Wegner corrections and may be chosen such that these ratios agree with the theoretical predictions.[17,22] In the present study we set $\omega = 0.33$.

The simplicity of Eqs. (5.1) stems from our adhering to the functional structure of the first-order-ε approximation expressions (2.12) and (2.15). At higher orders, thermodynamic responses change their structure and can no longer be reduced to their first-order-ε approximation forms.

Phenomenological expressions (5.1) make it possible to describe the heat-capacity and susceptibility data well within the experimental accuracy currently achievable. In the present study we analyzed heat-capacity data for CO_2 (Ref. 24) and Ar (Ref. 25). The results are summarized in Figs. 2 and 3, which show that the phenomenological generalization of the first-order-ε formulas is adequate not only in the asymptotic critical region but for $\tau \sim Gi$ as well. Also, phenomenological expressions (5.1) make it possible to extract the experimental values of the Ginzburg parameter and the (upper-cutoff related) parameter g_0 and thus to quantitatively estimate the departure of the experimental data from the "universal behavior" suggested in Refs. 15 and 16. The term "universality" implies that physical properties share a common form dependent on critical exponents and a Ginzburg-type parameter. As argued in Refs. 15 and 16, expressions of this kind should be applicable both near the phase transition and in the crossover region ($\tau \sim Gi$). Equations (5.1) become universal at $g_0 = 0$.

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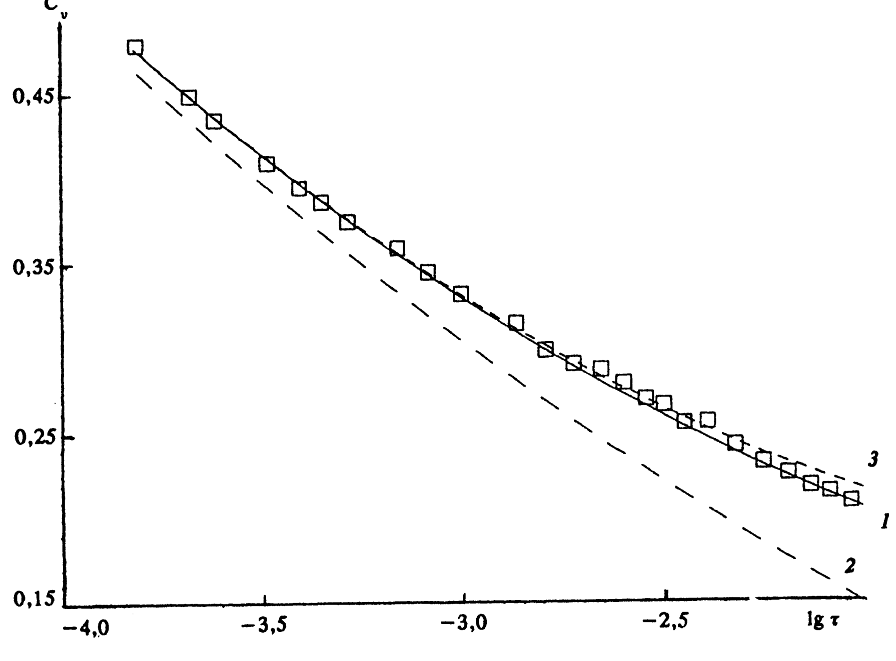

FIG. 3. Isochore heat capacity C versus $\log(\tau)$: $\square$—Ar (Ref. 25), curve *1*—Eq. (5.1), curve *2*—asymptotic behavior ($C \propto \tau^{-\alpha}$), curve *3*—asymptotic behavior including the leading Wegner expansion term $[C \propto \tau^{-\alpha}(1 + a_c \tau^{\Delta})]$.

[1] L. D. Landau and E. M. Lifshitz, *Statistical Physics* [in Russian], Nauka, Moscow (1976), Part 1 [Engl. transl. publ. by Pergamon Press].
[2] A. Z. Patashinskii and V. L. Pokrovskii, *Fluctuation Theory of Phase Transitions* [in Russian], Nauka, Moscow (1982) [Engl. transl. publ. by Pergamon Press].
[3] K. G. Wilson and J. Kogut, The renormalization group and ε-expansion, Phys. Lett. C **12**, 75 (1974).
[4] Sh. Ma, *Modern Theory of Critical Phenomena*, Benjamin, London *et al.* (1976).
[5] E. Brezin, J. C. Le Guillou, and J. Zinn-Justin, in *Phase Transition and Critical Phenomena*, eds. C. Domb and M. S. Green (Academic, New York, 1976), V. 6.
[6] J. V. Sengers and J. M. H. Levelt Sengers, Ann. Rev. Phys. Chem. **37**, 189 (1986).
[7] J. C. Le Guillou and J. Zinn-Justin, J. Phys. **48**, 19 (1987).
[8] J. Liu and M. E. Fisher, Physica A **156**, 35 (1989).
[9] M. Ley-Koo and M. S. Green, Phys. Rev. A **16**, 2483 (1977).
[10] M. A. Anisimov and S. B. Kiselev, in Sov. Phys. Rev. Ser. B, Therm. Phys., Eds. A. E. Sheindlin and V. E. Fortov, Hardwood Acad. Publ. 1992, Vol. 3(2).
[11] J. Rudnick and D. R. Nelson, Phys. Rev. B **13**, 2208 (1976).
[12] A. D. Bruce and D. J Wallace, J. Phys. A **9**, 1117 (1976).
[13] J. F. Nicoll and J. K. Bhattacharjee, Phys. Rev. B **32**, 389 (1981).
[14] J. F. Nicoll and P. C. Albright, Phys. Rev. B **31**, 4576 (1985).
[15] C. Bagnuls and C. Bervillier, Phys. Rev. B **32**, 7209 (1985).
[16] C. Bagnuls and C. Bervillier, Phys. Rev. B **35**, 3585 (1987).
[17] C. Bagnuls and C. Bervillier, Phys. Lett. A **107**, 299 (1985).
[18] J. F. Nicoll and P. C. Albright, Phys. Rev. B **34**, 1991 (1986).
[19] A. P. Levanyuk, Zh. Eksp. Teor. Fiz. **36**, 810 (1959) [Sov. Phys. JETP **9**, 571 (1959)].
[20] F. G. Wegner, Phys. Rev. B **5**, 4529 (1972).
[21] M. C. Chang and A. Houghton, Phys. Rev. B **21**, 1881 (1980).
[22] Z. Y. Chen, P. C. Albright, and J. V. Sengers, Phys. Rev. A **41**, 3161 (1990).
[23] S. Tang, J. V. Sengers, and Z. Y. Chen, Phys. A **179**, 344 (1991).
[24] Sh. P. Adamov, M. A. Anisimov, S. B. Kiselev, V. A. Rabinovich, and V. A. Smirnov, Teplofiz. Vys. Temp. **18**, 1115 (1980).
[25] M. A. Anisimov, B. A. Koval'chuk, V. A. Rabinovich, and V. A. Smirnov, *Thermophysical Properties of Substances and Materials* [in Russian], Standards, Moscow (1977).

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