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Crossover parametric equation of state for Ising-like systems

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We present a parametric equation for the thermodynamic properties in the critical region of three-dimensional Ising-like systems which include fluids and fluid mixtures. The equation of state incorporates a crossover from singular Ising behavior asymptotically close to the critical point to classical (mean-field) behavior further away from the critical point, characterized by two physical crossover parameters: a coupling constant related to the strength and range of molecular interactions and a ''cutoff'' wave number for the critical fluctuations. In the asymptotic Ising limit, the crossover equation reproduces the most recent theoretical estimates for the universal ratios of the leading and correction-to-scaling critical amplitudes. The equation has been tested by comparing it with recent experimental thermodynamic-property data for ^{3}He near its vapor-liquid critical point.

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I. INTRODUCTION

Critical phenomena in fluids have been the subject of many theoretical and experimental studies during the past thirty years. The most striking result of these studies has been the discovery of critical-point universality: the microscopic structure of systems becomes unimportant in the vicinity of a critical point [1–4].

The principle of critical-point universality finds its physical origin in the phenomenon that long-range fluctuations of the order parameter (magnetization in spin systems, density in one-component fluids, or density and concentration in fluid mixtures) dominate in the critical region so that the range of these fluctuations becomes much larger than any other microscopic scale. The spatial extent of these critical fluctuations is determined by a correlation length, which diverges at the critical point. As a consequence, at the critical point the behavior of the thermodynamic properties becomes singular and it can be characterized by scaling laws with universal critical exponents. Every singularity is also characterized by an amplitude, and certain combinations of critical amplitudes are universal.

Critical-point universality asserts that the thermodynamic properties of systems with finite interaction ranges have critical exponents that depend on only two physical parameters, namely, the spatial dimensionality d and the number of components n of the order parameter. Systems with the same d and n are said to belong to the same universality class. For example, fluids, fluid mixtures, and uniaxial ferromagnets belong to the three-dimensional Ising universality class with $d=3$ and $n=1$ and they can all be described by the same scaled equation of state asymptotically close to the critical point [3].

The range of asymptotic scaling behavior is usually quite small. However, the correlation length of the critical fluctuations exceeds in practice the short-range molecular interaction range in a sizable part of the phase diagram and one must also consider the effects of critical fluctuations at temperatures and densities where the correlation length is still significantly larger than the average intermolecular distance. Hence, to deal with the effects of critical fluctuations on the thermodynamic properties of systems one needs to formulate a description of the effects of critical fluctuations that goes beyond the asymptotic scaling behavior and includes crossover from fluctuation-dominated critical behavior in the near vicinity of the critical point to classical behavior far away from the critical point where the effects of fluctuations can be neglected.

For fluids a well-developed approach to this problem is provided by a transformed Landau expansion for the Helmholtz-energy density, originally formulated by Chen *et al.* [5,6] and reviewed by Anisimov *et al.* [7]. This crossover Landau model is based on a so-called renormalization-group matching technique as earlier implemented by Nicoll *et al*. [8,9]. The approach has been successful in representing experimental thermodynamic-property data not only for molecular fluids, but recently also for complex fluids like polymer or aqueous electrolyte solutions [10].

While the crossover Landau model, formulated about ten years ago, incorporates a representation of the asymptotic thermodynamic behavior that is realistic for many practical applications, strictly it does not reproduce the theoretical values of the universal critical-amplitude ratios within the high accuracy currently available for these ratios, as will be documented in Sec. III. The purpose of the present paper is to present an improved equation of state that incorporates the crossover from Ising-like to mean-field critical behavior, while reproducing the known theoretical values for the universal ratios of both the asymptotic critical amplitudes and the correction-to-scaling amplitudes.

To accomplish this goal we start with an extended parametric equation for the asymptotic scaling laws designed so as to reproduce the relevant critical-amplitude ratios by following a procedure similar to the one recently adopted by Fisher *et al.* [11]. As a next step we introduce into this asymptotic parametric equation a crossover transformation similar to the one deduced from the renormalization-group theory for the crossover Landau model.

We shall proceed as follows. In Sec. II we consider the asymptotic thermodynamic critical behavior of Ising-like systems in terms of two relevant scaling fields. To discuss the consequences of this general formulation we shall adopt physical variables appropriate for one-component fluids. However, the results can be applied to any Ising-like system by identifying the relationships between the scaling fields and the appropriate physical fields. In Sec. III we review the crossover Landau model and its predictions for the crossover behavior of various thermodynamic properties. Section IV presents the improved parametric crossover equation including a detailed comparison with theoretical predictions for both the asymptotic and nonasymptotic behavior. In Sec. V we make a comparison with crossover parametric equations of state developed by other investigators. Sec. VI deals with an application of the crossover parametric equation to the representation of experimental thermodynamic-property data. The paper concludes with a discussion of the results in Section VII.

II. SCALING FIELDS, CRITICAL EXPONENTS, AND CRITICAL AMPLITUDES

The near-critical behavior of Ising-like systems is characterized by two relevant scaling fields, an ordering field h_1 conjugate to the order parameter φ_1, and a nonordering field h_2 conjugate to the second scaling density φ_2. Asymptotically close to the critical point the critical part $\Delta\tilde{\Phi}$ of the dimensionless thermodynamic potential $\tilde{\Phi}$, whose characteristic variables are the scaling fields h_1 and h_2, then satisfies a scaling law of the form [3]

$$\Delta\tilde{\Phi}(h_1,h_2)=|h_2|^{\beta(\delta+1)}f(z), \tag{2.1}$$

with

$$z=h_1/|h_2|^{\beta\delta}, \tag{2.2}$$

where β and δ are two universal critical exponents, and where $f(z)$ is a universal scaling function except for the two system-dependent constants related to the amplitudes of the asymptotic power laws to be defined below.

The scaling "densities" conjugate to h_1 and h_2 are

$$\varphi_1=-\left(\frac{\partial\Delta\tilde{\Phi}}{\partial h_1}\right)_{h_2}=|h_2|^{\beta}f'(z), \tag{2.3}$$

$$\varphi_2=-\left(\frac{\partial\Delta\tilde{\Phi}}{\partial h_2}\right)_{h_1}=h_2|h_2|^{-\alpha}\psi(z), \tag{2.4}$$

where $f'(z)=df/dz$ and

$$\psi(z)=(2-\alpha)f(z)-(\beta+\gamma)zf'(z). \tag{2.5}$$

One may define the scaling susceptibilities χ_1 (strongly divergent) and χ_2 (weakly divergent) that are associated with the densities φ_1 and φ_2:

$$\chi_1=\left(\frac{\partial\varphi_1}{\partial h_1}\right)_{h_2}=|h_2|^{-\gamma}f''(z), \tag{2.6}$$

$$\chi_2=\left(\frac{\partial\varphi_2}{\partial h_2}\right)_{h_1}=|h_2|^{-\alpha}y(z), \tag{2.7}$$

with

$$y(z)=(1-\alpha)\psi(z)-(\beta+\gamma)z\psi'(z), \tag{2.8}$$

where $f''(z)=d^2f/dz^2$ and $\psi'(z)=d\psi/dz$. In addition, one may define a cross susceptibility as

$$\chi_{12}=\chi_{21}=\left(\frac{\partial\varphi_1}{\partial h_2}\right)_{h_1}=\left(\frac{\partial\varphi_2}{\partial h_1}\right)_{h_2}$$
$$=|h_2|^{\beta-1}[\beta f'(z)-(\beta+\gamma)zf''(z)]. \tag{2.9}$$

The exponents α and γ are related to β and δ by $\alpha=2-\beta(\delta+1)$ and $\gamma=\beta(\delta-1)$. We note that in the one-phase region in zero ordering field ($h_1=0$) $\varphi_1=0$, $\varphi_2=0$, and $\chi_{12}=0$, since $z=0$ and $f'(z)=0$.

The scaling law, given by Eqs. (2.1) and (2.2), represents the thermodynamic behavior asymptotically close to the critical point. The renormalization-group (RG) theory of critical phenomena predicts that Eq. (2.1) represents the first term of the so-called Wegner expansion of the form [12,13]

$$\Delta\tilde{\Phi}(h_1,h_2)=h_2^2|h_2|^{-\alpha}f(z)[1+|h_2|^{\Delta_s}f_1(z)+\cdots], \tag{2.10}$$

where $\Delta_s=0.52\pm0.02$ is another universal critical exponent [14,15] and where $f_1(z)$ is a universal correction-to-scaling function except for a multiplicative system-dependent constant related to the strength of the first irrelevant scaling field.

To elucidate the consequences of the scaled equation (2.10) and to subsequently formulate a crossover equation of state we shall adopt here physical variables appropriate to a one-component fluid near the vapor-liquid critical point. Let P be the pressure, T the temperature, ρ the density, μ the chemical potential, U the internal energy, A the Helmholtz energy, and C_V the isochoric heat capacity. The extensive thermodynamic properties are considered per unit of volume V and all thermodynamic fields and densities are made dimensionless with the aid of the critical pressure P_c, the critical temperature T_c, and the critical density ρ_c [16]:

$$\tilde{P}=\frac{PT_c}{TP_c},\quad \tilde{T}=-\frac{T_c}{T},\quad \tilde{\rho}=\frac{\rho}{\rho_c},\quad \tilde{\mu}=\frac{\mu\rho_cT_c}{P_cT}, \tag{2.11}$$

$$\tilde{U}=\frac{U}{VP_c},\quad \tilde{A}=\frac{AT_c}{VTP_c},\quad \tilde{C}_V=\frac{C_VT_c}{VP_c}. \tag{2.12}$$

We also introduce the variables

$$\Delta\tilde{T}=(T-T_c)/T=\tilde{T}+1, \tag{2.13}$$

$$\Delta\tilde{\rho}=(\rho-\rho_c)/\rho_c=\tilde{\rho}-1, \tag{2.14}$$

$$\Delta\tilde{\mu}=\tilde{\mu}-\tilde{\mu}_0(T), \tag{2.15}$$

where $\tilde{\mu}_0(T)$ is an analytic function of temperature equal to the chemical potential $\tilde{\mu}$ when $h_1=0$.

For spin systems, as represented by the Ising model, the ordering field h_1 is to be identified with the magnetic field and the order parameter φ_1 is to be identified with the magnetization. It is commonly assumed that fluids asymptotically close to the critical point have the same symmetry as the lattice gas for which the ordering field h_1 and the nonordering field h_2 are [17,18]

$$h_1=\Delta\tilde{\mu}, \quad h_2=\Delta\tilde{T}. \tag{2.16}$$

The corresponding scaling densities are

$$\varphi_1=\Delta\tilde{\rho}, \quad \varphi_2=\Delta\tilde{U}, \tag{2.17}$$

where $\Delta\tilde{U}=\tilde{U}-\tilde{U}_{\mathrm{c}}$ with $\tilde{U}_{\mathrm{c}}$ being the (arbitrary) value of $\tilde{U}$ at the critical point. The corresponding thermodynamic potential in Eq. (2.1) becomes the density of PV/T, which in dimensionless units equals $\tilde{P}$. Upon substituting the expressions (2.16) for the scaling fields into Eq. (2.1), we note that the critical part of the thermodynamic potential becomes asymptotically close to the critical point a universal function of the physical variables $\Delta\tilde{T}$ and $\Delta\tilde{\mu}$, except for two system-dependent coefficients.

Conventionally, one has used as the temperature variable T/T_{c} rather than the variable $\tilde{T}=-T_{\mathrm{c}}/T$ adopted here. The scaling field h_2 then is proportional to $(T-T_{\mathrm{c}})/T_{\mathrm{c}}$, while φ_2 is then related to the entropy density. The two choices become identical in the asymptotic limit but differ with regard to nonasymptotic corrections. To include a treatment of nonasymptotic critical behavior, use of the inverse temperature as the temperature variable appears to be more appropriate [5–7,13,16,19,20].

The scaling laws, given by Eqs. (2.1) and (2.10), imply asymptotic power-law behavior of various thermodynamic properties along the critical isochore $\rho=\rho_{\mathrm{c}}$, along the coexistence curve $\rho=\rho_{\mathrm{cxc}}$, and along the critical isotherm $T=T_{\mathrm{c}}$. For fluids the weak susceptibility χ_2 is proportional to $\tilde{C}_V/\tilde{T}^2$, which diverges at $\rho=\rho_{\mathrm{c}}$ as

$$\tilde{C}_V/\tilde{T}^2=A_0^{\pm}|\Delta\tilde{T}|^{-\alpha}[1+A_1^{\pm}|\Delta\tilde{T}|^{\Delta_{\mathrm{s}}}+\cdots], \tag{2.18}$$

where the plus and minus signs correspond to $\Delta\tilde{T}>0$ and $\Delta\tilde{T}<0$, respectively. The order parameter φ_1 is proportional to $\Delta\tilde{\rho}$, which along the coexistence curve $\rho=\rho_{\mathrm{cxc}}$ varies as

$$\Delta\tilde{\rho}=\pm B_0|\Delta\tilde{T}|^{\beta}[1+B_1|\Delta\tilde{T}|^{\Delta_{\mathrm{s}}}+\cdots], \tag{2.19}$$

where the plus and minus signs correspond to the liquid and vapor branches of the coexistence curve. The strong susceptibility χ_1 is proportional to $\tilde{\chi}=(\partial\tilde{\rho}/\partial\tilde{\mu})_T$, which diverges as

$$\tilde{\chi}=\Gamma_0^{\pm}|\Delta\tilde{T}|^{-\gamma}[1+\Gamma_1^{\pm}|\Delta\tilde{T}|^{\Delta_{\mathrm{s}}}+\cdots], \tag{2.20}$$

where the plus sign corresponds to $\rho=\rho_{\mathrm{c}}$ above T_{c} and the minus sign to $\rho=\rho_{\mathrm{cxc}}$ below T_{c}. Along the critical isotherm $\Delta\tilde{T}=0$, $\Delta\tilde{\mu}$ varies as

$$\Delta\tilde{\mu}=\pm D_0|\Delta\tilde{\rho}|^{\delta}[1+\cdots]. \tag{2.21}$$

In these equations, $A_0^{\pm}$, $A_1^{\pm}$, B_0, B_1, $\Gamma_0^{\pm}$, $\Gamma_1^{\pm}$, and D_0 are system-dependent coefficients. The amplitudes $A_0^{\pm}$, B_0, $\Gamma_0^{\pm}$, and D_0 of the asymptotic power laws are related to the scaling function $f(z)$ in Eq. (2.1) by

$$A_0^{\pm}=(2-\alpha)(1-\alpha)f_{\pm}(0), \tag{2.22}$$

$$B_0=f_{-}'(0), \tag{2.23}$$

$$\Gamma_0^{\pm}=f_{\pm}''(0), \tag{2.24}$$

$$D_0=\lim_{z\to\infty}\{z[f'(z)]^{-\delta}\}. \tag{2.25}$$

Since the scaling function contains only two system-dependent coefficients, which are multiplicative factors of the function f and of the argument z, respectively, it follows that the asymptotic critical amplitudes $A_0^{\pm}$, B_0, $\Gamma_0^{\pm}$, and D_0 are interrelated by universal ratios so that only two of these amplitudes are independent. Similarly, the correction-to-scaling amplitudes $A_1^{\pm}$, B_1, and $\Gamma_1^{\pm}$ are related by universal ratios so that only one of them is independent.

Asymptotically close to the critical point the correlation length ξ diverges as

$$\xi=\xi_0^{\pm}|\Delta\tilde{T}|^{-\nu}, \tag{2.26}$$

where the plus sign corresponds to $\rho=\rho_{\mathrm{c}}$ above T_{c} and the minus sign to $\rho=\rho_{\mathrm{cxc}}$ below T_{c}. The universal exponent ν is related to the susceptibility exponent γ by $\gamma=(2-\eta)\nu$, where η is the exponent that characterizes the wave number dependence of the structure factor [21]. We note that the correlation-length amplitude ξ_0^{+} is related to the specific heat capacity amplitude A_0^{+} by the so-called principle of two-scale-factor universality [22],

$$\alpha A_0^{+}(\xi_0^{+})^3/v_0=0.0188\pm0.0001. \tag{2.27}$$

Here v_0 is physically the molecular volume. However, since the Helmholtz energy A in Eq. (2.12) has been made dimensionless by dividing by $P_{\mathrm{c}}V$ rather than RT_{c}, in this paper v_0 is actually the molecular volume divided by the critical compression factor $Z_{\mathrm{c}}=P_{\mathrm{c}}/\rho_{\mathrm{c}}RT_{\mathrm{c}}$, so that [18]

$$v_0=k_{\mathrm{B}}T_{\mathrm{c}}/P_{\mathrm{c}}, \tag{2.28}$$

where k_{B} is Boltzmann's constant. The universal critical exponents and the universal critical amplitudes have been calculated by many investigators [14,15,22–28]. The values for the universal critical exponents for three-dimensional Ising-like systems, together with their classical values, are listed in Table I. Theoretical values currently available for the universal critical-amplitude ratios are contained in Table II.

TABLE I. Universal critical exponents for three-dimensional Ising systems and for the classical theory.

Critical exponent	3-dim. Ising systems	Classical value
α	0.110 ± 0.003	0
β	0.3255 ± 0.002	1/2
γ	1.239 ± 0.002	1
δ	4.80 ± 0.02	3
ν	0.630 ± 0.002	1/2
η	0.033 ± 0.004	0
Δ_s	0.52 ± 0.02	1

The simple Ising model and its equivalent, the lattice-gas model, have a special symmetry with respect to the sign of the ordering field h_1. Real fluids near the liquid-gas critical point, however, do not possess the symmetry of the lattice gas [29]. The physical fields, which are the chemical potential and temperature, have no definite scaling dimensionality and one should identify the scaling fields with the linear combinations [30,31]

$$h_1=a_1\Delta\tilde{\mu}+a_2\Delta\tilde{T}, \tag{2.29}$$

$$h_2=b_1\Delta\tilde{T}+b_2\Delta\tilde{\mu}, \tag{2.30}$$

where a_i and b_i are system-dependent coefficients to be determined from a comparison with experimental data. The scaling fields may be normalized in such a way that $a_1=1$ and $b_1=1$ as is done in Eq. (2.16) by putting two system-dependent coefficients in the scaling function $f(z)$ in Eq. (2.1). Taking $a_2=0$ corresponds to the choice of the energy $\tilde{U}_c=(\partial\tilde{P}/\partial\tilde{T})^c_{\tilde{\mu}}$ at the critical point, and we have for the scaling fields

$$h_1=\Delta\tilde{\mu}, \tag{2.31}$$

$$h_2=\Delta\tilde{T}+b_2\Delta\tilde{\mu}. \tag{2.32}$$

The densities conjugate to h_1 and h_2 are

$$\varphi_1=\Delta\tilde{\rho}-b_2\Delta\tilde{U}, \tag{2.33}$$

$$\varphi_2=\Delta\tilde{U}. \tag{2.34}$$

The order parameter φ_1 is not simply proportional to $\Delta\tilde{\rho}$ but has a contribution proportional to $\Delta\tilde{U}$. As a consequence, along the two branches of the phase boundary $\Delta\tilde{\rho}$ varies as

$$\Delta\tilde{\rho}=\pm B_0|\Delta\tilde{T}|^{\beta}+B_a|\Delta\tilde{T}|^{1-\alpha}+\cdots \tag{2.35}$$

with

$$B_a=b_2(2-\alpha)f_-(0). \tag{2.36}$$

The second term in Eq. (2.35) causes a singular asymptotic behavior of the coexistence curve diameter [32]. Most recently, Fisher and Orkoulas have also considered the possibility of adding a pressure contribution to the expressions (2.31) and (2.32) for the scaling fields [33].

In spite of the mixing of the physical fields defined by Eqs. (2.29) and (2.30), the main contribution to the compressibility of a near-critical fluid is the strongly divergent susceptibility χ_1, while the main contribution to the isochoric heat capacity is the weakly divergent susceptibility χ_2.

For a description of the general procedure for specifying the scaling fields of fluid mixtures we refer to some other publications [30,31].

III. CROSSOVER LANDAU MODEL

A. Renormalization of the Helmholtz free-energy density

The modern theory of critical phenomena is based on the renormalization-group theory applied to systems characterized by a Landau-Ginzburg Hamiltonian [1]. To make the connection with this theory we note that the asymptotic Landau expansion for the critical part of the classical local Helmholtz free-energy density [34]

$$\Delta\tilde{A}_{cl}=\frac{1}{2}a_0\Delta\tilde{T}(\Delta\tilde{\rho})^2+\frac{1}{4!}u_0(\Delta\tilde{\rho})^4+\frac{1}{2}c_0(\nabla\tilde{\rho})^2 \tag{3.1}$$

can be rewritten in the rescaled form

$$\Delta\tilde{A}_{cl}=\frac{1}{2}tM^2+\frac{u\Lambda}{4!}M^4+\frac{1}{2}(\tilde{\nabla}M)^2, \tag{3.2}$$

where we have introduced the following transformation of variables and coefficients:

$$M=c_\rho\Delta\tilde{\rho},\quad t=c_t\Delta\tilde{T},\quad \tilde{\nabla}=q_0^{-1}\nabla, \tag{3.3}$$

$$c_tc_\rho^2=a_0,\quad u\Lambda=c_\rho^{-4}u_0,\quad c_0=q_0^{-2}c_\rho^2. \tag{3.4}$$

The system-dependent coefficients a_0, u_0, and c_0 in the Landau expansion (3.1) have been replaced by the two scale factors c_ρ and c_t and the coefficient $u\Lambda$ in Eq. (3.2). In Eqs. (3.3) and (3.4) q_0 is a wave number associated with the

TABLE II. Universal ratios of the leading and correction-to-scaling amplitudes for three-dimensional Ising systems. To calculate the universal amplitude ratios for the crossover Landau model (CLM) and the crossover parametric model (CPM) we adopted $\gamma=1.239$, $\alpha=0.110$, and $\Delta_s=0.51$.

Ratio	Ising model	CLM	CPM
A_0^+/A_0^-	0.523 ± 0.009	0.50	0.524
Γ_0^+/Γ_0^-	4.95 ± 0.15	5.0	4.94
$\alpha A_0^+\Gamma_0^+/B_0^2$	0.0581 ± 0.0010	0.052	0.0580
$\Gamma_0^+D_0B_0^{\delta-1}$	1.57 ± 0.23	1.73	1.71
A_1^+/B_1	1.10 ± 0.25	0.83	0.844
B_1/Γ_1^+	0.90 ± 0.21	0.87	0.897
B_1/Γ_1^-	0.29 ± 0.08		0.175
A_1^+/A_1^-	1.12 ± 0.29		1.20

microscopic structure of the system. For the Ising model $q_0 = \pi/a$, where a is the lattice constant [35,36]. Hence, for fluids we conjecture that

$$q_0 \simeq \pi/v_0^{1/3}. \tag{3.5}$$

The parameter Λ in Eq. (3.2) is to be interpreted as a dimensionless wave number related to an actual cutoff wave number q_{D} for the critical fluctuations by

$$\Lambda = q_{\mathrm{D}}/q_0 = \xi_{\mathrm{D}}^{-1}/q_0. \tag{3.6}$$

The variable M represents the order parameter φ_1 and the variable t the scaling field h_2 [cf. Eqs. (2.16) and (2.17)]. The expression for the classical correlation length ξ_{cl} can be written as

$$\xi_{\mathrm{cl}} = q_0^{-1}\kappa_{\mathrm{cl}}^{-1} \tag{3.7}$$

with

$$\kappa_{\mathrm{cl}}^2 = \left(\frac{\partial^2 \Delta\tilde{A}_{\mathrm{cl}}}{\partial M^2}\right)_t = t + \frac{1}{2}u\Lambda M^2. \tag{3.8}$$

From Eqs. (3.7) and (3.8) it follows that at $M=0$ ξ_{cl} satisfies a power law of the form [7]

$$\xi_{\mathrm{cl}} = \overline{\xi_0^{+}}(\Delta\tilde{T})^{-1/2} \tag{3.9}$$

with $\overline{\xi_0^{+}} = q_0^{-1}c_t^{-1/2} = (c_0/a_0)^{1/2}$.

The rescaled expression (3.2) for $\Delta\tilde{A}_{\mathrm{cl}}$ can be related by a Legendre transformation to the familiar Landau-Ginzburg-Wilson Hamiltonian $\mathcal{H}$:

$$\mathcal{H} = \frac{1}{2}t\phi^2 + \frac{u\Lambda}{4!}\phi^4 + \frac{1}{2}(\nabla\phi)^2 - h\phi, \tag{3.10}$$

where t is the temperaturelike field, ϕ is the fluctuating order parameter whose average value yields M, u is the ϕ^4-theory coupling constant rescaled by a dimensionless ultraviolet cutoff wave number Λ, and h is the ordering field. In implementing the renormalization due to the presence of long-range fluctuations asymptotically close to the critical point, one integrates $\mathcal{H}$ over fluctuations with all wave numbers. However, to account for nonasymptotic effects of the fluctuations one must retain a lower nonzero limit $\Lambda_1 = \xi^{-1}/q_0$ and an upper limit Λ.

An approximate solution of the non-asymptotic renormalization procedure can be obtained with the aid of so-called match-point methods [8,37–39]. Implementing a match-point method proposed by Nicoll and co-workers [8,9,40], Chen *et al.* [5,6] have shown that the classical expression (3.2) for $\Delta\tilde{A}_{\mathrm{cl}}$ can be transformed into the following crossover expression for the singular part $\Delta\tilde{A}_{\mathrm{s}}$ of the actual Helmholtz-energy density:

$$\Delta\tilde{A}_{\mathrm{s}} = \frac{1}{2}tM^2\mathcal{T}\mathcal{D} + \frac{\bar{u}u^*\Lambda}{4!}M^4\mathcal{D}^2\mathcal{U} - \frac{1}{2}t^2\mathcal{K}, \tag{3.11}$$

where $\mathcal{T}$, $\mathcal{D}$, $\mathcal{U}$, and $\mathcal{K}$ are rescaling functions defined by

$$\mathcal{T} = Y^{(2\nu-1)/\Delta_{\mathrm{s}}}, \quad \mathcal{D} = Y^{-\eta\nu/\Delta_{\mathrm{s}}}, \quad \mathcal{U} = Y^{\nu/\Delta_{\mathrm{s}}}, \tag{3.12}$$

and

$$\mathcal{K} = \frac{\nu}{\alpha\bar{u}\Lambda}(Y^{-\alpha/\Delta_{\mathrm{s}}} - 1). \tag{3.13}$$

Here $\bar{u} = u/u^*$ is a rescaled coupling constant with $u^* = 0.472 \pm 0.001$ being the fixed-point coupling constant for Ising systems [41,42]. Note that there is a factor of $3/(n+8)$ difference between the fixed-point value g^* in Ref. [43] (see also [25,28]) and u^* used here, with n being the number of components of the order parameter. The crossover function Y is to be evaluated from the equation [6,7]

$$1 - (1-\bar{u})Y = \bar{u}(1 + \Lambda^2/\kappa^2)^{1/2}Y^{\nu/\Delta_{\mathrm{s}}} \tag{3.14}$$

with κ given by

$$\kappa^2 = t\mathcal{T} + \frac{1}{2}\bar{u}u^*\Lambda M^2\mathcal{D}U. \tag{3.15}$$

The classical limit corresponds to $\bar{u}\Lambda/\kappa \to 0$ or $Y \to 1$, the logarithmic derivative of Y tends to 0, the rescaling functions $\mathcal{T}$, $\mathcal{D}$, and $\mathcal{U}$ tend to unity while $\mathcal{K}$ tends to zero, so that the classical (mean-field) expression (3.2) for the Helmholtz free-energy density (without the gradient term) is recovered:

$$\lim_{\Lambda/\kappa \to 1} \Delta\tilde{A}_{\mathrm{s}} = \Delta\tilde{A}_{\mathrm{cl}}. \tag{3.16}$$

The critical limit corresponds to $\Lambda/\kappa \to \infty$ or

$$Y \to \left(\frac{\kappa}{\bar{u}\Lambda}\right)^{\Delta_{\mathrm{s}}/\nu}, \tag{3.17}$$

and one recovers from Eq. (3.11) the asymptotic scaled critical behavior in the form given by Eq. (2.10) including the leading Wegner correction terms. In this limit the crossover function Y can be expanded in powers of t, yielding in zero field for $t>0$

$$Y \simeq \left(\frac{t}{t_\times}\right)^{\Delta_{\mathrm{s}}}\left[1 - 2\Delta_{\mathrm{s}}(1-\bar{u})\left(\frac{t}{t_\times}\right)^{\Delta_{\mathrm{s}}} + \cdots\right], \tag{3.18}$$

where $t_\times = c_t\Delta\tilde{T}_\times$ is an effective crossover temperature scale such that

$$\Delta\tilde{T}_\times = g = (\bar{u}\Lambda)^2/c_t. \tag{3.19}$$

We note that the crossover from Ising to mean-field critical behavior is governed by two crossover parameters, namely, $\bar{u}$ and g.

For simple fluids the physical cutoff length scale ξ_{D} will be microscopically small ($\xi_{\mathrm{D}} \simeq \overline{\xi_0}$) and we may consider the infinite-cutoff approximation $\Lambda \to \infty$, but $\bar{u} \to 0$, so that the product $\bar{u}\Lambda$ remains finite [7,44]. In this approximation one can recover from the mean-field limit square-root corrections to the classical behavior of susceptibility and heat capacity in the form $(t/t_\times)^{-1/2}$ or $(\Delta\tilde{T}/g)^{-1/2}$, similar to results obtained earlier by Vaks *et al.* [45] and by Levanyuk [46]. In the infinite-cutoff crossover theory (for $\Lambda\to\infty$, $\bar{u}\to 0$, but finite $\bar{u}\Lambda$) the crossover behavior is controlled by a single crossover parameter $g=(\bar{u}\Lambda)^2/c_t$ which is related to the Ginzburg number N_{G} as [7]

$$N_{\mathrm{G}}=n_0 g=n_0\frac{u_0^2 v_0^2}{(u^*)^2 a_0^4(\bar{\xi}_0^+)^6}, \tag{3.20}$$

with $n_0\simeq 0.0314$.

While in the infinite-cutoff crossover theory the crossover behavior can be made *universal* by rescaling of the variable t by $t_\times$ or by $\Delta\tilde{T}$ and the Ginzburg number, in general the crossover behavior implied by Eq. (3.14) is controlled by two independent parameters, namely, the Ginzburg number and the rescaled coupling constant. This can be inferred from the fact that the crossover Eq. (3.14) allows one to describe systems with positive ($\bar{u}<1$) and negative ($\bar{u}>1$) first Wegner correction amplitudes [47–49]. Even for $\bar{u}=1$, when the Wegner correction amplitudes vanish, the crossover to mean-field behavior may still occur if $\Lambda/c_t^{1/2}$ is small. The behavior of the crossover function Y, obtained as a solution to the crossover Eq. (3.14) in zero field, is shown in Fig. 1. The case of small $\Lambda/c_t^{1/2}$ corresponds to crossover to mean-field tricriticality [50,51].

Close to the critical point $Y\to(\kappa/\bar{u}\Lambda)^{\Delta_s/\nu}\to 0$ and the isochoric heat capacity, the order parameter, the susceptibility, and the ordering field satisfy the asymptotic power-law expansions given by Eqs. (2.18)–(2.21). The expressions for the various critical amplitudes in terms of the coefficients c_t and c_ρ and the crossover parameters $\bar{u}$ and Λ are given in Table III [41,52]. Note that the correction-to-scaling amplitudes $A_1^\pm$, B_1, and $\Gamma_1^\pm$ are proportional to $1-\bar{u}$; hence, the leading Wegner corrections are positive for $\bar{u}<1$ and negative for $\bar{u}>1$. Negative correction-to-scaling contributions have been found experimentally for polymer solutions [50] and for aqueous electrolyte solutions [47–49,53]. The explicit values implied by the crossover Landau model for the universal critical amplitudes are shown in Table II.

In analogy to Eq. (3.7) the (crossover) correlation length ξ in zero field in the one-phase region is related to κ by

$$\xi=q_0^{-1}\kappa^{-1}. \tag{3.21}$$

The expression for the universal relationship between the isochoric heat-capacity amplitude A_0^+ and the correlation-length amplitude ξ_0^+ then becomes

$$\alpha A_0^+(\xi_0^+)^3/v_0=\frac{1}{2}\nu(1-\alpha)(2-\alpha)q_0^{-3}/v_0. \tag{3.22}$$

On comparing Eq. (3.22) with Eq. (2.27) we conclude that

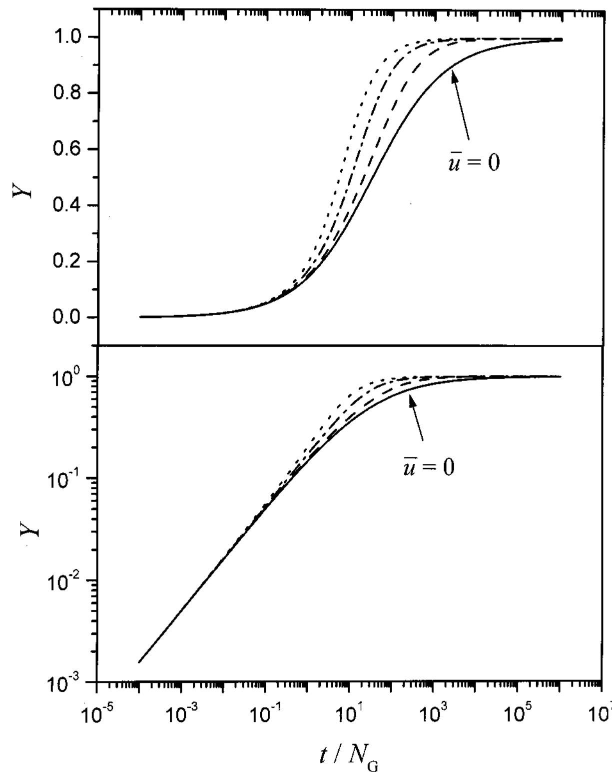

FIG. 1. The crossover function Y as calculated from Eq. (3.14) as a function of the normalized temperature scale t/N_{G} (semilogarithmic and log-log plots). The solid curve corresponds to the infinite-cutoff limit when $\bar{u}=0$. The three other curves correspond to the finite cutoff $\Lambda=1$ with $\bar{u}=0.3$ (dashed curve), with $\bar{u}=1$ (dash-dotted curve), and with $\bar{u}=2$ (dotted curve).

$$q_0=3.04/v_0^{1/3}, \tag{3.23}$$

in good agreement with the conjecture given by Eq. (3.5).

Upon increasing the distance from the critical point, the crossover model provides a continuous transformation from Ising-like critical behavior to mean-field critical behavior. The transformation is controlled by the ratio Λ/κ or, equivalently, by ξ/ξ_{D}, the ratio of the correlation length ξ to the cutoff length $\xi_{\mathrm{D}}=q_{\mathrm{D}}^{-1}$, and by the coupling constant $\bar{u}$. Due to the critical fluctuations, the position of the actual critical temperature T_{c} is shifted with respect to the mean-field critical temperature. The critical-temperature shift can be evaluated by extrapolation of the inverse susceptibility to zero at $\Delta\tilde{\rho}=0$ from the one-phase region far away from the critical point [54].

Expression (3.11) refers to the critical part $\Delta\tilde{A}_{\mathrm{s}}$ of the Helmholtz free-energy density. The total Helmholtz free-energy density is given by [5,6]

$$\tilde{A}=\Delta\tilde{A}_{\mathrm{s}}+\tilde{\rho}\tilde{\mu}_0(T)+\tilde{A}_0(T), \tag{3.24}$$

where $\tilde{\mu}_0(T)$ and $\tilde{A}_0(T)$ are analytic functions of temperature. From Eq. (3.24) we note that $\tilde{\chi}^{-1}=\partial^2\tilde{A}/(\partial\Delta\tilde{\rho})^2$

TABLE III. Leading and correction-to-scaling amplitudes for the crossover Landau model (CLM) and for the crossover parametric model (CPM). Here $g=(\bar{u}\Lambda)^2/c_t$.

CLM	CPM
$A_0^+=2.27g^{\alpha}(a_0^2/u_0)$	$A_0^+=1.68210m_0l_0=1.68210g^{\alpha}\tilde{m}_0\tilde{l}_0$
$A_0^-=4.55g^{\alpha}(a_0^2/u_0)$	$A_0^-=3.21197m_0l_0=3.21197g^{\alpha}\tilde{m}_0\tilde{l}_0$
$\Gamma_0^+=0.871g^{\gamma-1}a_0^{-1}$	$\Gamma_0^+=3.38317m_0/l_0=3.38317g^{\gamma-1}\tilde{m}_0/\tilde{l}_0$
$\Gamma_0^-=0.174g^{\gamma-1}a_0^{-1}$	$\Gamma_0^-=0.684262m_0/l_0=0.684262g^{\gamma-1}\tilde{m}_0/\tilde{l}_0$
$B_0=2.05g^{1/2-\beta}(a_0/u_0)^{1/2}$	$B_0=3.28613m_0=3.28613g^{1/2-\beta}\tilde{m}_0$
$D_0=0.129g^{(3-\delta)/2}a_0(u_0/a_0)^{(\delta-1)/2}$	$D_0=0.00544597l_0/m_0^{\delta}=0.00544597g^{(3-\delta)/2}\tilde{l}_0/\tilde{m}_0^{\delta}$
$A_1^+=0.439g^{-\Delta_s}(1-\bar{u})$	$A_1^+=0.446g^{-\Delta_s}(1-\bar{u})$
$\Gamma_1^+=0.610g^{-\Delta_s}(1-\bar{u})$	$\Gamma_1^+=0.590g^{-\Delta_s}(1-\bar{u})$
$B_1=0.531g^{-\Delta_s}(1-\bar{u})$	$B_1=0.529g^{-\Delta_s}(1-\bar{u})$
	$A_1^-=0.539g^{-\Delta_s}(1-\bar{u})$
	$\Gamma_1^-=3.03g^{-\Delta_s}(1-\bar{u})$

$=\partial^2\Delta\tilde{A}_s/(\partial\Delta\tilde{\rho})^2$. Thus $\Delta\tilde{A}_s$ is the part of $\tilde{A}$ related to the susceptibility $\tilde{\chi}$ and, hence, to the critical fluctuations.

The crossover Landau model (CLM), specified by Eq. (3.11), involves a transformation of the first two terms in the Landau expansion (3.2). This two-term crossover Landau model provides a crossover from Ising critical behavior to asymptotic mean-field critical behavior. A procedure for dealing with crossover from Ising critical behavior to nonasymptotic mean-field critical behavior by including higher-order terms in the Landau expansion has also been developed [6,7,55,56]. However, in the present paper we shall deal only with crossover from Ising critical behavior to asymptotic mean-field critical behavior.

B. Effective exponents

Consider the inverse reduced susceptibility $\tilde{\chi}^{-1}=(\partial^2\Delta\tilde{A}_s/\partial M^2)_t$, where $\Delta\tilde{A}_s$ is the renormalized free-energy density as given by the crossover two-term Landau model. One can define an effective exponent $\gamma_{\rm eff}^{\pm}$ that characterizes the singular behavior of the zero-field susceptibility by [47,57–59]

$$\gamma_{\rm eff}^{\pm}=-d\ln\tilde{\chi}/d\ln|t|. \tag{3.25}$$

Asymptotically close to the critical point $\gamma_{\rm eff}^{\pm}\to\gamma=1.239$, while far away $\gamma_{\rm eff}^{\pm}$ tends to its classical value of 1. If we write the asymptotic expansion (2.20) in terms of the Landau variable t rather than the physical variable $\Delta\tilde{T}$,

$$\tilde{\chi}=\hat{\Gamma}_0^{\pm}|t|^{-\gamma}(1+\hat{\Gamma}_1^{\pm}|t|^{\Delta_s}+\cdots), \tag{3.26}$$

we can deduce a useful asymptotic relation between $\gamma_{\rm eff}^{\pm}$ and the value of the correction-to-scaling amplitude $\hat{\Gamma}_1^{\pm}$, namely,

$$\gamma_{\rm eff}^{\pm}\simeq\gamma-\frac{\hat{\Gamma}_1^{\pm}|t|^{\Delta_s}\Delta_s}{1+\hat{\Gamma}_1^{\pm}|t|^{\Delta_s}}. \tag{3.27}$$

From Eq. (3.27) it is evident that if the correction-to-scaling amplitude $\hat{\Gamma}_1^{\pm}$ is positive then $\gamma_{\rm eff}^{\pm}$ approaches the asymptotic value $\gamma=1.239$ from *below*, while if $\hat{\Gamma}_1^{\pm}$ is negative the asymptotic value is approached from *above*. In Fig. 2 we show the effective susceptibility exponent $\gamma_{\rm eff}^{+}$ as a function of the reduced temperature $t/N_{\rm G}$ for various values of the normalized coupling constant $\bar{u}$, demonstrating the behavior of $\gamma_{\rm eff}^{+}$ for the cases that $\hat{\Gamma}_1^{+}>0$, $\hat{\Gamma}_1^{+}<0$, and $\hat{\Gamma}_1^{+}=0$. The normalized crossover scale is characterized by the crossover temperature $t_{\times}\simeq10N_{\rm G}$ which can be inferred from the position of an inflection point in the dependence of $\gamma_{\rm eff}^{+}$ on t.

In a similar fashion, an effective order-parameter exponent $\beta_{\rm eff}$ can be defined by

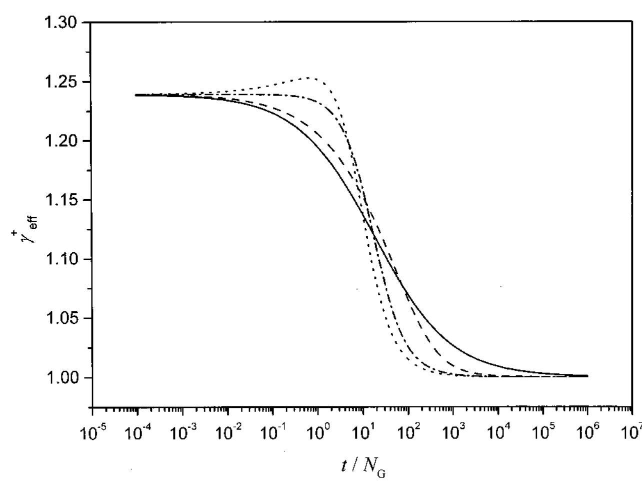

FIG. 2. The effective exponent $\gamma_{\rm eff}^{+}$ defined by Eq. (3.25) for the crossover Landau model as a function of the normalized temperature scale $t/N_{\rm G}$. The solid curve corresponds to the infinite-cutoff limit when $\bar{u}=0$. The three other curves correspond to the finite cutoff $\Lambda=1$ with $\bar{u}=0.3$ (dashed curve), with $\bar{u}=1$ (dash-dotted curve), and with $\bar{u}=2$ (dotted curve).

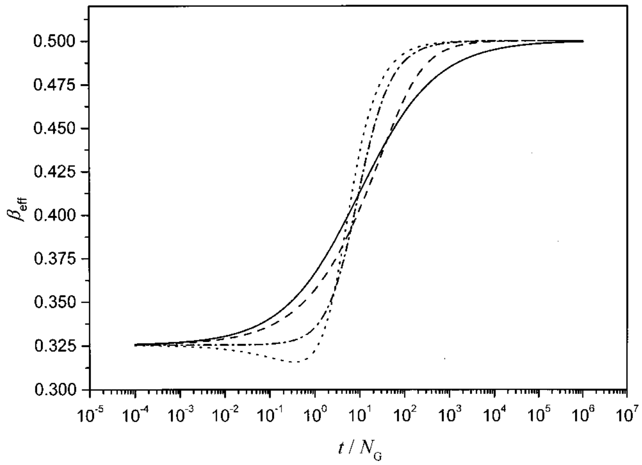

FIG. 3. The effective exponent β_{eff} defined by Eq. (3.28) for the crossover Landau model as a function of the normalized temperature scale t/N_{G}. The solid curve corresponds to the infinite-cutoff limit when $\bar{u}=0$. The three other curves correspond to the finite cutoff $\Lambda=1$ with $\bar{u}=0.3$ (dashed curve), with $\bar{u}=1$ (dash-dotted curve), and with $\bar{u}=2$ (dotted curve).

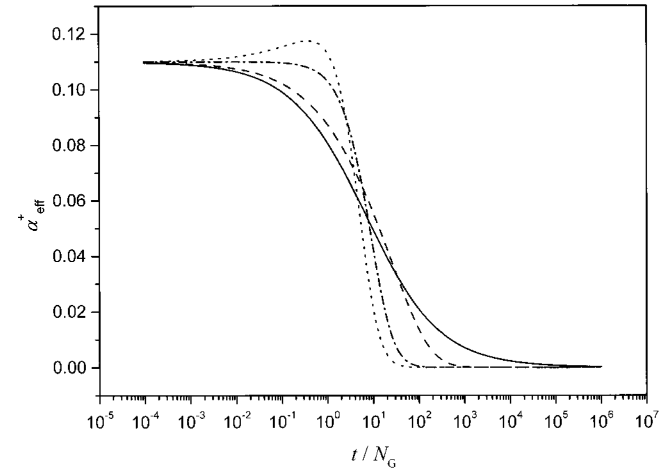

FIG. 4. The effective exponent α^{+}_{eff} defined by Eq. (3.30) for the crossover Landau model as a function of the normalized temperature scale t/N_{G}. The solid curve corresponds to the infinite-cutoff limit when $\bar{u}=0$. The three other curves correspond to the finite cutoff $\Lambda=1$ with $\bar{u}=0.3$ (dashed curve), with $\bar{u}=1$ (dash-dotted curve), and with $\bar{u}=2$ (dotted curve).

$$\beta_{\text{eff}}=d\ \ln|M|/d\ \ln|t|. \tag{3.28}$$

If in the expansion

$$M=\pm\hat{B}_0|t|^{\beta}(1+\hat{B}_1|t|^{\Delta_{\text{s}}}+\cdots) \tag{3.29}$$

$\hat{B}_1$ is positive then β_{eff} approaches its asymptotic value $\beta=0.3255$ from above, while if $\hat{B}_1$ is negative the asymptotic value is approached from below.

Finally, an effective zero-field heat-capacity exponent $\alpha^{\pm}_{\text{eff}}$ can also be defined. Here one must be cautious because there are two contributions to the critical part of the heat capacity: one part is singular and behaves as $\hat{A}^{\pm}_0|t|^{-\alpha}$ asymptotically close to the critical point and the other part is constant and represents an analytic fluctuation-induced critical background term $\hat{B}_{\text{cr}}$. The effective exponent $\alpha^{\pm}_{\text{eff}}$ is pertinent to the diverging term:

$$\alpha^{\pm}_{\text{eff}}=-d\ \ln\left[-\left(\frac{\partial^2\Delta\tilde{A}_{\text{s}}}{\partial t^2}\right)_M+\hat{B}_{\text{cr}}\right]\Big/ d\ \ln|t|. \tag{3.30}$$

As in the case of the susceptibility, for positive values of the correction-to-scaling amplitude $\hat{A}^{\pm}_1$ the asymptotic value $\alpha=0.110$ is approached from below, while for negative $\hat{A}^{\pm}_1$ the asymptotic value is approached from above. In Figs. 3 and 4 we show the effective exponents β_{eff} and α^{+}_{eff}, respectively, for various values of the normalized coupling constant $\bar{u}$.

IV. CROSSOVER PARAMETRIC MODEL

A. Introduction

Expressions (2.5) and (2.8) for the scaling functions $\psi(z)$ and $y(z)$, as given by various approximations of the RG theory, are very cumbersome and inconvenient for practical use, in particular, if one needs to obtain caloric properties by integration. In fact, an accurate closed form of the scaling functions has not been formulated for the three-dimensional Ising model. Moreover, the change from positive to negative values of h_2 involves the mathematical difficulty of passing across the singular critical point [18,60]. Instead, phenomenological parametric representations of an asymptotic scaled equation of state, which operate with a positive variable characterizing the distance from the critical point, have become popular [18,61–65]. One of the simplest parametric representations, the so-called linear model [63], appears to be consistent with the asymptotic RG theory to second order in $\epsilon=4-d$, where d is the dimensionality [66]. Various revisions of the asymptotic parametric representations have been proposed to include Wegner correction-to-scaling terms [16,67,68]. However, such revisions of the asymptotic equation are often inconsistent with the current theoretical predictions for the correction-to-scaling amplitude ratios, and the range of validity of such revised asymptotic equations is still limited [16].

Recently, Fisher *et al.* [11] proposed an asymptotic parametric model that complies with the most recent theoretical estimates for the universal amplitude ratios. We shall use an approach similar to that used by Fisher *et al.* to construct a crossover parametric equation of state valid in the entire critical region. First, we develop an extended asymptotic parametric model. Then, starting with this asymptotic parametric model as a basis, we shall develop a crossover parametric model (CPM) that reproduces almost exactly all relevant asymptotic amplitude ratios and is in good agreement with the estimates for the correction-to-scaling amplitude ratios. This crossover model is advocated for practical use as an alternative to the crossover Landau model.

B. Asymptotic parametric equation of state

A general asymptotic parametric model for the equation of state can be defined by a set of functions $k(\theta)$, $l(\theta)$, and

$m(\theta)$ [65], which specify the relation between the ordering field h_1, the scaling field h_2, and the order parameter φ_1 as follows:

$$h_1 = r^{\beta\delta} l(\theta), \tag{4.1}$$

$$h_2 = r k(\theta), \tag{4.2}$$

and

$$\varphi_1 = r^{\beta} m_1(\theta), \tag{4.3}$$

where r and θ are parametric variables. The variable r is non-negative and represents the distance to the critical point. Critical singularities in the form of power laws are incorporated into the parametric form through the r variable, while the parameter θ specifies a location on a contour of constant r. The sign of θ is taken to be the same as that of the order parameter φ_1. Assuming symmetry in terms of $\pm\theta$, we can formulate the requirements to be imposed on the angular functions $k(\theta)$, $l(\theta)$ and $m_1(\theta)$. Specifically, $k(\theta)$ must be symmetric with respect to θ, while $l(\theta)$, and $m_1(\theta)$ must be antisymmetric with respect to θ. The locus $\theta=0$ corresponds to zero-field ordering ($h_1=\varphi_1=0$) above T_c, where $r=h_2$. The locus $h_2=0$ (corresponding to the critical isotherm) is specified by $\theta=\theta_c$, which corresponds to $k(\pm\theta_c)=0$. To fix the overall factor of $k(\theta)$ we impose the condition $k(0)=1$. On the coexistence boundary the angle θ takes the values $\pm\theta_1$, so that the one-phase region is described by $|\theta|<\theta_1$. Since r is always positive, $k(\theta)$ must change sign at $\theta=\pm\theta_c$ and be positive for $0<|\theta|<\theta_c$ and negative for $\theta_c<|\theta|<\theta_1$. In the same way, solutions of $l(\theta)=0$ specify the zero-field line above T_c and $\pm\theta_1$ below T_c with $l(\theta)$ being positive for positive θ and negative for negative θ. As is commonly done in the literature, these conditions are satisfied by the following transformation:

$$h_1 = r^{\beta\delta} l(\theta), \quad h_2 = r k(\theta) \tag{4.4}$$

with

$$l(\theta) = l_0 \theta (1-\theta^2), \quad k(\theta) = 1 - b^2\theta^2, \tag{4.5}$$

where l_0 is a system-dependent constant and where b^2 is a universal constant. A parametric scaled equation of state can be obtained by specifying the function $m_1(\theta)$ in Eq. (4.3) for the order parameter φ_1. However, rather than specifying this function directly, we prefer to consider the potential $\Delta\Phi(h_1,h_2)$, which has the scaling fields h_1 and h_2 as its characteristic variables [cf. Eq. (2.1)]. Expressing Φ in terms of dimensionless units by introducing $\tilde{\Phi}=(T_c/P_c)(\Phi/VT)$, we write $\Delta\tilde{\Phi}$ in the form

$$\Delta\tilde{\Phi}(h_1,h_2) = r^{2-\alpha} w(\theta) + \frac{1}{2} B_{\mathrm{cr}} r^2 k^2(\theta), \tag{4.6}$$

where the angular function $w(\theta)$ is represented by a polynomial of the form

$$w(\theta) = m_0 l_0 [w_0 + w_1\theta^2 + w_2\theta^4 + w_3\theta^6 + w_4\theta^8], \tag{4.7}$$

TABLE IV. Universal parameters in the crossover parametric model.

$b^2=1.691\,047$	$w_0=-1$	$w_1=1.504\,493$
$w_2=-1.321\,901$	$w_3=-0.189\,833\,6$	$w_4=0.057\,533\,47$

and where m_0 is a second system-dependent coefficient, while $w_0=-1$. The second term on the right-hand side of Eq. (4.6) represents an additive fluctuation contribution [8,69] with a coefficient B_{cr} that is actually related to the crossover parameters, as will be specified by Eq. (4.25) in Sec. III C.

Equations (4.4)–(4.7) define an extended parametric model with five universal coefficients b^2, w_1, w_2, w_3, and w_4 which are chosen in such a way that the amplitudes of the critical power laws implied by this parametric model satisfy the theoretically predicted universal amplitude ratios. The actual values assigned to these universal coefficients are given in Table IV. Our extended parametric model has some similarities with an extended cubic model recently proposed by Fisher *et al.* [11], but has the following advantages. First, upon substituting $w_4=0$ we recover the cubic model, and upon substituting $w_3=w_4=0$ we recover the linear model. Second, for our extended parametric model we can derive explicit expressions for all critical-amplitude ratios, while for the extended cubic model of Fisher *et al.* [11] the value $\theta=\theta_1$ on the coexistence boundary can be obtained only by solving the nonlinear equation $l(\theta)=0$ numerically ($\theta_1=1$ in our extended parametric model).

In order to obtain corresponding expressions for other thermodynamic properties we note that one can write quite generally for the scaling densities and susceptibilities

$$\varphi_1 = r^{\beta} m_1(\theta), \tag{4.8}$$

$$\varphi_2 = r^{1-\alpha} m_2(\theta) - B_{\mathrm{cr}} r k(\theta), \tag{4.9}$$

$$\chi_1 = r^{-\gamma} q_1(\theta), \tag{4.10}$$

$$\chi_2 = r^{-\alpha} q_2(\theta) - B_{\mathrm{cr}}, \tag{4.11}$$

$$\chi_{12} = r^{\beta-1} q_{12}(\theta). \tag{4.12}$$

We can write the higher field derivatives of the susceptibility χ_1 as

$$(\partial^n \chi_1 / \partial h_1^n)_{h_2} = r^{-\gamma - n\beta\delta} s_n(\theta) \tag{4.13}$$

with $n=1,2,\ldots$. The explicit expressions for the angular functions $m_i(\theta)$, $q_i(\theta)$, and $s_i(\theta)$ in terms of $l(\theta)$, $k(\theta)$, and $w(\theta)$ are specified in Appendix A. Equations (4.8)–(4.13) are general and do not depend on the particular forms of the functions $k(\theta)$, $l(\theta)$, and $w(\theta)$. From considerations of symmetry, $m_2(\theta)$, $q_1(\theta)$, and $q_2(\theta)$ are even functions of θ, while $m_1(\theta)$ and $q_{12}(\theta)$ are odd functions of θ. For $s_n(\theta)$ we deduce $s_n(-\theta)=(-1)^n s_n(\theta)$. From Eqs. (4.8)–(4.12) we deduce the following expressions for the leading critical amplitudes:

$$\Gamma_0^+=q_1(0), \quad \Gamma_0^-=|k(\theta_1)|^\gamma q_1(\theta_1), \tag{4.14}$$

$$A_0^+=q_2(0), \quad A_0^-=|k(\theta_1)|^\alpha q_2(\theta_1), \tag{4.15}$$

$$B_0=m_1(\theta_1)/|k(\theta_1)|^\beta, \tag{4.16}$$

$$D_0=l(\theta_c)/[m_1(\theta_c)]^\delta, \tag{4.17}$$

where $\theta_c=1/b$ and $\theta_1=1$. Using the values of the universal coefficients listed in Table IV, one readily deduces from Eqs. (4.14)–(4.17) the values for the universal ratios of the asymptotic amplitudes listed in the last column of Table II.

C. Crossover parametric equation of state

The asymptotic parametric equation of state formulated in Sec. IV B is valid only in the near vicinity of the critical point. In Sec. III we discussed how we can formulate a crossover equation of state that incorporates both Ising critical behavior with the Wegner corrections and mean-field critical behavior by applying a transformation to the critical part of the Helmholtz free-energy density or, more generally, to the thermodynamic potential that has the ordering field h_1 and the order parameter φ_1 as characteristic variables. Our crossover parametric equation of state will be based on the critical part $\Delta\tilde{\Phi}(h_1,h_2)$ of the thermodynamic potential that has h_1 and h_2 as characteristic variables, which is the potential for which the asymptotic parametric equation of state was formulated in Sec. IV B.

In the crossover Landau model, developed from the RG theory of critical phenomena, the parameter κ plays the role of the distance from the critical point and contains two singular contributions, namely, one associated with the temperaturelike variable t and the other with the order parameter M [see Eq. (3.15)]. In the parametric equation of state it is the variable r that serves as a measure of the distance to the critical point. We incorporate the crossover from asymptotic Ising-like critical behavior to classical (mean-field) behavior by applying a proper rescaling transformation to this variable r, while preserving the existing analytic dependence on the angular variable θ.

To formulate a crossover parametric equation of state we relate κ^2 to the distance variable r as

$$\kappa^2(r)=c_t r\mathcal{T}=c_t rY^{(2\nu-1)/\Delta_s}, \tag{4.18}$$

to be compared with the corresponding expression (3.15) in the crossover Landau model, where $t=c_t\Delta\tilde{T}$. From Eq. (4.18) it follows that in the asymptotic critical limit κ will vary as r^ν, while far away from the critical point κ will vary as $r^{1/2}$. Since κ depends only on the variable r, contours of constant r coincide with contours of constant distance variable κ. The crossover function Y is again defined by Eq. (3.14):

$$1-(1-\bar{u})Y=\bar{u}(1+\Lambda^2/\kappa^2)^{1/2}Y^{\nu/\Delta_s}, \tag{4.19}$$

but with κ^2 given by Eq. (4.18). Hence, the crossover function Y, like κ^2, is also only a function of r and independent of θ. From Eqs. (4.18) and (4.19) we note that the crossover function depends on two crossover variables, namely, $\bar{u}$ and $\Lambda/c_t^{1/2}$.

To completely define the crossover parametric equation of state we need to specify the equations for the scaling fields h_1 and h_2 and the thermodynamic potential $\Delta\tilde{\Phi}$. For this purpose we rescale the field h_1 as

$$h_1=r^{3/2}Y^{(2\beta\delta-3)/2\Delta_s}\tilde{l}(\theta), \tag{4.20}$$

which replaces Eq. (4.1) and where

$$\tilde{l}(\theta)=\tilde{l}_0\theta(1-\theta^2), \tag{4.21}$$

while the dependence of the field h_2 on r and θ is left unchanged:

$$h_2=rk(\theta). \tag{4.22}$$

The critical part of the thermodynamic potential $\Delta\tilde{\Phi}(h_1,h_2)$ is now given by

$$\Delta\tilde{\Phi}_s(r,\theta)=r^2Y^{-\alpha/\Delta_s}\tilde{w}(\theta)+\frac{1}{2}B_{cr}r^2k^2(\theta) \tag{4.23}$$

with

$$\tilde{w}(\theta)=\tilde{m}_0\tilde{l}_0[w_0+w_1\theta^2+w_2\theta^4+w_3\theta^6+w_4\theta^8]. \tag{4.24}$$

The term $\frac{1}{2}B_{cr}r^2k^2(\theta)$ in Eq. (4.23) with

$$B_{cr}=-2\tilde{m}_0\tilde{l}_0w_0>0 \tag{4.25}$$

should not be rescaled, since it represents an analytic fluctuation-induced background contribution. The coefficients $\tilde{m}_0$ and $\tilde{l}_0$ in Eqs. (4.21), (4.24), and (4.25) are related to m_0 and l_0 by

$$\tilde{l}_0=l_0g^{\beta\delta-3/2}, \quad \tilde{m}_0=m_0g^{\beta-1/2}, \tag{4.26}$$

where $g=(\bar{u}\Lambda)^2/c_t$ is again the system-dependent parameter related to the Ginzburg number defined by Eq. (3.20).

Equations (4.20), (4.22), and (4.23) completely specify the crossover parametric equation of state, to be referred to as the crossover parametric model. Using Eq. (4.5), we can write Eq. (4.23) also as

$$\begin{aligned}\Delta\tilde{\Phi}_s(r,\theta)/\tilde{m}_0\tilde{l}_0=&r^2Y^{-\alpha/\Delta_s}[w_1\theta^2+w_2\theta^4+w_3\theta^6+w_4\theta^8]\\&+w_0r^2(Y^{-\alpha/\Delta_s}-1)\\&+w_0r^2(2b^2\theta^2-b^4\theta^4).\end{aligned} \tag{4.27}$$

In this form Eq. (4.27) can be compared with Eq. (3.11) for the Helmholtz free-energy density in the crossover Landau model. The last term in Eq. (4.27) can be incorporated into the background part of the thermodynamic potential and is of no importance here. The term $w_0r^2(Y^{-\alpha/\Delta_s}-1)$ is responsible for the singular behavior of the critical part of the heat-capacity asymptotically close to the critical point and for vanishing of the critical part of the heat-capacity far away from the critical point.

Recalling the definitions, Eqs. (2.3)–(2.9) for the scaling densities and susceptibilities and calculating the corresponding derivatives in the crossover parametric equation of state, we obtain

$$\varphi_1 = r^{1/2} Y^{(2\beta-1)/2\Delta_s} \tilde{m}_1(\theta, Y_1), \tag{4.28}$$

$$\varphi_2 = r Y^{-\alpha/\Delta_s} \tilde{m}_2(\theta, Y_1) - B_{\rm cr} r k(\theta), \tag{4.29}$$

$$\chi_1 = r^{-1} Y^{(1-\gamma)/\Delta_s} \tilde{q}_1(\theta, Y_1), \tag{4.30}$$

$$\chi_2 = Y^{-\alpha/\Delta_s} \tilde{q}_2(\theta, Y_1) - B_{\rm cr}, \tag{4.31}$$

$$\chi_{12} = r^{-1/2} Y^{(2\beta-1)/2\Delta_s} \tilde{q}_{12}(\theta, Y_1), \tag{4.32}$$

to be compared with Eqs. (4.8)–(4.12). In these equations

$$Y_1(r) \equiv \frac{d \ln Y}{d \ln r^{\Delta_s}} = \frac{1}{\Delta_s} \frac{r}{Y} \frac{dY}{dr}$$

and the explicit expressions for the functions $\tilde{m}_i(\theta, Y_1)$ and $\tilde{q}_i(\theta, Y_1)$ are presented in Appendix A. In the asymptotic critical limit $Y \to (r/g)^{\Delta_s}$ and we recover the original expressions (4.8)–(4.12) for the asymptotic parametric equation of state. The total thermodynamic potential $\Delta\tilde{\Phi}(h_1, h_2)$ is obtained by adding to the crossover expression (4.23) for $\Delta\tilde{\Phi}_s$ a background contribution that depends analytically on the physical field variables.

D. Critical amplitudes and effective critical exponents

In the asymptotic critical limit $r \to 0$, the crossover function $Y(r)$ can be expanded as

$$Y(r) = (r/g)^{\Delta_s}[1 - Y_{10} r^{\Delta_s} + \mathcal{O}(r^{2\Delta_s})] \tag{4.33}$$

and the corresponding expansion of $Y_1(r)$ is obtained by differentiation as

$$Y_1(r) = 1 - Y_{10} r^{\Delta_s} + \mathcal{O}(r^{2\Delta_s}), \tag{4.34}$$

where

$$Y_{10} = 2\Delta_s g^{-\Delta_s}(1 - \bar{u}). \tag{4.35}$$

Asymptotically close to the critical point the crossover function Y_1 and the corresponding expressions for the functions $\tilde{m}_i$ and $\tilde{q}_i$ can be expanded in power series in r, namely,

$$\tilde{m}_i(\theta, Y_1) \propto m_i(\theta)[1 + m_{i,1}(\theta) Y_{10} r^{\Delta_s} + \cdots], \tag{4.36}$$

$$\tilde{q}_i(\theta, Y_1) \propto q_i(\theta)[1 + q_{i,1}(\theta) Y_{10} r^{\Delta_s} + \cdots], \tag{4.37}$$

where $i = 1,\ 2$, and 12. The angular functions $m_{i,1}(\theta)$ and $q_{i,1}(\theta)$ are given in Appendix A. Using the expressions (4.36) and (4.37) one can readily derive explicit expressions for the leading and correction-to-scaling amplitudes of the power-law expressions defined in Sec. II, as shown in Appendix A. The final expressions for these amplitudes are given in the second column of Table III. The values of the resulting amplitude ratios are presented in the last column of Table II. From the information in Table II we conclude that all universal amplitude ratios of the crossover parametric model agree with the theoretical values for the three-dimensional Ising model within their estimated accuracies.

Far away from the critical point the crossover function Y and its logarithmic derivative Y_1 behave as

$$Y \simeq 1 - \frac{\bar{u}\Lambda^2}{r} f(\bar{u}) \tag{4.38}$$

and

$$Y_1 \simeq \frac{\bar{u}\Lambda^2/\Delta_s}{r} f(\bar{u}) \tag{4.39}$$

with

$$f(\bar{u}) = \frac{1}{2}[1 + \bar{u}(\nu/\Delta_s - 1)]^{-1}, \tag{4.40}$$

so that for $r \to \infty$ one has $Y \to 1$ and $Y_1 \to 0$. In this limit, expressions (4.8)–(4.11) for the scaling densities and susceptibilities reduce to

$$\varphi_1 = r^{1/2} \bar{m}_1(\theta), \tag{4.41}$$

$$\varphi_2 = r \bar{m}_2(\theta) - B_{\rm cr} r k(\theta), \tag{4.42}$$

$$\chi_1 = r^{-1} \bar{q}_1(\theta), \tag{4.43}$$

$$\chi_2 = \bar{q}_2(\theta) - B_{\rm cr}, \tag{4.44}$$

where the functions $\bar{m}_i(\theta)$ and $\bar{q}_i(\theta)$ are also given in Appendix A. Thus, for large r we recover classical (mean-field) power laws with the amplitudes

$$\bar{A}_0^+ = \bar{q}_2(0) - B_{\rm cr}, \quad \bar{A}_0^- = \bar{q}_2(1) - B_{\rm cr}, \tag{4.45}$$

$$\bar{B}_0 = (b^2 - 1)^{1/2} \bar{m}_1(1), \tag{4.46}$$

$$\bar{\Gamma}_0^+ = \bar{q}_1(0), \quad \bar{\Gamma}_0^- = (b^2 - 1)\bar{q}_1(1), \tag{4.47}$$

and

$$\bar{D}_0 = \tilde{l}(\theta_c)/[\bar{m}_1(\theta_c)]^3. \tag{4.48}$$

We find $\bar{q}_2(0) = B_{\rm cr}$ so that $\bar{A}_0^+ = 0$, as it should be in the classical theory. The classical jump of the heat capacity is recovered as

$$\Delta \bar{C}_V = \bar{q}_2(1) - B_{\rm cr}. \tag{4.49}$$

The ratio $\bar{\Gamma}_0^+/\bar{\Gamma}_0^-$ is universal and in the CPM it is given by

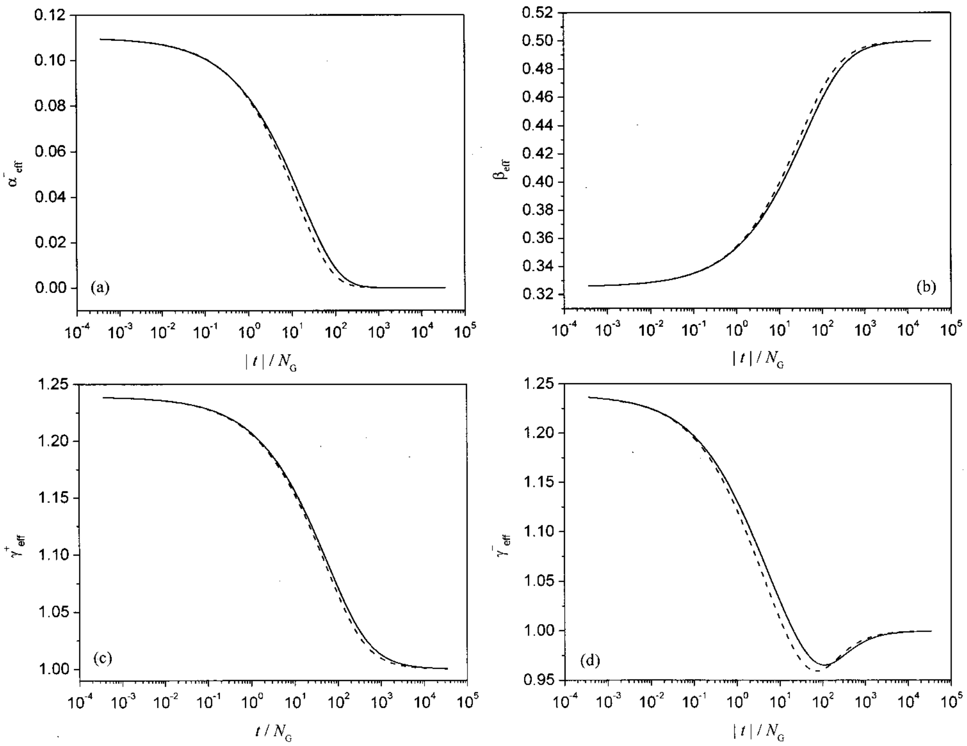

FIG. 5. Effective critical exponents for the crossover parametric model (solid curves) and for the crossover Landau model (dashed curves) calculated for the case $\bar{u}=0.3$ and $\Lambda=1$: (a) $\alpha^-_{\rm eff}$, (b) $\beta_{\rm eff}$, (c) $\gamma^+_{\rm eff}$, and (d) $\gamma^-_{\rm eff}$. The effective exponent $\alpha^+_{\rm eff}$ for the crossover parametric model coincides identically with that for the crossover Landau model for any value of the coupling constant $\bar{u}$ and reduced temperature t and is not shown.

$$\bar{\Gamma}^+_0/\bar{\Gamma}^-_0 \simeq 2.056, \tag{4.50}$$

which differs from the theoretical value of 2 by 2.8%. The ratio $\bar{R}_c \equiv \bar{\Gamma}^+_0 \Delta \bar{C}_V/\bar{B}^2_0$ is also universal in the classical theory and plays the same role as the universal ratio $R_c = \alpha A^+_0 \Gamma^+_0/B^2_0$ in the asymptotic scaling theory. Calculating this ratio, we find

$$\bar{R}_c \simeq 0.5109, \tag{4.51}$$

which differs by 2.1% from the theoretical value of $\bar{R}_c = 1/2$. For the ratio $\bar{\Gamma}^+_0 \bar{D}_0 \bar{B}^2_0$ we obtain

$$\bar{\Gamma}^+_0 \bar{D}_0 \bar{B}^2_0 \simeq 1.015, \tag{4.52}$$

to be compared with the exact value of 1 in the classical theory.

Finally, we consider the crossover behavior of the effective critical exponents implied by the crossover parametric model. As an illustration, we have plotted in Fig. 5 the effective exponents as calculated from the CPM and from the CLM for $\bar{u}=0.3$. The curves are almost identical, especially in the vicinity of the critical temperature, which is reasonable because the correction-to-scaling amplitudes and their ratios in the CPM are very close to those in the CLM. The critical exponent $\alpha^+_{\rm eff}$ of the CPM coincides identically with that of the CLM and is not shown.

Numerical values for the effective critical exponents of three-dimensional Ising lattices with a variety of interaction ranges have recently been obtained by Luijten and Binder [70]. In a previous publication we demonstrated that the crossover Landau model gives a good representation of these numerical critical-exponent values both as a function of temperature and as a function of the interaction range [71]. Since the difference between the effective critical exponents of the CLM and of the CPM is small, and certainly smaller than the accuracy with which the numerical effective exponents can be calculated, we conclude that the crossover parametric model is also consistent with the effective critical exponents for Ising lattices.

V. COMPARISON WITH OTHER PARAMETRIC FORMULATIONS

A previous attempt to transform the crossover Landau model into a parametric representation has been made by Luettmer-Strathmann *et al.* [72], and it has been applied to represent the thermodynamic properties of ethane [72–74] and of argon [75] in the critical region. Since the variable κ, given by Eq. (3.15), plays a role similar to the distance parameter r in parametric models, one can set $\kappa = r^\nu$ and identify the ratio

$$\frac{u^* \bar{u} \Lambda M^2 \mathcal{D} U}{\kappa^2} \equiv \Theta^2 \tag{5.1}$$

with the angular variable Θ [9,72]. The parametric crossover model of Luettmer-Strathmann *et al.* is mathematically equivalent to a variant of the crossover Landau model described in Sec. III in which the implicit Eq. (3.14) for the crossover function Y is approximated by an explicit equation of the form

$$Y = \{1 + \bar{u}[(1+\Lambda^2/\kappa^2)^{\omega/2} - 1]\}^{-1}, \tag{5.2}$$

where $\omega=\Delta_s/\nu$. This version of the crossover Landau model has been designated as crossover model I by Tang *et al.* [41]. Parametrization of the temperaturelike variable t and the densitylike variable M follows as

$$t=rZ^{(1/\nu-2)/\omega}(1-\Theta^2/2), \tag{5.3}$$

$$M=(u^*\bar{u}\Lambda)^{-1/2}(r^{2\nu}+\Lambda^2)^{(1-\omega)/4}r^\beta Z^{(\eta-\omega)/2\omega}\Theta, \tag{5.4}$$

where Z is a function of r:

$$Z(r)=[(1-\bar{u})r^{\omega\nu}+\bar{u}(r^{2\nu}+\Lambda^2)^{\omega/2}]^{-1}. \tag{5.5}$$

The parametrized variables t and M are to be substituted into Eq. (3.11) for the crossover free-energy density, yielding $\Delta\tilde{A}_s$ as a function of r and Θ [72]. It should be noted that in applying this transformation Luettmer-Strathmann *et al.* also retained higher-order terms in the expansion (3.11) for the crossover Helmholtz-energy density so as to increase the range of applicability of the crossover model in the actual representation of thermodynamic-property data of fluids in the critical region [72,75]. The numerical values for the asymptotic amplitude ratios are identical with the values listed in Table II for the crossover Landau model, while $A_1^+/B_1=1.25$ and $B_1/\Gamma_1^+=0.60$ as quoted by Tang *et al.* for crossover model I [41].

Another parametric crossover model has been proposed by Belyakov *et al.* [76]. This parametric crossover model is a generalization of a theoretical solution obtained earlier by Belyakov and Kiselev [77] from renormalization-group theory to first order in $\epsilon=4-d$, where d is the dimensionality of the system. This solution corresponds to the infinite-cutoff approximation [7] and, hence, as discussed in Sec. III A, the crossover model of Belyakov and Kiselev contains only one system-dependent crossover parameter related to the Ginzburg number N_G. In the asymptotic critical limit the crossover model of Belyakov and Kiselev reduces to the linear-model parametric equation of state [$w_3=w_4=0$ in Eq. (4.7)] with $b^2=1.3766$ [76]. No detailed information about the values implied for the ratios of the correction-to-scaling amplitudes or about the behavior of effective critical exponents was provided by the authors. However, an analysis made by Anisimov *et al.* [7] of an earlier version of the crossover model of Belyakov and Kiselev [77] indicated good agreement of the temperature dependence of the effective critical exponents with those implied by the crossover Landau model.

A more phenomenological parametric crossover model was formulated by Kiselev and co-workers [78–82]. In the most recent version, the expression [Eq. (2.17) in Ref. [82]] for the crossover function in the model of Kiselev contains a universal constant q_0. For $q_0=1$ the crossover model of Kiselev reduces to an asymptotic equation of state with correction-to-scaling terms derived by Berestov [83] up to second order in $\epsilon=4-d$. The values implied by this crossover model for the universal amplitude ratios are [41]

$$A_0^+/A_0^-=0.52,\ \ \Gamma_0^+/\Gamma_0^-=4.87,$$
$$\alpha A_0^+\Gamma_0^+/B_0^2=0.056,\ \ \Gamma_0^+D_0B_0^{\delta-1}=1.69, \tag{5.6}$$

and

$$A_1^+/B_1=0.53,\ \ B_1/\Gamma_1^+=1.23. \tag{5.7}$$

The asymptotic amplitude ratios (5.6) are identical to those of the linear model and comparison with the information provided in Table II shows that these ratios are quite satisfactory. However, the ratios (5.7) of the correction-to-scaling amplitudes differ significantly from the theoretical estimates in Table II. The temperature dependence of the effective critical exponents of the phenomenological crossover model of Kiselev is different from that implied by the crossover Landau model as discussed by Anisimov *et al.* [7].

VI. APPLICATION TO ONE-COMPONENT FLUIDS

The crossover model developed in Sec. IV yields a set of parametric equations for the thermodynamic potential $\Delta\tilde{\Phi}(h_1,h_2)$. The crossover parametric model can be applied to one-component fluids h_1 and h_2 with the expressions as given by Eqs. (2.29) and (2.30) or, equivalently, Eqs. (2.31) and (2.32). The appropriate thermodynamic relations needed to deduce the various thermodynamic properties from the potential $\Delta\tilde{\Phi}(h_1,h_2)$ are presented in Appendix B.

As an illustration, we show here how the crossover parametric model can be applied to represent susceptibility data and heat-capacity data recently obtained by Barmatz *et al.* [84,85] for ^{3}He at the critical density as a function of temperature. Because of the high degree of vapor-liquid symmetry in the case of ^{3}He, we neglect the effect of any mixing of the physical fields, so that $h_1=\Delta\tilde{\mu}$, $h_2=\Delta\tilde{T}$, $\varphi_1=\Delta\tilde{\rho}$, and $\varphi_2=\Delta\tilde{U}$. The thermodynamic expression for the isothermal susceptibility χ then becomes

$$\chi=\left(\frac{\partial\rho}{\partial\mu}\right)_T=\frac{\rho_c^2}{P_c}\frac{T_c}{T}\left(\frac{\partial\tilde{\rho}}{\partial\tilde{\mu}}\right)_{\tilde{T}}=\frac{\rho_c^2T_c}{P_c}(\chi_1/T), \tag{6.1}$$

with χ_1 given by Eq. (4.30). For the isochoric specific heat capacity C_V we obtain

$$C_V=\frac{P_cT_c}{\rho_c}(\chi_2/T^2)+C_0+C_1\Delta\tilde{T}+C_2\Delta\tilde{T}^2+C_3\Delta\tilde{T}^3, \tag{6.2}$$

where χ_2 is given by Eq. (4.31) and where the noncritical analytic background to the isochoric specific heat capacity has been represented by a truncated Taylor series with coefficients C_i.

We have fitted the experimental data obtained by Barmatz *et al.* [84] to Eqs. (6.1) and (6.2) using the critical temperature T_c, the CPM parameters l_0, m_0, $\bar{u}$, and $\Lambda/c_t^{1/2}$, and the background coefficients C_i as adjustable constants. Since the parameters $\bar{u}$ and $\Lambda/c_t^{1/2}$ for a molecular fluid like ^{3}He are

TABLE V. Parameters for ^{3}He deduced from the experimental susceptibility and heat capacity of Barmatz *et al.* [84].

Critical parameters
$P_c = 114.657$ kPa (fixed)
$\rho_c = 13.7598$ mol/L (fixed)
$T_c = 3.315581$ K
Asymptotic scaling parameters
$l_0 = 6.89 \pm 0.12$
$m_0 = 0.306 \pm 0.01$
Crossover parameter [a]
$\bar{u}\Lambda / c_t^{1/2} = 0.528 \pm 0.003$
Caloric background parameters
$C_0 = 3.69 \pm 0.02$
$C_1 = 10.9 \pm 0.5$
$C_2 = -299 \pm 11$
$C_3 = 3570 \pm 323$

[a] $\Lambda / c_t^{1/2} = \pi$ (fixed).

strongly correlated, we only fitted for $g = (\bar{u}\Lambda)^2 / c_t$, adopting somewhat arbitrarily $\Lambda / c_t^{1/2} = \pi$. The values obtained for the system-dependent parameters are presented in Table V. The resulting value of the Ginzburg number of ^{3}He is

$$N_G = 8.75 \times 10^{-3}. \tag{6.3}$$

A comparison with the experimental susceptibility data (in the one-phase region above T_c) is shown in Fig. 6 and a comparison with the experimental C_V data above and below T_c is shown in Figs. 7 and 8 on a linear and double-logarithmic scale, respectively. It is seen that the crossover parametric model yields an excellent representation of these experimental data. With the values obtained for the system-dependent constants listed in Table V, we can readily calculate the critical amplitudes A_0^+, A_1^+, Γ_0^+, and Γ_1^+ for ^{3}He using the expressions given in Table III:

$$A_0^+ = 3.548 \pm 0.031, \quad A_1^+ = 0.712 \pm 0.006, \tag{6.4}$$

$$\Gamma_0^+ = 0.150 \pm 0.002, \quad \Gamma_1^+ = 0.941 \pm 0.007. \tag{6.5}$$

With the aid of Eq. (2.27) we calculate

$$\xi_0^+ = 0.268 \pm 0.004 \ \text{nm}, \tag{6.6}$$

which is consistent with the estimate $\xi_0^+ = 0.26$ nm reported by previous investigators [86–88].

VII. DISCUSSION

In this paper we have developed a crossover parametric equation of state that satisfies the most recent theoretical estimates for the universal ratios of the critical amplitudes and of the correction-to-scaling amplitudes. The crossover behavior implied for the effective critical exponents is in good agreement with that previously obtained from a renormalization-group matching technique [7]. The parametric equation incorporates crossover to classical mean-field critical behavior away from the critical point, recovering the classical amplitude ratios to within a few percent. Using ^{3}He as an example, we have demonstrated how the crossover parametric equation can be used to represent experimental thermodynamic-property data of fluids in the critical region.

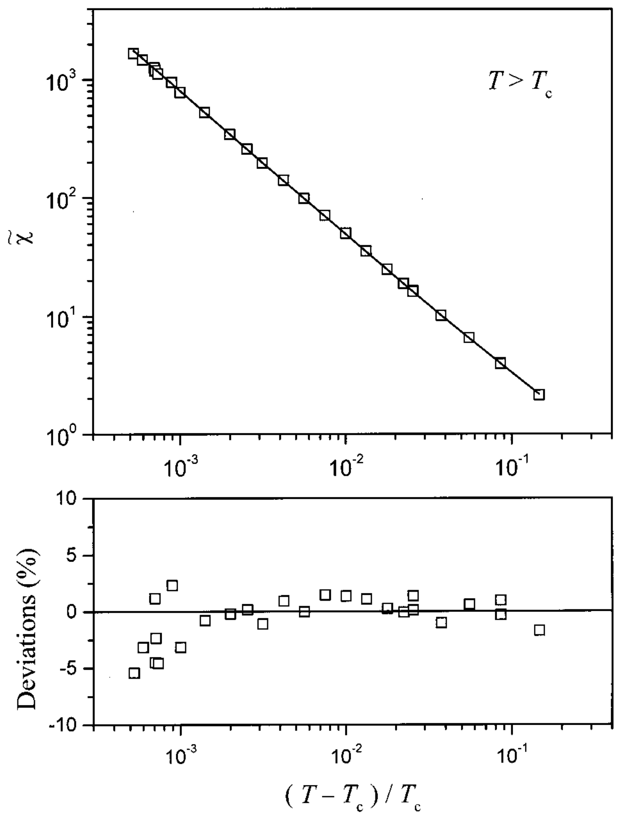

FIG. 6. Susceptibility χ (in dimensionless units) of ^{3}He as a function of $(T-T_c)/T_c$. The symbols represent the experimental data and the solid curves the values calculated from the crossover parametric model.

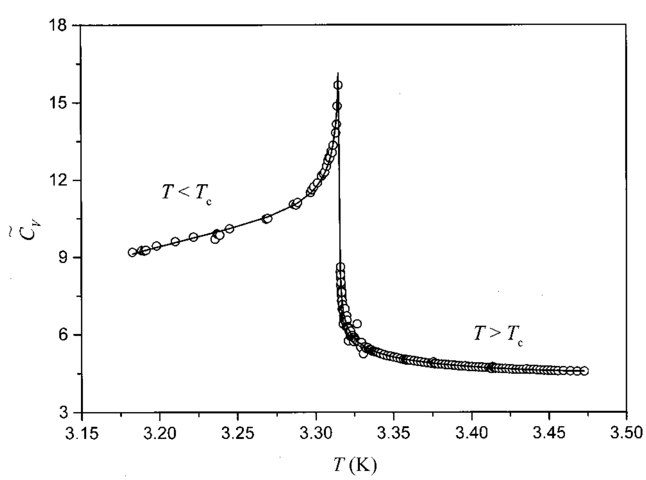

FIG. 7. Specific isochoric heat capacity C_V (in dimensionless units) of ^{3}He as a function of T. The symbols indicate the experimental data and the solid curve represents the values calculated from the crossover parametric model.

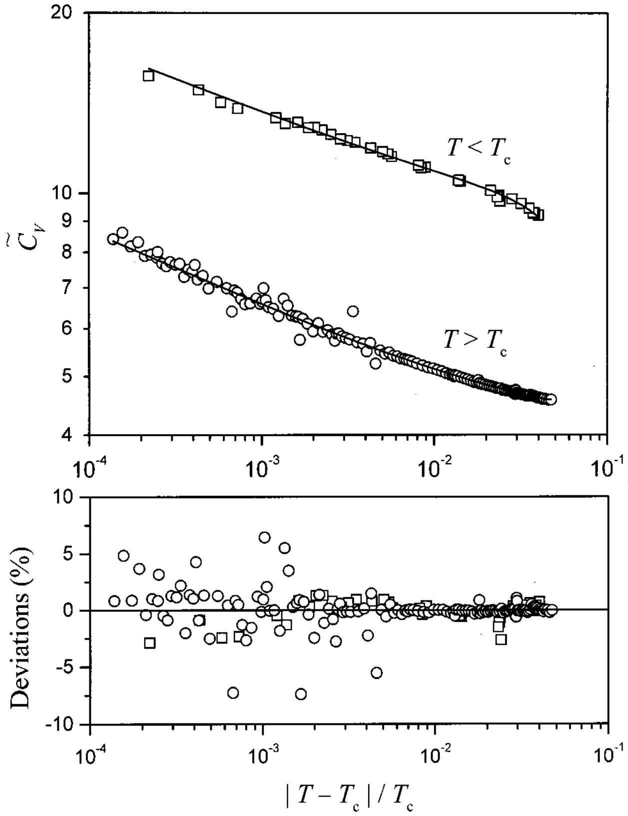

FIG. 8. Specific isochoric heat capacity C_V (in dimensionless units) of ^{3}He as a function of $|T-T_c|/T_c$. The symbols represent the experimental data and the solid curves the values calculated from the crossover parametric model.

The crossover parametric equation of state can be readily extended to a description of thermodynamic-property data of fluid mixtures including crossover from vapor-liquid critical behavior to consolute critical behavior by applying the principle of isomorphism of critical phenomena [30,31].

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APPENDIX A: EQUATIONS FOR THE PARAMETRIC MODEL

The definition of the asymptotic parametric model is

$$h_1 = r^{\beta\delta} l(\theta), \quad h_2 = r k(\theta), \tag{A1}$$

$$\Delta\tilde{\Phi}(h_1,h_2) = r^{2-\alpha} w(\theta) + \frac{1}{2} B_{\mathrm{cr}} r^2 k^2(\theta), \tag{A2}$$

with

$$l(\theta) = l_0 \theta(1-\theta^2), \quad k(\theta) = 1 - b^2\theta^2, \tag{A3}$$

$$w(\theta) = m_0 l_0 [w_0 + w_1\theta^2 + w_2\theta^4 + w_3\theta^6 + w_4\theta^8]. \tag{A4}$$

The auxiliary asymptotic angular functions are given by

$$m_1(\theta) = \frac{(2-\alpha)wk' - w'k}{l'k - \beta\delta lk'}, \tag{A5}$$

$$m_2(\theta) = -\frac{(2-\alpha)wl' - \beta\delta w'l}{l'k - \beta\delta lk'}, \tag{A6}$$

$$q_1(\theta) = -\frac{\beta m_1 k' - m_1' k}{l'k - \beta\delta lk'}, \tag{A7}$$

$$q_2(\theta) = \frac{(1-\alpha) m_2 l' - \beta\delta m_2' l}{l'k - \beta\delta lk'}, \tag{A8}$$

$$q_{12}(\theta) = \frac{\beta(m_1 l' - \delta m_1' l)}{l'k - \beta\delta lk'}, \tag{A9}$$

$$s_1(\theta) = \frac{\gamma q_1 k' + q_1' k}{l'k - \beta\delta lk'}, \tag{A10}$$

$$s_{n+1}(\theta) = \frac{(\gamma + n\beta\delta) s_n k' + s_n' k}{l'k - \beta\delta lk'}. \tag{A11}$$

In this appendix quantities with a prime indicate the derivative with respect to θ (at constant r).

Expressions for the auxiliary angular functions at $\theta=0$ and $\theta=1$ are

$$q_1(0) = \frac{m_0}{l_0}[4w_1 - 2(2-\alpha)b^2 w_0], \tag{A12}$$

$$q_1(1) = \frac{m_0}{l_0}\left\{\frac{[2\beta b^2(1-\delta) + 5b^2 - 3][(b^2-1)\sigma_2 - (2-\alpha)b^2\sigma_1]}{2(b^2-1)^2} + \frac{(2-\alpha)b^2(\sigma_1 + 2\sigma_2) - (b^2-1)\sigma_3 - 2b^2\sigma_2}{2(b^2-1)}\right\}, \tag{A13}$$

$$q_2(0)=-l_0m_0(2-\alpha)(1-\alpha)w_0, \tag{A14}$$

$$q_2(1)=-l_0m_0\frac{(2-\alpha)(1-\alpha)\sigma_1}{(b^2-1)^2}, \tag{A15}$$

$$m_1(1)=m_0\left[\sigma_2-\frac{(2-\alpha)b^2\sigma_1}{(b^2-1)}\right], \tag{A16}$$

where

$$\sigma_1=\sum_{j=0}^{3} w_j, \quad \sigma_2=\sum_{j=0}^{3} jw_j, \quad \sigma_3=\sum_{j=0}^{3}(2j-1)jw_j. \tag{A17}$$

The critical amplitudes are given by

$$A_0^+=q_2(0), \tag{A18}$$

$$A_0^-=(b^2-1)^{\alpha}q_2(1), \tag{A19}$$

$$B_0=(b^2-1)^{-\beta}m_1(1), \tag{A20}$$

$$\Gamma_0^+=q_1(0), \tag{A21}$$

$$\Gamma_0^-=(b^2-1)^{\gamma}q_1(1), \tag{A22}$$

$$D_0=l(b^{-1})m_1(b^{-1})^{-\delta}. \tag{A23}$$

The definition of the crossover parametric model is

$$h_1=r^{3/2}Y^{(2\beta\delta-3)/2\Delta_s}\tilde{l}(\theta), \quad h_2=rk(\theta), \tag{A24}$$

$$\Delta\tilde{\Phi}_s(r,\theta)=r^2Y^{-\alpha/\Delta_s}\tilde{w}(\theta)+\frac{1}{2}B_{cr}r^2k^2(\theta), \tag{A25}$$

with

$$\tilde{l}(\theta)=\tilde{l}_0\theta(1-\theta^2), \quad k(\theta)=1-b^2\theta^2, \tag{A26}$$

$$\tilde{w}(\theta)=\tilde{m}_0\tilde{l}_0[w_0+w_1\theta^2+w_2\theta^4+w_3\theta^6+w_4\theta^8], \tag{A27}$$

$$B_{cr}=-2\tilde{m}_0\tilde{l}_0w_0, \tag{A28}$$

where

$$\tilde{l}_0=l_0g^{\beta\delta-3/2}, \quad \tilde{m}_0=m_0g^{\beta-1/2}, \tag{A29}$$

and

$$g=(\bar{u}\Lambda)^2/c_t. \tag{A30}$$

The radial crossover functions are given by

$$1-(1-\bar{u})Y(r)=\bar{u}(1+\Lambda^2/\kappa^2)^{1/2}Y^{\nu/\Delta_s}(r), \tag{A31}$$

$$Y_1(r)\equiv\frac{1}{\Delta_s}\frac{r}{Y}\frac{dY}{dr}=\frac{1}{\Delta_s}\frac{f_1\kappa^2}{1+f_1f_2} \tag{A32}$$

with

$$\kappa^2=c_trY(r)^{(2\nu-1)/\Delta_s}, \tag{A33}$$

$$f_1=\frac{\Lambda^2}{2\kappa^4}\left(1+\frac{\Lambda^2}{\kappa^2}\right)^{-1}\left[\frac{\nu}{\Delta_s}+\frac{(1-\bar{u})Y(r)}{1-(1-\bar{u})Y(r)}\right]^{-1}, \tag{A34}$$

$$f_2=-\left(\frac{2\nu-1}{\Delta_s}\right)\kappa^2. \tag{A35}$$

The auxiliary angular crossover functions are

$$\tilde{m}_1(\theta,Y_1)=\frac{(2-\alpha Y_1)\tilde{w}k'-\tilde{w}'k}{\tilde{l}'k-[3/2+(\beta\delta-3/2)Y_1]\tilde{l}k'}, \tag{A36}$$

$$\tilde{m}_2(\theta,Y_1)=-\frac{(2-\alpha Y_1)\tilde{w}\tilde{l}'-[3/2+(\beta\delta-3/2)Y_1]\tilde{w}'\tilde{l}}{\tilde{l}'k-[3/2+(\beta\delta-3/2)Y_1]\tilde{l}k'}, \tag{A37}$$

$$\tilde{q}_1(\theta,Y_1)=-\frac{\{\tilde{m}_1[1/2+(\beta-1/2)Y_1]+r(\partial\tilde{m}_1/\partial r)_\theta\}k'-\tilde{m}_1'k}{\tilde{l}'k-[3/2+(\beta\delta-3/2)Y_1]\tilde{l}k'}, \tag{A38}$$

$$\tilde{q}_2(\theta,Y_1)=\frac{\{\tilde{m}_2(1-\alpha Y_1)+r(\partial\tilde{m}_2/\partial r)_\theta\}\tilde{l}'}{\tilde{l}'k-[3/2+(\beta\delta-3/2)Y_1]\tilde{l}k'}-\frac{[3/2+(\beta\delta-3/2)Y_1]\tilde{m}_2'\tilde{l}}{\tilde{l}'k-[3/2+(\beta\delta-3/2)Y_1]\tilde{l}k'}, \tag{A39}$$

$$\tilde{q}_{12}(\theta,Y_1)=\frac{\{\tilde{m}_1[1/2+(\beta-1/2)Y_1]+r(\partial\tilde{m}_1/\partial r)_\theta\}\tilde{l}'}{\tilde{l}'k-[3/2+(\beta\delta-3/2)Y_1]\tilde{l}k'}-\frac{[3/2+(\beta\delta-3/2)Y_1]\tilde{m}_1'\tilde{l}}{\tilde{l}'k-[3/2+(\beta\delta-3/2)Y_1]\tilde{l}k'}. \tag{A40}$$

The angular correction-to-scaling functions are

$$m_{1,1}(\theta)=\frac{\alpha wk'}{(2-\alpha)wk'-w'k}-\frac{(\beta\delta-3/2)lk'}{l'k-\beta\delta lk'}, \tag{A41}$$

$$m_{2,1}(\theta)=\frac{\alpha wl'+(\beta\delta-3/2)w'l}{(2-\alpha)wl'-\beta\delta w'l}-\frac{(\beta\delta-3/2)lk'}{l'k-\beta\delta lk'}, \tag{A42}$$

$$q_{1,1}(\theta)=\frac{[(1+\Delta_s)m_{1,1}-(\beta-1/2)]m_1k'}{\beta m_1k'-m_1'k}-\frac{(m_1'm_{1,1}+m_1m_{1,1}')k}{\beta m_1k'-m_1'k}-\frac{(\beta\delta-3/2)lk'}{l'k-\beta\delta lk'}, \tag{A43}$$

$$q_{2,1}(\theta)=\frac{[(1+\Delta_s)m_{2,1}+\alpha]m_2 l'}{(1-\alpha)m_2 l'-\beta\delta m_2' l}-\frac{(\beta\delta-3/2)lk'}{l'k-\beta\delta lk'}+\frac{[(\beta\delta-3/2)m_2'-(m_2' m_{2,1}+m_2 m_{2,1}')]l}{(1-\alpha)m_2 l'-\beta\delta m_2' l}. \tag{A44}$$

The correction-to-scaling amplitudes are given by

$$A_1^+=[\alpha/\Delta_s+q_{2,1}(0)]Y_{10}, \tag{A45}$$

$$A_1^-=(b^2-1)^{-\Delta_s}[\alpha/\Delta_s+q_{2,1}(1)]Y_{10}, \tag{A46}$$

$$B_1=(b^2-1)^{-\Delta_s}[(1-2\beta)/2\Delta_s+m_{1,1}(1)]Y_{10}, \tag{A47}$$

$$\Gamma_1^+=[(\gamma-1)/\Delta_s+q_{1,1}(0)]Y_{10}, \tag{A48}$$

$$\Gamma_1^-=(b^2-1)^{-\Delta_s}[(\gamma-1)/\Delta_s+q_{1,1}(1)]Y_{10}. \tag{A49}$$

The angular functions in the classical limit are given by

$$\overline{m}_1(\theta)=\tilde{m}_1(\theta,0)=\frac{2\tilde{w}k'-\tilde{w}'k}{\tilde{l}'k-(3/2)\tilde{l}k'}, \tag{A50}$$

$$\overline{m}_2(\theta)=\tilde{m}_2(\theta,0)=-\frac{2\tilde{w}\tilde{l}'-(3/2)\tilde{w}'\tilde{l}}{\tilde{l}'k-(3/2)\tilde{l}k'}, \tag{A51}$$

$$\overline{q}_1(\theta)=\tilde{q}_1(\theta,0)=-\frac{(1/2)\overline{m}_1 k'-\overline{m}_1' k}{\tilde{l}'k-(3/2)\tilde{l}k'}, \tag{A52}$$

$$\overline{q}_2(\theta)=\tilde{q}_2(\theta,0)=\frac{\overline{m}_2\tilde{l}'-(3/2)\overline{m}_2'\tilde{k}}{\tilde{l}'k-(3/2)\tilde{l}k'}. \tag{A53}$$

APPENDIX B: THERMODYNAMIC RELATIONS

The differential relations are

$$d\tilde{P}=\tilde{U}d\tilde{T}+\tilde{\rho}d\tilde{\mu}, \tag{B1}$$

$$d\tilde{A}=-\tilde{U}d\tilde{T}+\tilde{\mu}d\tilde{\rho}, \tag{B2}$$

$$d\tilde{\Phi}=-\varphi_2 dh_2-\varphi_1 dh_1, \tag{B3}$$

$$d\tilde{\Psi}=-\varphi_2 dh_2+h_1 d\varphi_1 \tag{B4}$$

with

$$\tilde{A}=\tilde{\rho}\tilde{\mu}-\tilde{P}, \tag{B5}$$

$$\tilde{\Psi}=\varphi_1 h_1+\tilde{\Phi}. \tag{B6}$$

Decomposition into critical and regular parts gives

$$\tilde{A}(\tilde{T},\tilde{\rho})=\Delta\tilde{A}(\Delta\tilde{T},\Delta\tilde{\rho})+\tilde{\rho}\tilde{\mu}_0(\tilde{T})+\tilde{A}_0(\tilde{T}), \tag{B7}$$

$$\tilde{P}(\tilde{\mu},\tilde{T})=\Delta\tilde{P}(\Delta\tilde{\mu},\Delta\tilde{T})-\tilde{A}_0(\tilde{T}). \tag{B8}$$

The relationship between the critical part of the pressure $\tilde{P}$ and the critical part of the field-dependent potential $\tilde{\Phi}$

$$\begin{aligned} d\Delta\tilde{P}(\Delta\tilde{\mu},\Delta\tilde{T})&=\Delta\tilde{U}d(\Delta\tilde{T})+\Delta\tilde{\rho}d(\Delta\tilde{\mu})\\ &=\Delta\tilde{U}d(\Delta\tilde{T}+b_2\Delta\tilde{\mu})+(\Delta\tilde{\rho}-b_2\Delta\tilde{U})d(\Delta\tilde{\mu})\\ &=\varphi_2 dh_2+\varphi_1 dh_1, \end{aligned} \tag{B9}$$

so that

$$\Delta\tilde{P}(\Delta\tilde{\mu},\Delta\tilde{T})=-\Delta\tilde{\Phi}(\Delta\tilde{\mu},\Delta\tilde{T}+b_2\Delta\tilde{\mu})\equiv-\Delta\tilde{\Phi}(h_1,h_2). \tag{B10}$$

The Helmholtz free-energy density $\tilde{A}$ and the potential $\tilde{\Psi}$ are related by a Legendre transformation

$$\tilde{A}=\tilde{\Psi}+b_2 h_1\varphi_2, \tag{B11}$$

as can be seen from

$$\begin{aligned} &d\Delta\tilde{A}(\Delta\tilde{T},\Delta\tilde{\rho})-b_2 d(\Delta\tilde{\mu}\Delta\tilde{U})\\ &\quad=-\Delta\tilde{U}d(\Delta\tilde{T}+b_2\Delta\tilde{\mu})+\Delta\tilde{\mu}d(\Delta\tilde{\rho}-b_2\Delta\tilde{U})\\ &\quad=-\varphi_2 dh_2+h_1 d\varphi_1, \end{aligned} \tag{B12}$$

so that

$$\Delta\tilde{A}(\Delta\tilde{T},\Delta\tilde{\rho})=\Delta\tilde{\Psi}(h_2,\varphi_1)+b_2 h_1\varphi_2 \tag{B13}$$

with

$$\Delta\tilde{U}\equiv-\left(\frac{\partial\Delta\tilde{A}}{\partial\Delta\tilde{T}}\right)_{\tilde{\rho}}=-\left(\frac{\partial\Delta\tilde{\Psi}}{\partial h_2}\right)_{\varphi_1}\equiv\varphi_2, \tag{B14}$$

$$\Delta\tilde{\mu}\equiv\left(\frac{\partial\Delta\tilde{A}}{\partial\Delta\tilde{\rho}}\right)_{\tilde{T}}=\left(\frac{\partial\Delta\tilde{\Psi}}{\partial\varphi_1}\right)_{h_2}\equiv h_1. \tag{B15}$$

From Eqs. (B10), (B14), and (B15) it follows that the expressions for the internal-energy density $\tilde{U}$, the external field $\tilde{\mu}$, and the pressure $\tilde{P}$ are invariant under mixing transformations, while for the Helmholtz free-energy density one has

$$\Delta\tilde{A}(\Delta\tilde{T},\Delta\tilde{\rho})=\Delta\tilde{\Psi}(h_2,\varphi_1)-b_2\left(\frac{\partial\Delta\tilde{\Psi}}{\partial\varphi_1}\right)_{h_2}\left(\frac{\partial\Delta\tilde{\Psi}}{\partial h_2}\right)_{\varphi_1}. \tag{B16}$$

Derived thermodynamic quantities are given by

$$\left(\frac{\partial\tilde{P}}{\partial\tilde{T}}\right)_{\tilde{\rho}}=\left(\frac{\partial\tilde{P}}{\partial\tilde{T}}\right)_{\tilde{\mu}}+\left(\frac{\partial\tilde{P}}{\partial\tilde{\mu}}\right)_{\tilde{T}}\left(\frac{\partial\tilde{\mu}}{\partial\tilde{T}}\right)_{\tilde{\rho}}, \tag{B17}$$

$$\left(\frac{\partial\tilde{\mu}}{\partial\tilde{T}}\right)_{\tilde{\rho}}=-\left(\frac{\partial\tilde{\rho}}{\partial\tilde{T}}\right)_{\tilde{\mu}}\left(\frac{\partial\tilde{\mu}}{\partial\tilde{\rho}}\right)_{\tilde{T}}, \tag{B18}$$

$$\left(\frac{\partial\tilde{\rho}}{\partial\tilde{P}}\right)_{\tilde{T}}=\frac{1}{\tilde{\rho}}\left(\frac{\partial\tilde{\rho}}{\partial\tilde{\mu}}\right)_{\tilde{T}}, \tag{B19}$$

$$\tilde{C}_V/\tilde{T}^2=-\left(\frac{\partial^2\tilde{A}}{\partial\tilde{T}^2}\right)_{\tilde{\rho}}=\left(\frac{\partial^2\tilde{P}}{\partial\tilde{T}^2}\right)_{\tilde{\rho}}-\tilde{\rho}\left(\frac{\partial^2\tilde{\mu}}{\partial\tilde{T}^2}\right)_{\tilde{\rho}}, \tag{B20}$$

$$\tilde{\chi}=\left(\frac{\partial\tilde{\rho}}{\partial\tilde{\mu}}\right)_{\tilde{T}}=\left(\frac{\partial^2\tilde{P}}{\partial\tilde{\mu}^2}\right)_{\tilde{T}}=\chi_1+b_2^2\chi_2+2b_2\chi_{12}, \tag{B21}$$

$$\left(\frac{\partial\tilde{U}}{\partial\tilde{T}}\right)_{\tilde{\mu}}=\left(\frac{\partial^2\tilde{P}}{\partial\tilde{T}^2}\right)_{\tilde{\mu}}=-\frac{d^2\tilde{A}_0(\tilde{T})}{d\tilde{T}^2}+\chi_2, \tag{B22}$$

$$\left(\frac{\partial\tilde{\rho}}{\partial\tilde{T}}\right)_{\tilde{\mu}}=\left(\frac{\partial\tilde{U}}{\partial\tilde{\mu}}\right)_{\tilde{T}}=\chi_{12}+b_2\chi_2. \tag{B23}$$

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