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Critical phenomena of fluids: Asymmetric Landau-Ginzburg-Wilson model

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The critical behavior of simple single-component fluids near the liquid-vapor critical point (and of other systems in the same universality class) is examined via an asymmetric spin Hamiltonian in Landau-Ginzburg-Wilson form. The leading important odd terms to be added to an Ising-type system are a five-spin interaction $\int\varphi^5(x)$ and a nonlocal cubic interaction $-\int\varphi^2\nabla^2\varphi$. These two operators can be combined into two different eigenoperators with distinct physical interpretations. One combination can be shown to be exactly equivalent to the mixing of field variables (e.g., chemical potential and temperature) in the temperaturelike variable of an Ising or Ising-type system. This mixing has been used phenomenologically, found in certain models, and justified on general geometric grounds. This is the first proof that all asymmetric models, assuming universality and barring accidents, will have such mixing; this implies the universal occurrence of a $t^{1-\alpha}$ fluid diameter. The second combination is treated by renormalization-group methods and its contributions to the Helmholtz free energy, magnetic equation of state, and correlation length are calculated to $O(\epsilon^2)$, $\epsilon\equiv 4-d$. There are several novel features of this interaction which persist to all orders in perturbation theory. In addition to the expected renormalized M^5 contribution to the free energy, there are also terms linear in h (the magnetic field) and M which could be described as nonanalytic fluctuation-induced shifts in the order parameter and field. These might appear experimentally as apparent shifts in the background terms for h and M.

I. INTRODUCTION

There has been a long and profitable association between the critical behavior of simple liquid-vapor systems and the magnetic Ising model. This identification, founded partly on the notion of universality, can only extend so far without encountering the real differences between the systems. The magnetic system described in terms of the magnetic field h, magnetization M, and reduced temperature $t=T-T_c$ has a global symmetry $h\to -h$, $M\to -M$, which the fluid system, described by chemical potential μ, density ρ, and t, does not. In the simplest form of the lattice-gas model[1] the order parameter M of the Ising system is identified with $\rho-\rho_c$, and the ordering field h with $\mu-\mu(\rho_c,t)$ with t unchanged. This neglects entirely the real asymmetries of the fluid.

One way to introduce asymmetry is to assume that chemical potential and temperature mix both in the ordering field and temperaturelike variables. For example, one might assume that the singular part of the pressure was given by an Ising-type (lattice-gas) pressure $P_{\rm sing}(\mu,t)=P_I(h,t')$ with h as above and t' a linear combination of μ and t. The phenomenological consequences of such a revision of the scaling fields are reviewed in Ref. 2. The behavior is found in certain models[3] and it has been argued[4] that such mixing can generally be expected on geometrical grounds.[5] Although this mixing would lead to asymmetric terms, experimental verification of its existence is hard to establish since the asymmetries are relatively weak. One characteristic consequence is the prediction of a weak singularity in the fluid diameter, defined as the sum of the liquid and gas densities in the two-phase region:

$$\frac{\rho_L+\rho_G}{2}=\rho_c+d_0|t|^{1-\alpha}+d_1|t|+\cdots, \qquad (1.1)$$

where α is the specific heat exponent. A simple rectilinear diameter ($d_0=0$) is sufficient for most fluids over a large range[6] although some evidence of curvature has been observed[7] and fit[8] with (1.1). The primary result of this paper is to demonstrate that the asymmetric Landau-Ginzburg-Wilson (LGW) Hamiltonian model of the fluid systems *does* exhibit this mixing. The mixing does not represent an exact change of variables in the Hamiltonian[3] but rather is a consequence of the effects of the asymmetric terms on the free energy and correlation functions. As will be shown in Sec. II this proof of mixing is independent of perturbation theory and the renormalization group. If the universality of results derived for the LGW model is accepted,[9] then the universal occurence of mixing and its consequences in fluids is established.

This does not imply that mixing is the only source of asymmetric terms. Truly nontrivial non-Ising interactions are also present and cannot be removed by adjustments of the variables and background terms. The second emphasis of this paper will be the determination of the proper form of these new terms and their calculation within the renormalization group. To begin, consider the usual LGW Hamiltonian corresponding to a simple nonmixed but asymmetric system,[10] in dimension $d \equiv 4-\epsilon$. The usual terms can be written as[11]

$$H = \int \left(\frac{t(x)\varphi^2(x)}{2} + \tfrac{1}{2}(\nabla\varphi)^2_\Lambda + \frac{u\Lambda^\epsilon \varphi^4(x)}{4!} - h(x)\varphi(x) \right) + \int \left(f_1(t)\varphi(x) + \frac{u\Lambda^\epsilon}{3!} f_3(t)\varphi^3(x) \right). \tag{1.2}$$

In Eq. (1.2) the constant fields t and h have been replaced by spatially varying fields $t(x)$ and $h(x)$ for the usual convenience of defining generating functions for the correlation and vertex functions.[12] The uniform limit is taken at the end of any specific calculation. A latticelike behavior is preserved through the cutoff Λ imposed on the wave vectors of the Fourier transformed spin field $\varphi(k)$. This can be imposed as an absolute sharp cutoff or by modifying the form of the gradient-squared term in (1.2); this is indicated by the subscript Λ. When an explicit form is needed, the following will be used: $(\nabla\varphi)^2_\Lambda \rightarrow (\nabla\varphi)^2 + \Lambda^{-2}(\nabla^2\varphi)^2$. In Eq. (1.2), it may be supposed that $M = \langle\varphi\rangle$ is proportional to the density ρ. The non-Ising terms may be removed if the fields h and φ are shifted:

$$\varphi = \varphi' - f_3(t), \tag{1.3a}$$

$$h = h' + f_1(t) - t f_3(t). \tag{1.3b}$$

The LGW Hamiltonian is thereby transformed to an Ising form [$O(f_i^2)$ terms are dropped for simplicity].

$$H = \int \left(\tfrac{1}{2}t(x)[\varphi'(x)]^2 + \tfrac{1}{2}(\nabla\varphi')^2_\Lambda + \frac{u\Lambda^\epsilon}{4!}[\varphi'(x)]^4 - h'(x)\varphi'(x) \right) + h f_3(t), \tag{1.4}$$

where a unit volume is taken. The constant term $hf_3(t)$ can be dropped if the behavior of the order parameter $M' \equiv \langle\varphi'\rangle$ is considered; in the original variables this represents an analytic background term in the Gibbs free energy. Thus the new Hamiltonian is precisely an Ising-type Hamiltonian with the provisos that the experimentally interesting quantity $\rho - \rho_c$ differs from the order parameter M' by a background analytic in t and that the ordering field h' is a function of both μ and t. With these conventions, the primes may be discarded.

The new interactions that need to be considered are

$$v_3 0_3 = \frac{v_3}{3!} \int \varphi^2(-\nabla^2)_\Lambda \varphi, \tag{1.5a}$$

$$v_5 0_5 = v_5 \frac{u\Lambda^\epsilon}{5!} \int \varphi^5. \tag{1.5b}$$

These interactions are the leading nontrivial odd interactions not included in Eq. (1.2). As shown elsewhere[13] both interactions must be included to have a consistent theory of their influence on the fluid system. The factor of $u\Lambda^\epsilon$ included in 0_5 keeps the balance in the Hamiltonian between the four and five spin terms independent of u. The new interactions are smaller than those of the original Hamiltonian by factors of $v_i\varphi$ ($i=3,5$) and it is therefore expected that the effects on the thermodynamic functions will be smaller by (renormalized) $v_i M$. In any event $v_i M$ will be considered as a small term having no particular order in the ϵ expansion.

There are two other terms that are of comparable size:

$$0_3' = \int \frac{t(x)\varphi^3(x)}{3!}, \tag{1.6a}$$

$$0_1' = \int t^2(x)\varphi(x). \tag{1.6b}$$

These are just special cases of the previously treated odd terms and could be removed as in (1.3). However, their existence determines the form of the renormalization group equations (Sec. IV) and $0_3'$ is needed in the demonstration of LGW mixing (Sec. II).

The critical-point exponents associated with the insertion of the 0_i have been given[13] to $O(\epsilon^2)$. It is shown that both operators correspond to irrelevant perturbations and therefore represent correction-to-scaling terms. It is thus justifiable to treat these interactions linearly, that is to $O(v_i)$. (The φ^5 theory is considered near $d=10/3$ in Ref. 13 and is shown to have no fixed point.) However, the full crossover behavior of the $O(v_i)$ terms will be considered when explicit calculations are made. As will become clear below, this is necessary for a proper understanding of their contributions.

In Sec. II, the equation of motion approach[14] as applied to the cutoff (rather than renormalized) theory is used to provide a simple proof of the generality of the field mixing discussed above. In Sec. III, a brief discussion of the formal features of crossover equations in the context of the renormalization group is given. The method used[15] is a modification of that of Bruce and Wallace[16] which leads to the most compact and easily interpretable crossover forms. The crossover equations for the Ising-type model are discussed both as an example and because they form the basis of the non-Ising calculation. In Sec. IV the renormalization group treatment of the 0_i is given and the proper form of the renormalization group equations is derived. In Sec. V explicit expressions to $O(\epsilon^2)$ for the nontrivial contributions are given. A concluding discussion is given in Sec. VI. The perturbation series used are collected and details of the renormalization-group matching are given for the Ising case in Appendix A and for the non-Ising terms in Appendix B. Further consequences of the equation of motion are given in Appendix C.

II. MIXING IN ASYMMETRIC LANDAU-GINZBURG-WILSON HAMILTONIANS

In this section it is shown that a general LGW Hamiltonian with odd interaction terms $v_i 0_i$ will exhibit a statistical mixing of field variables. The term "statistical" is used to distinguish this mixing from one that is implemented by a mixing at the level of the Hamiltonian. In the latter case, an exact line of symmetry exists in precise analogy with the magnetic case. In the present situation, the operator which induces mixing at linear order itself deviates from mixing at second order and destroys the line of symmetry at third order, i.e., very weakly (cf. Appendix C). Of course, the nontrivial, non-Ising interaction breaks the symmetry at linear order. However, in practical terms linear mixing is sufficient since the corrections to the Ising-type behavior are weak and only the linear consequences of mixing are usually considered.[2,8] The proof does not depend on the form of the cutoff used or on the properties of the renormalization group and, insofar as the φ^4 LGW Hamiltonian describes the system of interest, holds everywhere, not just in the region of the critical point. Of course, special systems can be constructed with no mixing; in the present context, if v_3 and v_5 are related in a specific way so that the amplitude of the mixing eigenoperator is zero, then there is no mixing. However, there is no reason to think this is the case for the fluid systems of interest. The equation of motion method is used,[12-14] but without taking the $\Lambda\to\infty$ limit.

The Ising-type LGW Hamiltonian with spatially varying $t(x)$ and $h(x)$ is

$$H=\int\left(\tfrac{1}{2}t(x)\varphi^2+\tfrac{1}{2}(\nabla\varphi)^2_\Lambda+\frac{u\Lambda^\epsilon\varphi^4}{4!}-h(x)\varphi(x)\right). \tag{2.1}$$

The generating functional for correlation functions (Gibbs free-energy functional) is given by the functional integral

$$\exp[-G(h(x),t(x))]=\int D\varphi(x)\exp[-H]. \tag{2.2}$$

It is often convenient to use the Helmholtz free-energy functional A, which is related to G by Legendre transform:

$$A(M(x),t(x))=G(h(x),t(x))+\int h(x')M(x'), \tag{2.3a}$$

$$M(x)=-\frac{\delta G}{\delta h(x)}, \tag{2.3b}$$

$$h(x)=\frac{\delta A}{\delta M(x)}. \tag{2.3c}$$

The functional derivatives of G with respect to $h(x)$ are the correlation functions while the derivatives of A with respect to $M(x)$ are the one-particle irreducible vertex functions.[12]

The equation of motion approach takes its name from its starting point. The identity

$$0=\int D\varphi\,\frac{\delta}{\delta\varphi(x)}\exp(-H), \tag{2.4}$$

true for all Hamiltonians, is applied to (2.1). This implies

$$\left\langle t(x)\varphi(x)+(-\nabla^2)_\Lambda\varphi(x)+\frac{u\Lambda^\epsilon\varphi^3(x)}{3!}-h(x)\right\rangle=0. \tag{2.5}$$

The quantity inside the brackets is exactly the classical equation of motion. That is, if $\varphi(x)$ is a spatially varying field which minimizes the Hamiltonian, then the quantity inside the brackets would vanish. Equation (2.5) says that the classical equation is satisfied in an average sense. It is convenient to define

$$h_\varphi(x)=t(x)\varphi(x)-(\nabla^2)_\Lambda\varphi(x)+\frac{u\Lambda^\epsilon\varphi^3(x)}{3!}, \tag{2.6}$$

so that Eq. (2.5) expresses $\langle h_\varphi(x)-h(x)\rangle=0$. Now differentiate Eq. (2.4) by applying $\delta/\delta t(y)$,

$$\langle\tfrac{1}{2}\varphi^2(y)h_\varphi(x)-\delta(y-x)\varphi(x)\rangle=\langle h(x)\tfrac{1}{2}\varphi^2(y)\rangle. \tag{2.7}$$

To relate Eq. (2.7) to the 0_i, set $y=x$ and integrate over x

$$\left\langle\tfrac{1}{2}\int\varphi^2(x)h_\varphi(x)\right\rangle=\left\langle\int h(x)\tfrac{1}{2}\varphi^2(x)\right\rangle+\delta(0)M. \tag{2.8}$$

The $\delta(0)$ is not infinite in a cutoff theory but is the volume of the Brillouin zone, $\delta(0)\sim\Lambda^d$. Defining $\overline{0}_3=3(0_3+\frac{10}{3}0_5+0_3')$,

$$\langle\overline{0}_3\rangle=\left\langle\int h(x)\frac{\delta}{\delta t(x)}\right\rangle+\Lambda^d M. \tag{2.9}$$

The final term represents an analytic global shift in the magnetic field which has no observable consequences and will be dropped henceforth.[17] Denoting the shift in G induced by $\overline{0}_3$ as $\overline{G}_3$, and in A by $\overline{A}_3$:

$$\overline{G}_3=\int h(x)\frac{\delta}{\delta t(x)}G, \tag{2.10a}$$

$$\bar{A}_3 = \int h(x) \frac{\delta}{\delta t(x)} A . \quad (2.10b)$$

Finally, if an interaction $\bar{v}_3 \bar{0}_3$ is added to the Hamiltonian and its effects taken linearly, then to $O(\bar{v}_3)$, Eq. (2.10) shows that

$$A \to A[M(x), \bar{t}(x) + \bar{v}_3 h(x)], \quad (2.11a)$$

$$G \to G[h(x), t(x) + \bar{v}_3 h(x)], \quad (2.11b)$$

which is precisely the statement of field mixing in the temperature variable. By using the spatially varying $t(x)$ and $h(x)$, Eq. (2.11) shows that the mixing extends to all the correlation and vertex functions.

If a new temperaturelike variable is defined by

$$t'(x) = t(x) + \bar{v}_3 h(x), \quad (2.12)$$

then the true Ising-type order parameter is given by $-M'(x) = \delta G/\delta h(x)$ at constant t'. The original order parameter (related to the density difference) now has a mixed behavior

$$M(x) = M'(x) - \bar{v}_3 \frac{\delta G}{\delta t(x)}$$

$$= M'(x) - \bar{v}_3 \frac{\delta A}{\delta t(x)} . \quad (2.13)$$

This is the source of the asymmetries observed in M in the phenomenological models.[4] It is convenient to evaluate the Helmholtz functional at $M'(x)$ rather than $M(x)$; this restores the relationship

$$h(x) = \frac{\delta A(M'(x), t'(x))}{\delta M'(x)} . \quad (2.14)$$

With these conventions as to the meaning of t and M, the primes may be dropped. Unless $\bar{v}_3 = 0$, these mixing terms will be present, and thus the LGW Hamiltonian will, in general, exhibit field mixing. The presumption of universality extends this to all asymmetric models. Although the proof given above does not depend upon the renormalization-group or perturbation theory, it is easy to check that these results are reproduced to $O(\epsilon^2)$ by the calculations of Secs. IV and V (cf. Appendices A and B). Note that the simple form of the present result depends upon the inclusion of the trivial operator $0_3'$ in $\bar{0}_3$.

There is a simple way to see the relationship between the operator $\bar{0}_3$ and field mixing. The LGW Hamiltonian with perturbation $\bar{v}_3 \bar{0}_3$ can be written as

$$H = \int \tfrac{1}{2}[t(x) + \bar{v}_3 h_\varphi]\varphi^2(x) + \tfrac{1}{2}(\nabla\varphi)^2_\Lambda$$

$$+ \frac{u\Lambda^\epsilon \varphi^4(x)}{4!} - h(x)\varphi(x) , \quad (2.15)$$

if h_φ could be replaced with $h(x)$ then the contributions of $\bar{0}_3$ would be exactly equivalent to variable mixing, as may be seen on the Hamiltonian level. The equation of motion guarantees this replacement to linear order. The equivalence of the introduction of $\bar{0}_3$ to fluid mixing extends only to first order. This is clear since mixing terms in the free energy vanish if $h=0$ but $\langle(\bar{0}_3) - \langle\bar{0}_3\rangle\rangle^2 \neq 0$. The use of the equations of motion to determine the second order contribution is given in Appendix C; it differs from mixing by terms giving the next even contributions to H: the φ^6 and associated operators.

An alternative to the equation of motion approach is to apply the general result

$$\left\langle \int h_\phi(x)\psi(x) \right\rangle_H = \left\langle \int h(x)\psi(x) \right\rangle_H + \left\langle \int \delta\psi(x)/\delta\phi(x) \right\rangle_H , \quad (2.16)$$

which holds for any Hamiltonian H and operator ψ [with $h_\phi(x) = \delta H/\delta\phi(x)$]. Then, setting $\psi = \phi^2(x)/2$ yields Eq. (2.8). Equation (2.16) and its relationship to other methods will be discussed in Appendix C.

III. RENORMALIZATION-GROUP CROSSOVER FUNCTIONS: ISING CASE

In this section a brief review of the technical features of the renormalization group and its application to the calculation of crossover scaling functions is given. Further details may be found in Ref. 15. This serves to define the technical tools needed for the non-Ising effects described in Secs. IV and V as well as listing the principal Ising-type results.

The method employed is a variation of the matching point method of Bruce and Wallace.[16] The basic idea is that a good crossover form can be obtained by combining the perturbation series calculations with the solutions of the renormalization group equations and choosing a matchpoint value of the renormalization-group parameter. A typical thermodynamic function F satisfies (within the approximations of the renormalization group, see Refs. 15 and 16 and below) an equation of the form

$$[\mathcal{R} + e(u)]F = K(t, u, M, \Lambda) , \quad (3.1)$$

where the renormalization-group operator $\mathcal{R}$ is given by

$$\mathcal{R} \equiv \Lambda\frac{\partial}{\partial\Lambda} + \beta(u)\frac{\partial}{\partial u} + [2 - 1/\nu(u)]t\frac{\partial}{\partial t} - \eta(u)\frac{M}{2}\frac{\partial}{\partial M}. \quad (3.2)$$

The formal solution of Eq. (3.1) is

$$F(t,u,M,\Lambda=1) = \mathcal{E}(l)F(t(l),u(l),\mathfrak{D}^{1/2}M,\Lambda=\exp[-l]) + \int_0^l K(l')\mathcal{E}(l')dl', \quad (3.3)$$

where

$$\mathcal{E} \equiv \exp - \int_0^l e(u(l'))\,dl', \quad (3.4a)$$

$$t(l) \equiv t\mathcal{T} = t\exp - \int_0^l [2 - 1/\nu(u(l'))]\,dl', \quad (3.4b)$$

$$\frac{\partial u}{\partial l} = -\beta, \quad (3.4c)$$

$$\mathfrak{D} = \exp + \int_0^l \eta(u(l'))\,dl'. \quad (3.4d)$$

The integral over the kernel K is occasionally termed a trajectory integral. Although the values of $\beta(u)$, $\eta(u)$, K, etc., are generally only determined perturbatively, the form of (3.1) is true independent of perturbation theory. This also applies to the form of K as will be made clear below. Given the existence of a short diagram series for F, however, the use of renormalized quantities as in (3.3) changes the relative size of the terms in that series. The most direct approach is to divide F into a lowest-order part (mean-field portion) and a term due to fluctuations,

$$F = \mathcal{E}(l)[F_{\rm mf}(l) + \Delta F(l)] + \int_0^l K\mathcal{E}. \quad (3.5)$$

As l changes, the value of F itself is left invariant; the changing contribution of the fluctuation term being precisely compensated for by the changes in the renormalized mean-field part and the integral of K. The mean-field portion is easily understood in terms of its renormalized variables, while the fluctuation term is only known perturbatively and needs interpretation. The match-point method consists of choosing a value of $l = l^*$ such that the fluctuation terms can be easily handled.

The choice which gives the most compact and conceptually simplest result for the crossover is to pick l^* such that $\Delta F(l^*) = 0$. Then

$$F = \mathcal{E}(l^*)F_{\rm mf}(l^*) + \int_0^{l^*} K(l)\mathcal{E}(l)\,dl. \quad (3.6)$$

All the information from the fluctuations is used to determine l^*, while the form of the final answer is determined by mean-field considerations and the renormalization-group equations. As is shown in Ref. 15, this match point resums the N-point vertex functions to their exact values in the spherical limit. The function F will have crossed over to its mean-field limit when $l^* \to 0$. Although this match point gives the most convenient crossover forms and has several technical advantages it has the disadvantage that the values of l^* will differ for different functions. It is therefore useful to evaluate functions not only at the optimal match point (3.6) but also at the optimal match point of some other function.

As a first example, consider the magnetic equation of state h/M, for which $e(u) = -\eta(u)$, $K=0$. In this case to $O(\epsilon^2)$,

$$\frac{h}{M} = t + \frac{u\Lambda^\epsilon M^2}{6} + \frac{\Delta h}{M}, \quad (3.7a)$$

$$\frac{\Delta h}{M} = -u\kappa^2\left(\frac{(\kappa/\Lambda)^{-\epsilon} - B_0}{\epsilon}\right) + \frac{u^2\kappa^2}{4}[(L+1)(L+2) + L^2 - f] + \frac{u^3M^2\Lambda^\epsilon}{4}(L^2 + 2L - f). \quad (3.7b)$$

In (3.7b) and elsewhere, $\kappa^2 = t + u\Lambda^\epsilon M^2/2$ (or its renormalized value), $L = \ln(\kappa^2/\Lambda^2)$, $B_0 = 1 + \epsilon/2$, and $f \simeq 4.5$ (the values of B_0 and f depend on the form of the cutoff). Choosing a match point is equivalent to choosing a value for L. The Bruce and Wallace choice would be $L = 0$; to cancel the fluctuations, it is necessary to pick $L \neq 0$; in fact, L will be a function of the thermodynamic variables. To this order they are given by[15,16]

$$\mathcal{T} = Y^{(2-1/\nu)\omega}\exp D_1(p - \bar{u}), \quad (3.8a)$$

$$\mathfrak{D} = Y^{-\eta/\omega}\exp[-\eta/\omega(p - \bar{u})], \quad (3.8b)$$

$$u(l)e^{-\epsilon l} = uY^{\epsilon/\omega}, \quad (3.8c)$$

where $p = u(l)/u^*$, $\bar{u} = u/u^*$, $Y = (1-p)/(1-\bar{u})$, and u^* is the fixed point value of u, $\beta(u^*) = 0$. The exponents of the Y's are the critical-point exponents $\eta(u^*) = \eta$. etc., and ω is the correction-to-scaling eigenvalue, $\omega = \partial\beta/\partial u$. The constant D_1 is given by

$$D_1 = \frac{2 - 1/\nu}{\omega} - \frac{\hat{u}}{\epsilon} = \frac{19}{54}\hat{u}, \quad (3.8d)$$

$$\hat{u} = B_0 u^* = \frac{\epsilon}{3}\left(1 + \frac{17}{27}\epsilon\right). \quad (3.8e)$$

The final form of the equation of state is

$$\frac{h}{M} = \mathfrak{D}\left(t\mathcal{T} + \frac{uY^{\epsilon/\omega}\mathfrak{D}M^2}{6}\right). \quad (3.9)$$

The match point L is expressed by the specification of the renormalization-group invariant p,

$$Y^{\epsilon/\omega}\frac{\bar{u}}{p}=\exp(-\epsilon l^*)=\kappa^{\epsilon}(l^*)\exp(-\epsilon L/2)$$

$$=\kappa^{\epsilon}B_0\left[1-\frac{\epsilon}{4}\hat{u}p\left((f-1)+\frac{q(f+1)}{2}\right)\right], \quad (3.10a)$$

$$\kappa^2(l^*)=t\mathcal{T}+\frac{uY^{\epsilon/\omega}\mathfrak{D}M^2}{2}, \quad (3.10b)$$

$$q=\frac{uY^{\epsilon/\omega}\mathfrak{D}M^2}{\kappa^2}. \quad (3.10c)$$

As shown in Ref. 15, κ is an exact global nonlinear scaling field while p and q are exact global nonlinear scaling invariants.

In principle, Eqs. (3.8)-(3.10) provide a complete specification of the equation of state; this is, however, implicitly given through the scaling field κ for which no direct interpretation can be given. Its meaning is elucidated by evaluating other quantities at the same value of L. For example, κ^2 is related to the inverse susceptibility (two-point vertex function) by (at the h/M match point)

$$\Gamma_2=\mathfrak{D}\kappa^2\left[1+q\frac{\hat{u}p}{2}\left(1-\frac{\hat{u}p}{2}\right)-\frac{(\hat{u}p)^2}{4}q(1-q/2)(f+1)\right]. \quad (3.11)$$

The field κ is also essentially proportional to the inverse correlation length (cf. Appendix A).

It is important to note that these expressions cannot be sensibly used for $l^*\leq 0$, which occurs for $\kappa\sim 1$; this corresponding to a correlation length of the order of the lattice spacing in these units. In this range of κ the renormalization-group approximations break down and Eq. (3.1) no longer applies. The crossover to mean-field was described as the limit $l^*\to 0$, however, and therefore this sort of renormalization-group treatment of the crossover is flawed in the asymptotic mean-field regime. The source of these difficulties and a heuristic approach to repair them can be found by examining the spherical model. The disordered phase two-point vertex function is given exactly by

$$\Gamma_2=\frac{t}{1+u\int\frac{d^d\vec{k}}{k_\Lambda^2(k_\Lambda^2+\Gamma_2)}}, \quad (3.12)$$

where a subscript Λ again indicates that various cutoff forms could be used. The crossover to $\Gamma_2=t$ (the mean-field limit) occurs only as $\Gamma_2\to\infty$. The usual renormalization-group expression corresponds to the small t limit

$$\Gamma_2=\frac{t}{1+\bar{u}\left(\frac{\Gamma_2^{-\epsilon/2}}{B_0}-1\right)}, \quad (3.13)$$

where B_0, as mentioned above, is nonuniversal and depends on the cutoff used. This form cannot be used for large Γ_2 and the mean-field form $\Gamma_2=t$ is achieved at $\Gamma_2^{-\epsilon/2}=B_0\sim O(1)$, corresponding exactly to the $l^*=0$ limit. The problem is circumvented by retaining the renormalization-group form given in Eq. (3.6) while smoothing the transition of l^* to 0 so that it occurs only asymptotically as $\kappa\to\infty$ rather than at $\kappa\sim 1$. This can be done by comparing Eqs. (3.12) and (3.13) and making a corresponding substitution in the matching condition (3.10a). This is exact for the spherical model and is correct to one-loop order for the Ising case.[15]

A related consequence of the breakdown of the renormalization-group equations for $\kappa\sim 1$ is that the different functions have different values of l^*, rather than $l^*=\infty$. Thus, Eq. (3.11) never reaches a simple mean-field form, even at $l^*=0$. The best crossover expression for Γ_2 would be given by choosing the match point L appropriate to it (and smoothing out the mean-field limit); alternately, the smoothed version of the equation of state could be differentiated; only a smoothed version should be used for differentiation because of the abrupt nature of the $l^*=0$ limit. This smoothing is highly nonuniversal but a selection of various forms of cutoff shows that the variation between smoothing choices is smaller than between smoothed and pure renormalization-group calculations, even in the $\kappa\leq 1$ region.[15] The seriousness of this effect is reduced if $\bar{u}\ll 1$ (which may apply to the fluid cases of interest) and vanishes for u, $\Lambda^{-1}\to 0$, $u\Lambda^{\epsilon}$ fixed. While the results given here will be presented in unsmoothed form the passage to asymptotic mean-field behavior should be understood in a smoothed sense.

An important example with nonzero kernel is the free energy A for which $K=-B_0t^2\Lambda^{-\epsilon}/2$. At its optimal match point the result is

$$A=\mathfrak{D}\frac{t\mathcal{T}M^2}{2}+\frac{uY^{\epsilon/\omega}\mathfrak{D}^2M^4}{4!}-\frac{t^2\hat{u}}{2\epsilon u}\exp 2D_1(1-\bar{u})\left[\frac{(Y^{-\alpha/\omega\nu}-1)}{\alpha/\omega\nu}\frac{\epsilon}{\omega}+\frac{(Y^{1-\alpha/\omega\nu}-1)}{1-\alpha/\omega\nu}\left(\frac{\epsilon}{\omega}-1+2D_1\right)(1-\bar{u})\right]. \quad (3.14)$$

The match-point is given by

$$Y^{\epsilon/\omega}\frac{\bar{u}}{p}=\kappa^{\epsilon}B_0\left(1-\frac{\epsilon}{4}\right)\left(1+\frac{\hat{u}p\epsilon}{16}[1+q(1-4f)]\right). \quad (3.15)$$

Connection formulas like (3.11) can be found in Appendix A. In Eq. (3.14), the trajectory integral has produced terms which scale (have power-law singularities) proportional to a power of Y and analytic terms proportional to t^2. These terms are not true background terms since as the mean-field limit is approached and $Y \to 1$ the entire integral vanishes, the limit of the scaling terms cancelling the apparent background. This fluctuation-induced apparent shift in background is well known in the specific heat. Qualitatively, if C were written as $C = C_1 t^{-\alpha} + C_0$ in the critical regime, the constant C_0 would not be the true background specific heat observed far from the critical point. Writing C as $C = C_1(t^{-\alpha} - 1) + C_0'$ would give agreement between C_0' and the background observed at $t \sim 1$. This is what is expressed in Eq. (3.14).

The existence of a nonzero kernel is intimately connected with the possibility of shifting the background specific heat by the addition of a constant term to the Hamiltonian.[12] If it was desired to make the free energy A scale (i.e., make $K=0$) a suitable constant, $A_0 t^2$, could be added to the Hamiltonian and A_0 adjusted order by order in perturbation theory so that $K=0$. This would yield a free-energy equivalent to Eq. (3.14) in perturbation theory with the analytic terms dropped, leaving only the singular portion. There are several reasons that such a procedure is not generally followed. First, the free energy will now cross over to a mean-field expression with an extra t^2 term; for the most part it is more convenient to take this term to be zero so that the renormalization-group calculation gives only the anomalous parts. Secondly, the form in Eq. (3.14) allows for the $\alpha \to 0$ limit in a direct manner. Third, the expansion for A_0 for the general n-component system has a singularity at $n = -2$ which is entirely unphysical; this is avoided in Eq. (3.14), if, as indicated, the critical point exponents are not expanded as functions of ε to the appropriate order. In Ref. 15, the corresponding expression for the specific heat is exact for $n = -2$ (disordered phase only).

The Ising results, Eqs. (3.8)–(3.15), illustrate another general feature. The present two-loop calculations determine the exponents and some critical amplitudes to $O(\varepsilon^2)$. This is reflected, for example, in the match-point expressions (3.10) or (3.15) or expressions for functions, cf. (3.11). However, the results for the scaling fields (3.8) and for kernel integrals (3.14) contain factors determined to $O(\varepsilon)$. Thus, while both the explicitly M dependent and kernel terms are $O(1/u) \sim O(1/\varepsilon)$, the former terms are determined to $O(\varepsilon^2) \times 0(1/u) = 0(\varepsilon)$ while the latter is given only to $O(\varepsilon) \times O(1/u) = O(1)$. The resolution of this seeming anomaly is to note that $Y - 1$ is formally $O(u)$, $Y - 1 \sim u \log\kappa^2/\Lambda^2 \sim O(\varepsilon)$; this also holds for $p - \bar{u} \sim O(\varepsilon)$. In the case of the scaling fields the $p \to 1$ limit does give $O(\varepsilon) \times (1 - \bar{u})$ nonuniversal scale factors which do not change the amplitude ratios. For the $Y \to 0$ limits in the kernel integrals the factors of $\exp 2D_1(1 - \bar{u})$ again cancel, but the remaining terms provide amplitudes determined only to $O(\varepsilon)$. Similarly, the nonuniversal constant f cancels at this order.

Finally, there is a crossover feature of the kernel integrals that should be described. Consider, for example, the $T > T_c$ specific heat. In mean-field theory it is zero; dropping inessential factors it is given by

$$C \approx \frac{1}{u} \frac{(Y^{-\alpha/\omega\nu} - 1)}{(\alpha/\varepsilon\nu)}. \tag{3.16}$$

The singular $Y^{-\alpha/\omega\nu}$ term has an amplitude that is $O(1/u) \sim O(1/\varepsilon)$. One could say that the fluctuations do not simply modify the exponent and amplitude of the singularity smoothly [as would be true if the amplitude were $O(1)$], but they instead introduce a discountinuity in the amplitude. Insofar as only critical amplitudes are considered this is true; however, this discontinuity has a crossover nature; in the mean-field region $Y \to 1$, $C \to 0$, restoring the mean-field behavior. From this point of view, the kernel integral does provide a smooth rather than discontinuous change from mean field to full critical behavior. The discontinuity is, of course, real, but only in a local, asymptotic critical sense; globally there is a gradual buildup of the singularity.

To summarize the character of the kernel integral terms: they represent fluctuation-induced nonanalytic background shifts which vanish smoothly in the mean-field region. In the critical region they split into regular and singular terms with a corresponding discontinuity in the amplitudes associated with the singularity. This splitting reduces by one order in ε the accuracy of the determination of amplitude ratios. The same features will occur for the non-Ising terms; in this case, the kernel terms contribute not only to the specific heat but also to all the M derivatives as well.

IV. RENORMALIZATION-GROUP TREATMENT OF NON-ISING OPERATORS

In this section the renormalization-group formalism is applied to the Ising Hamiltonian (2.1) augmented by the non-Ising interactions $v_3 0_3$ and $v_5 0_5$ [cf. Eq. (1.5)]. The form of the renormalization-group equations is determined and the eigenoperators, exponent function, and kernel are evaluated to second order. The operators $0_3'$ and $0_1'$ [Eq. (1.6)] which generate shifts in the order parameter M and field h will also be considered. The explicit calculations of the free energy will be given in Sec. V.

The free energy can be divided into Ising and non-Ising parts, $A = A_I + v_3 A_3 + v_5 A_5$, where the $A_i (i=3,5)$ are odd functions of the magnetization M. The form of the renormalization-group is then

$$v_i \mathcal{R} A_i + v_i \gamma_i^j A_j = v_i K_i \ . \tag{4.1}$$

The form of the kernels depends on the possible inclusion of the operators $0_i'$ and will therefore be discussed below. It is sufficient to note that $K_i = 0$ for $t=0$ and that the simpler renormalization-group equation as applied to the vertex functions $\Gamma_3(k_1, k_2, k_3)$ and $\Gamma_5(k_1, k_2, k_3, k_4, k_5)$ at $t=0$ can be used to determine the matrix γ_i^j. This is described in detail in Ref. 13 and only the results will be given here[18]

$$\gamma_5^5 = 7uB_0 - \tfrac{129}{4}u^2 - \tfrac{10}{6}u^2 , \tag{4.2a}$$

$$\gamma_3^5 = -20uB_0 + 110u^2 , \tag{4.2b}$$

$$\gamma_3^3 = uB_0 - \tfrac{11}{12}u^2 + \tfrac{10}{6}u^2 , \tag{4.2c}$$

$$\gamma_5^3 = -\tfrac{1}{2}u^2 . \tag{4.2d}$$

The renormalization-group flow equations for the v_i are

$$\frac{\partial v_i}{\partial l} = -\gamma_j^i v_j \ . \tag{4.3}$$

The eigenvalues (λ_3, λ_5) of the γ_j^i matrix evaluated at the fixed point determine the anomalous dimension (corrections to Gaussian exponents). The new correction-to-scaling eigenvalues are

$$\omega_i = \frac{d-2}{2} + \lambda_i \ . \tag{4.4}$$

The new correction-to-scaling exponents are $\Delta_i = \omega_i \nu$. The exact result on mixing of Sec. II implies that

$$\lambda_3(u) = 2 - \frac{1}{\nu(u)} - \frac{\eta(u)}{2}$$

$$= \gamma_5^5 + \tfrac{3}{10}\gamma_3^5$$

$$= \gamma_3^3 + \tfrac{10}{3}\gamma_5^3 \ . \tag{4.5}$$

Comparison with (4.2) and the expressions for $\nu(u)$ and $\eta(u)$ (cf. Appendix A) confirms (4.5) to $O(\epsilon^2)$. Since the effects of $\overline{0}_3$ are known exactly, the remaining non-Ising effects are due to the other eigencombination of the 0_i, $\overline{0}_5 = 0_5 + S_5(u) 0_3$, where $S_5(u)$ will be determined perturbatively. The non-Ising interactions $v_i 0_i$ are replaced by $\overline{v}_i \overline{0}_i$, with $v_5 = \overline{v}_5 + 10\overline{v}_3/3$, $v_3 = \overline{v}_3 + S_5(u)\overline{v}_5$. Then, only the contribution to the free energy corresponding to $\overline{0}_5$ need be calculated and the renormalization-group equation will be

$$(\mathcal{R} + \Lambda_5)\overline{A}_5 = \overline{K}_5 \ . \tag{4.6}$$

In general, Λ_5 and S_5 are determined by

$$\Lambda_5 = \gamma_5^5 + \gamma_3^5 S_5 \ , \tag{4.7a}$$

$$\beta \frac{\partial S_5}{\partial u} + \Lambda_5 S_5 = \gamma_3^3 S_5 + \gamma_5^3 \ . \tag{4.7b}$$

To the order obtainable here,

$$\Lambda_5 = \lambda_5 - \tfrac{5}{27}\beta , \tag{4.8a}$$

$$\lambda_5 = 7B_0 u - \tfrac{129}{4}u^2 , \tag{4.8b}$$

$$S_5 = -\tfrac{1}{12}u + \tfrac{1}{108}\beta/u \ . \tag{4.8c}$$

The expansion for the eigenvalue λ_5 is not very well behaved; the fixed point value gives the following ϵ expansion for the correction-to-scaling eigenvalue ω_5,

$$\omega_5 = 1 + \tfrac{11}{6}\epsilon - \tfrac{685}{324}\epsilon^2 + O(\epsilon^3) \ . \tag{4.9}$$

As written at $\epsilon = 1$, $\omega_5 = 0.78$; a simple Pade approximant gives $\omega_5 = 1.85$. The precise value of ω_5 being so uncertain,[19] the qualitative features of the $\overline{0}_5$ interaction will be stressed below.

The determination of the kernel $\overline{K}_5$ is intertwined with the operators $0_i'$. It would be possible to set $\overline{K}_5 = 0$ by adding a suitable amount of these operators to $\overline{0}_5$ just as the kernel for the Ising free energy could be removed by the addition of a constant ($\propto t^2$) to the Hamiltonian. In fact, it is the addition of $0_3'$ to $\overline{0}_3$ that makes its contribution so simple. However, to avoid the inclusion of terms linear and cubic in M in the mean-field region, no additions of the $0_i'$ will be made; in this way, the crossover will leave only an M^5 term in the mean-field region. Either procedure, taken exactly, would give the same physical result; the convenience of the crossover and the technical considerations alluded to above for the Ising free energy motivate the choice adopted here.

The form of the kernel is now determined and Eq. (4.6) takes the form

$$[\mathcal{R} + \Lambda_5(u)]\overline{A}_5 = B_M(u) t \Lambda^{-\epsilon} \frac{\partial A_I}{\partial M} + B_h(u) t^2 \Lambda^{-\epsilon} M \ . \tag{4.10}$$

The kernel is restricted to this form since the $0_i'$ are equivalent to shifting M and h. To $O(u,\epsilon)$ the coefficients have the values

$$B_M(u) = -B_0\left(1 - \frac{8u}{3} - \frac{1}{27}\frac{\beta}{u}\right), \quad (4.11a)$$

$$B_h(u) = B_0\left(1 - \frac{8u}{3} - \frac{1}{27}\frac{\beta}{u} + \frac{2}{3}S_5(u)\right). \quad (4.11b)$$

The second term in the kernel contributes only to the free energy, the magnetic field, and their temperature derivatives. The first term, on the other hand, persists in all the functions of interest. For example, the two-point vertex function at nonzero wave vector k divides into Ising and non-Ising parts $\Gamma_2(k) = \Gamma_2^I(k) + \bar{v}_5\bar{\Gamma}_2(k)$, with

$$(\mathcal{R} - \eta + \Lambda_5)\bar{\Gamma}_2(k) = B_M t\Lambda^{-\epsilon}\frac{\partial\Gamma_2^I}{\partial M}(k). \quad (4.12)$$

In particular, the second-moment correlation length is determined from the ratio $R = \Gamma_2/\xi^{-2}$:

$$R = \left(\frac{\partial}{\partial k^2}\Gamma_2\right)\Bigg|_{k^2=0}. \quad (4.13)$$

Dividing R into Ising and non-Ising parts, $R = R_I + v_5\bar{R}$,

$$(\mathcal{R} - \eta + \Lambda_5)\bar{R} = B_M t\Lambda^{-\epsilon}\partial R_I/\partial M. \quad (4.14)$$

As detailed in Sec. V, this persistent portion of the kernel is equivalent to a fluctuation induced nonanalytic shift in the background term in the definition of M. The same could be said of the analogous term in the Ising free energy, which represents a nonanalytic shift in the background t^2 term in the free energy. In the latter case, the singularity associated with this shift is relatively large, being the specific heat singularity. The singularity in the non-Ising system is weaker, representing a correction-to-scaling term.

V. NON-ISING CONTRIBUTIONS OF $\bar{0}_5$: TWO LOOPS

In this section, the two-loop $O(\epsilon^2)$ calculations for the change in the free energy $\bar{A}_5$, magnetic field $\bar{h}_5$, and correlation length ratio $\bar{R}$, are given. The results will be discussed at optimal match points and at the Ising h/M point. The former gives the expressions with the most compact and transparent crossover while the latter is useful for comparison with the Ising case and the computation of amplitudes.

The free energy in the presence of a perturbation $\bar{v}_5\bar{0}_5$ can be written as $A = A_I + \bar{v}_5\bar{A}_5$. The diagrammatic expansion for $\bar{A}_5$ is discussed in Appendix B. Its ϵ expansion [Eq. (B7)] determines its optimal match point [Eq. (B8)]. At that point

$$\bar{A}_5 = \mathcal{V}\,\frac{u\mathfrak{D}^{5/2}\,Y^{\epsilon/\omega}M^5}{5!} + t\,\frac{\partial A_I}{\partial M}\,\delta_M + t^2M\delta_h, \quad (5.1)$$

where $\mathcal{V}$ is defined by $\bar{v}_5(l) = \bar{v}_5\mathcal{V}$:

$$\mathcal{V} = Y^{\lambda_5/\omega}\exp[c(p - \bar{u})], \quad (5.2a)$$

$$c = \frac{\lambda_5}{\omega} - \frac{7\hat{u}}{\epsilon} - \frac{5}{27}\hat{u} = -\frac{235}{108}\epsilon + O(\epsilon^2), \quad (5.2b)$$

and δ_M and δ_h are effective nonanalytic shifts in M and h,

$$\delta_M = \frac{\hat{u}\exp}{\epsilon u}\left[\left(D_1 + \frac{\eta}{2\omega} + c\right)(1 - \bar{u})\right] \times [E_1(Y^{e_1} - 1) + E_1'(1 - \bar{u})(Y^{e_1+1} - 1)], \quad (5.3a)$$

$$\delta_h = \frac{-\hat{u}\exp}{\epsilon u}\left[\left(2D_1 - \frac{\eta}{2\omega} + c\right)(1 - \bar{u})\right] \times [E_2(Y^{e_2} - 1) + E_2'(1 - \bar{u})(Y^{e_2+1} - 1)]. \quad (5.3b)$$

The exponents e_i and amplitudes E_i, E_i' are

$$e_1 = \left(2 - \frac{1}{\nu} + \frac{\eta}{2} - \epsilon + \lambda_5\right)\Big/\omega = \tfrac{5}{3}\left(1 - \tfrac{76}{135}\epsilon\right), \quad (5.4a)$$

$$e_2 = \left(\frac{-\alpha}{\nu} - \frac{\eta}{2} + \lambda_5\right)\Big/\omega = 2\left(1 - \tfrac{17}{54}\epsilon\right), \quad (5.4b)$$

$$E_1 = \frac{\epsilon(1 - \frac{8}{3}\hat{u})}{e_1\omega} = \frac{3}{5}\left(1 + \frac{41}{135}\epsilon\right), \quad (5.4c)$$

$$E_2 = \frac{\epsilon(1 - \frac{49}{18}\hat{u})}{e_2\omega} = \frac{1}{2}\left(1 + \frac{1}{27}\epsilon\right), \quad (5.4d)$$

$$E_1' = -\frac{\left(\frac{\epsilon}{\omega} - 1 + D_1 + \frac{\eta}{2\omega} + c - \frac{25}{9}\hat{u}\right)}{e_1 + 1} = \frac{95}{108}\epsilon, \quad (5.4e)$$

$$E_2' = -\frac{\left(\frac{\epsilon}{\omega} - 1 + 2D_1 - \frac{\eta}{2\omega} + c - \frac{76}{27}\hat{u}\right)}{e_2 + 1} = \frac{61}{81}\epsilon. \quad (5.4f)$$

The ϵ expansions in Eq. (5.4) should not be considered reliable at $\epsilon = 1$ due to the poor convergence of λ_5 and the generally poor convergence of correction-to-scaling amplitudes.[20] The magnetic field can be decomposed as well $h = h_I + \bar{v}_5\bar{h}_5$, so that $\partial A_I/\partial M = h_I$ in (5.1). As expected, $\bar{v}_5\bar{A}_5$ is smaller than A_I by $\bar{v}_5\mathcal{V}\mathfrak{D}^{1/2}M \sim |t|^{\Delta_5}$.

The $\bar{A}_5$ free energy divides into a renormalized M^5 term, which enters in qualitatively the same fashion as a quintic term in mean-field theory, and the nonanalytic shift terms. The latter could be removed formally by shifts in the order parameter and ordering field: $M \to M - \bar{v}_5 t\delta_M$, $h \to h + v_5 t^2 \delta_h$. This would leave the free energy in a renormalized mean-field form but with nonanalytic h and M.[21,22]

The point of view taken here, on the other hand, is to consider the analytic definitions of h and M to be fixed in the asymptotic mean-field regime (which has a well-defined nature for the present model). In this limit, δ_h and δ_M are zero leaving only an analytic M^5 term ($\mathfrak{V} = \mathfrak{D} = Y = 1$) as a consequence of the $\bar{\mathfrak{V}}_5$ interaction. The t-dependent background for M as well as the mixing of density and entropy induced by $\bar{\mathfrak{V}}_3$ are not complicated by the fluctuation terms in this region and may be imagined to be determinable. Thus the meaning of M in Eq. (5.11) is, in principle, unambiguous, being that order parameter which is associated with the asymptotic asymmetric mean-field theory.

The δ_M and δ_h terms in Eq. (5.1) could be described as a gradual shift in the "best" background contributions to M and h. Suppose, for example, that Δ_5 is relatively large so that the critical singularities in δ_M and δ_h are not easily measured. Then it would still be true that a measurable effect would arise from the analytic parts of the δ's. If the background contributions to M and h (proportional to t and t^2, respectively) are determined relatively far from the critical point where $\delta_M \simeq \delta_h \simeq 0$, they will differ from those found asymptotically close to $t=0$ by $\bar{v}_5 t\delta_M(Y=0)$ and $\bar{v}_5 t^2 \delta_h(Y=0)$. This effect has been observed in the fluid diameter data[8,23] but may also be partly attributed to a similar effect arising from the variable mixing (cf. discussion below). For convenience, $\bar{A}_5$ and $\bar{h}_5$ are given the Ising h/M point

$$\bar{A}_5 = \mathfrak{V}\ \frac{uY^{\epsilon/\omega}\mathfrak{D}^{5/2}}{5!}\ M^5[1 + 10(1-f)(\hat{u}p)^2/q] + th\delta_M + t^2 M\delta_h\ , \tag{5.5a}$$

$$\bar{h}_5 = \mathfrak{V}\ \frac{uY^{\epsilon/\omega}\mathfrak{D}^{5/2}M^4}{4!}\left\{1 + 2\hat{u}p - (\hat{u}p)^2\left[1 + \left(3 - \frac{q}{2}\right)(f+1)\right] + \frac{4!\,\hat{u}p}{q}\left(\frac{\hat{u}p}{4}(1-f) - \frac{S_5(\hat{u}p)}{3}\right)\right\} + t\Gamma_2\delta_M + t^2\delta_h\ , \tag{5.5b}$$

where $S_5(\hat{u}p) = -\hat{u}p/12 - \epsilon(1-p)/108$ and Y, $\mathfrak{D}$, p, etc. are taken from Eqs. (3.8)–(3.11), and h, Γ_2, and κ^2 on the right-hand side are determined for the Ising-type case.

As discussed above, the mean-fieldlike terms ($\propto \mathfrak{V}$) are determined to $O(1/u) \times O(\epsilon^2)$ while the kernel terms are $O(1/u) \times O(\epsilon)$ only. For amplitude ratios which involve both sorts of terms the $O(\hat{u}^2)$ terms in (5.5) can be dropped. (Note that at the $\bar{h}_5$ optimal match point all the terms in the curly brackets would be dropped.)

These changes in the free energy and field have effects everywhere in the t-M plane. Only a few will be considered here. The breaking of the Ising symmetry means that $h=0$ no longer describes either the coexistence surface or "isochore" $M=0$. For $t>0$ the iso-M line will have $h = \bar{v}_5 \bar{h}_5(M=0)$, or

$$h = \bar{v}_5[t\Gamma_2(M=0)\delta_M + t^2\delta_h]\ . \tag{5.6}$$

This has a crossover nature so that $h=0$ is the asymptotic mean-field iso-M. To examine the character of Eq. (5.6) it is instructive to evaluate δ_M and δ_h at the one-loop level. Then

$$h = \bar{v}_5\left(\frac{t^2}{\epsilon\bar{u}}\ Y^{1/3}\ \frac{3}{5}(Y^{5/3} - 1) - \frac{t^2}{\epsilon\bar{u}}\ \frac{(Y^2 - 1)}{2}\right)\ . \tag{5.7}$$

The scaling part $h = \frac{1}{10}(t^2/\epsilon\bar{u})Y^2$ is mixed with a singular term proportional to $Y^{1/3}t^2$ and an analytic (t^2) term. The detailed behavior is quite complicated. The full expressions Eq. (5.3) increase the complexity by adding an explicit correction-to-scaling term $E_i'(Y^{\epsilon_i} - 1)$. The leading scaling part is

$$h = \frac{\bar{v}_5 t^2}{u}\exp[(2D_1 - \eta/2\omega + c)(1-\bar{u})]Y^{(\alpha/\nu - \eta/2 + \lambda_5)/\omega} \times \frac{\hat{u}}{\epsilon}(E_1 - E_2)\ . \tag{5.8}$$

In the ordered phase the Gibbs potential $G = A_I + \bar{v}_5\bar{A}_5 - hM$ must be the same in both phases, or to $O(\bar{v}_5)$,

$$h = \bar{v}_5\bar{A}_5/M\ . \tag{5.9}$$

To lowest order this is

$$\frac{\bar{v}_5 t^2}{\epsilon\bar{u}}\left(\frac{9}{10}\ Y^2 - \frac{(Y^2 - 1)}{2}\right)\ , \tag{5.10}$$

a combination of mean field and kernel terms. The scaling part of the full result is

$$h=\frac{\bar{v}_5 t^2}{u}\exp[(2D_1-\eta/2\omega+c)(1-\hat{u})]Y^{(\alpha/\nu-\eta/2+\lambda_5)/\omega}$$
$$\times\frac{3}{10}\left[1+\frac{10}{3}\left(\hat{u}^2(1-f)-\frac{E_2\hat{u}}{\epsilon}\right)\right]. \qquad (5.11)$$

The amplitude ratio[22] (in terms of Y; for Y itself see Ref. 15)

$$\frac{J_>}{J_>}=\frac{E_1-E_2}{\dfrac{3\epsilon}{10\hat{u}}-E_2}$$
$$=\tfrac{1}{4}(1+\tfrac{31}{10}\epsilon)+O(\epsilon^2). \qquad (5.12)$$

This dependence of h is only weakly nonanalytic: $h\sim|t|^{2-\alpha-\beta+\Delta_5}$, $2-\alpha-\beta+\Delta_5\cong 2+\epsilon-269\epsilon^2/324$. The second derivative is therefore probably not divergent at $t=0$. Equation (5.12) shows again the very poor convergence of the ϵ expansion for this problem.

Since $\Delta_5>0$, this dependence of h on t satisfies an exponent inequality derived by Griffiths.[24] If $\Delta_5<0$ this would not imply a violation of the Griffiths relationship since this would also imply the $\bar{0}_5$ was a relevant operator and a new fixed point might dominate the critical behavior. In this case α and β would change from the Ising-type values.

Another important qualitative change caused by $\bar{0}_5$ is the shift in the value of the order parameter from the simple Ising symmetry. Writing $M=\pm M_I+M_D\bar{v}_5$ (D for diameter),

$$M_D=\left(\frac{\bar{A}_5}{M}-\bar{h}_5\right)/\Gamma_2\,. \qquad (5.13)$$

Using the h/M match points for A_5, h_5, and Γ_2,

$$M_D=-\frac{\mathfrak{D}^{1/2}\mathfrak{V}M_I^2}{10}\left[1+\hat{u}p-\tfrac{13}{2}(\hat{u}p)^2-\tfrac{10}{3}\hat{u}pS_5(\hat{u}p)+\tfrac{47}{12}(\hat{u}p)^2(f-1)\right]-\delta_M t\,. \qquad (5.14)$$

Again the direct term $\propto\mathfrak{V}$ is determined more precisely than the kernel term, $-\delta_M t$. Note that $M_I^2=-6t\mathcal{T}/uY^{\epsilon/\omega}\mathfrak{D}$ so that the nonuniversal scale factor $\exp[(D_1+\eta/2\omega+c)(1-\bar{u})]$ multiplies both terms. At leading one-loop order, Eq. (5.15) reduces to

$$\bar{v}_5 M_D=\frac{\bar{v}_5 t}{u}\left(\frac{3}{5}Y^{5/3}-\frac{1}{5}(Y^{5/3}-1)\right)\,. \qquad (5.15)$$

There are again singular and backgroundlike contributions. Note that even if the $Y^{5/3}$ singularity were too weak to observe directly, then far from the critical point $M_D\sim\frac{3}{5}t/u$, while near the critical point $M_D\sim\frac{1}{5}t/u$, thereby shifting the diameter "background".

The complete density diameter is affected by true background terms and the mixing of fields

$$\rho_d=\frac{Bt}{u}+M_D\bar{v}_5-\bar{v}_3\frac{\partial A_I}{\partial t}\,. \qquad (5.16)$$

The h/M match-point expression for $\partial A/\partial t$ is

$$\frac{\partial A_I}{\partial t}=\frac{\mathcal{T}\mathfrak{D}M_I^2}{2}\left(1+\frac{(\hat{u}p)^2}{2q}(f-1)\right)-\frac{t\hat{u}}{\epsilon u}\exp[2D_1(1-\bar{u})]\left[\frac{(Y^{-\alpha/\omega\nu}-1)}{(\alpha/\omega\nu)}\frac{\epsilon}{\omega}+\frac{(Y^{1-\alpha/\omega\nu}-1)}{1-\alpha/\omega\nu}\left(\frac{\epsilon}{\omega}-1+2D_1\right)(1-\bar{u})\right]\,. \qquad (5.17)$$

To leading one-loop order this simplifies to

$$\frac{\partial A_I}{\partial t}=-\frac{3Y^{-1/3}t}{u}-\frac{t}{u}(Y^{-1/3}-1)\,, \qquad (5.18)$$

showing the contrast between direct and kernel integral terms. To the same order the full-fluid diameter is

$$u\rho_d=Bt+\bar{v}_5 t[\tfrac{3}{5}Y^{5/3}-\tfrac{1}{5}(Y^{5/3}-1)]$$
$$+3\bar{v}_3 t[Y^{-1/3}-\tfrac{1}{3}(Y^{-1/3}-1)]\,. \qquad (5.19)$$

The full result obtained by combining (5.18) with (5.14) gives better values for α and λ_5, extra correction-to-scaling terms, and an adjustment of the amplitudes of doubtful value. The general features are the same as (5.20). Far from the critical point

$$u\rho_d=(B+\tfrac{3}{5}\bar{v}_5+3\bar{v}_3)t\,, \qquad (5.20a)$$

near the critical point

$$u\rho_d=(B+\tfrac{1}{5}\bar{v}_5+\bar{v}_3)t-\tfrac{2}{5}\bar{v}_5|t|^{\beta+\Delta_5}-2\bar{v}_3|t|^{1-\alpha}\,. \qquad (5.20b)$$

The kernel integrals shift the apparent linear term (for simplicity, Y is taken to behave like $|t|^{\epsilon/2}$; a nonuniversal proportionality constant is suppressed).

The relative strength of the mixing singularity $|t|^{1-\alpha}$ and the new singularity $|t|^{\beta+\Delta_5}$ is hard to assess due to the poor convergence of Δ_5. To $O(\epsilon^2)$,

$$\Delta_5+\beta-(1-\alpha)=\epsilon-\tfrac{289}{324}\epsilon^2\,. \qquad (5.21)$$

Finally the result for the non-Ising part of the correlation length-Γ_2 ratio $R=\Gamma_2/\xi^{-2}=R_I+\bar{v}_5\bar{R}$, is

$$\bar{R}=\mathfrak{D}^{1/2}M\mathfrak{V}\left(\frac{2}{3}S_5(\hat{u}p)+\frac{\hat{u}pq}{18}\right)+\frac{\partial R_I}{\partial M}t\delta_M. \quad (5.22)$$

The Ising part R_I is given in Appendix A and the perturbation analytic for $\bar{R}$ in Appendix B.

VI. DISCUSSION

The inclusion of the leading asymmetric terms to an Ising-type Hamiltonian provides a framework for the understanding of critical phenomena in fluids. Although some of the results are limited by the ϵ expansion, the important qualitative features are independent of perturbation theory.

First, the mixing of variables in the temperaturelike variable is shown to be a universal feature of asymmetric LGW Hamiltonians. This is not a simple revision of the Hamiltonian variables, but rather a "statistically generated" mixing which is independent of perturbation theory. The proper use of this mixing in, for example, the analysis of the fluid diameter, requires that the nonscaling nature of the Ising-free energy be considered. The limitation to linear mixing $[O(\bar{v}_3)$ only$]$ is not in contradiction to the geometrical ideas of Griffiths and Wheeler[5] since their analysis applies to leading symmetric and antisymmetric behavior.

Second, the nontrivial interaction with a correction-to-scaling exponent Δ_5 absent in symmetric systems, generates not only a scaling contribution but also effective fluctuation-induced nonanalytic shifts in the order parameter and field. These will persist in all the functions of interest and complicate the determination of background terms. The ϵ expansions of these effects are poor both for the exponent Δ_5 and the amplitudes of interest.

If further additions were made to the Hamiltonian a similar division of effects could be made. Some combination of operators can be determined exactly by the equations of motion and are expressible in global form. The remaining terms divide into scaling and nonscaling effects. For example, at least one of the eigenoperators associated with φ^7 will have a kernel $K\sim K_M t^2\partial A_I/\partial M+K_M t^3 M$ corresponding to a diameter $\sim t^2$. The spectrum of singular contributions[25,26] indicates [at $O(\epsilon)$] that the new correction-to-scaling exponents associated with higher-order terms are unlikely to be important.

In the present calculation the full crossover forms of the new terms are given. In one sense, this is inconsistent. Even the leading behavior is weaker by $O(|t|^{\Delta_5})$ in the case of the $\bar{0}_5$ interaction. By the use of crossover equations, $O(|t|^{\Delta_5+n\Delta_1})$ corrections are included, where $\Delta_1=\omega\nu\sim\frac{1}{2}$. There are many higher degree operators $(\int\varphi^p)$ whose leading behavior is larger than these crossover Wegner expansion[27] terms. However, this view can be misleading. Each interaction in the Hamiltonian produces a global contribution to the free energy. This may separate into scaling power-law singularities and background terms (kernel $\neq 0$) but in any case it deforms into a mean-field behavior away from criticality. This was shown in the diameter, where the fluid mixing of variables induces a scaling contribution (coming from the $tM^2/2$ part of the free energy) which behaves like $|t|^{1-\alpha}$ near the critical point and crosses smoothly to a $|t|$ behavior farther away. In this case the critical exponent α is returning to its mean-field value of $\alpha=0$. This linear behavior is not a background term but is understandable as the mean-field internal energy. There is also a nonscaling term behaving like $t(|t|^{-\alpha}-1)$ near the critical point but vanishing in the mean-field regime. This sort of behavior cannot be reproduced by a Wegner expansion of finite order and yet clearly needs to be considered if a consistent analysis is to be undertaken. This global view distinguishes the present approach from the work of Ley-Koo and Green[28] which includes the mixing of variables and the $\int\varphi^5$ interaction in a phenomenological scaling setting consistent with the Wegner expansion to first order. (The value of Δ_5 is, of course, only given to $O(\epsilon)$ with $\Delta_5=1/2+\epsilon$.) A scaling format is equivalent to dropping the analytic parts of the fluctuation terms (setting $K=0$) and cannot give a good account of the background and background-mimicking terms. The crossover method supposes that the computation of the free energy and other quantities should be ordered by the relative size of the mean-field contributions in order to provide a smooth matching away from the critical point; full crossover expressions then follow the development of these mean-field terms into their critical limits. The crossover calculation method used here,[15,16] although it has limitations, appears to provide a straightforward approach to higher order in ϵ. Other crossover methods might also be used,[29] but do not seem as easily extended. Although a global crossover equation is exchanged, the poor convergence of the ϵ-expansion may prevent it from being more effective than a local Wegner expansion in practice, at least near the critical point.[23,30] An extension of the asymptotic series analysis for critical exponents[31] to the equation of state, if possible, may be needed before detailed quantitative comparisons can be made.

Finally, as is made evident by Eqs. (5.6) and (5.9), neither the iso-M nor coexistence curves is analytic in t. Thus, $\mu(\rho_c, t)$ is generally not analytic and if $h \equiv \mu - \mu_c - \mu_1 t - \mu_2 t^2/2$ (the degree of precision necessary here), μ_1 is the slope of the coexistence curve,[5] but μ_2 is not the curvature (it is, in principle, identifiable with the curvature of the iso-M line in the mean-field region). The asymptotic mean-field curvature of the coexistence curve, as well as the asymptotic linear diameter is a mixture of genuine background and fluctuation terms. The proper and complete interpretation of experimental data must take these considerations into account.

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APPENDIX A: ISING PERTURBATION SERIES

In this appendix the perturbation series for the Ising case are summarized. Some relationships between matching points are given. The free energy to $O(\epsilon^2)$ is given by

$$\Delta A = -\frac{1}{2}\frac{(\kappa^2)^2}{\epsilon}\left(\frac{(\kappa/\Lambda)^{-\epsilon}}{1-\frac{\epsilon}{4}} - B_0\right)\Lambda^{-\epsilon} + \tfrac{1}{8}u\,(\kappa^2)^2(L+1)^2\Lambda^{-\epsilon} + \frac{u^2M^2\kappa^2}{8}(L^2-f)\ , \qquad \text{(A1)}$$

where $\kappa^2 = t + u\Lambda^\epsilon M^2/2$, $L = \ln\kappa^2/\Lambda^2$, and $f = 4+\pi^2 - 8\lambda$ ($\lambda \cong 1.17$). By differentiation

$$\Delta\frac{\partial A}{\partial t} = -\frac{1}{\epsilon}[\,(\kappa/\Lambda)^{-\epsilon} - B_0]\,\kappa^2\Lambda^{-\epsilon} + \tfrac{1}{4}u\kappa^2\Lambda^{-\epsilon}(L+1)(L+2) + \frac{u^2M^2}{8}(L^2-f+2L)\ , \qquad \text{(A2)}$$

$$\Delta h = Mu\Lambda^\epsilon\Delta\frac{\partial A}{\partial t} + \frac{u^2\kappa^2M}{4}(L^2-f)\ , \qquad \text{(A3)}$$

$$\frac{\Delta h}{uM\kappa^2} = -\left(\frac{(\kappa/\Lambda)^{-\epsilon} - B_0}{\epsilon}\right) + \frac{u}{4}[(L+1)(L+2) + L^2 - f] + \frac{uq}{8}(L^2-f+2L)\ , \qquad \text{(A4)}$$

where $q = u\Lambda^\epsilon M^2/\kappa^2$.

$$\frac{\Delta\Gamma_2}{u\kappa^2} = -\frac{\{[1+q(1-\epsilon/2)](\kappa/\Lambda)^{-\epsilon} - (1+q)B_0\}}{\epsilon} + \frac{u}{4}(2L^2+3L+2-f) + \frac{u}{8}q(7L^2+20L+10-5f) + \frac{q^2}{4}(L+1)u\ , \qquad \text{(A5)}$$

$$\frac{\Delta\Gamma_2}{u\kappa^2} = \frac{\Delta h}{u\kappa^2M} - q\left[\left(\frac{(1-\epsilon/2)(\kappa/\Lambda)^{-\epsilon} - B_0}{\epsilon}\right) - \frac{u}{4}[2(L^2+2L-f) + (L+1)(L+2) + 2L + 3 + q(L+1)]\right]. \qquad \text{(A6)}$$

The match point for A is

$$e^{-\epsilon L/2} = B_0\left(1-\frac{\epsilon}{4}\right)\left(1+\frac{\epsilon\hat{u}p}{16}[1+q(1-4f)]\right), \qquad \text{(A7)}$$

for h/M:

$$\epsilon^{-\epsilon L/2} = B_0\left[1-\epsilon\frac{\hat{u}p}{4}\left((f-1)+q\frac{(f+1)}{2}\right)\right]. \qquad \text{(A8)}$$

For $\partial A/\partial t$:

$$e^{-\epsilon L/2} = B_0\left(1-\frac{\hat{u}p\epsilon q}{8}(f+1)\right). \qquad \text{(A9)}$$

The match point for Γ_2 is more complicated since L is a function of q even at lowest order:

$$e^{-\epsilon L/2} = B_0\left(1+q+\frac{\hat{u}p\epsilon}{4}(2L^2+3L+2-f) + \epsilon\frac{\hat{u}pq}{8}(7L^2+20L+10-5f) + (\hat{u}p)\frac{\epsilon q^2}{4}(L+1)\right)[1+q(1-\epsilon/2)]^{-1}, \qquad \text{(A10)}$$

with $L = -(1+2q)/(1+q)$ on the right-hand side.

A more convenient match for Γ_2 involves two matches:

$$\Gamma_2 = \frac{h}{M} + \frac{u\mathfrak{D}^2(l')M^2Y^{\epsilon/\omega}(l')}{3}, \qquad \text{(A11)}$$

where the h/M match point is used for h/M and the l' match point is

$$e^{-\epsilon L'/2} = \frac{B_0}{1-(\epsilon/2)}\left(1+\epsilon\frac{\hat{u}p'}{4}(2f+1+q')\right). \qquad \text{(A12)}$$

This is the point at which the large bracket in Eq. (A6) vanishes. The series for $R = \Gamma_2\xi^{+2}$ is

$$R = 1 + \frac{uq}{12}e^{-\epsilon L/2}\left(1-\frac{\epsilon}{2}\right) - \frac{2}{3}u^2\left(\frac{L+3}{8}\right) + \frac{u^2q}{36}\left(\frac{15}{2}(L+1) + (1-4I)\right) + \frac{u^2q^2}{36}[\tfrac{11}{4} + I - \tfrac{3}{2}(L+1)]\ . \qquad \text{(A13)}$$

In (A13) $I = -2\lambda$. By dividing the Γ_2 series by R an expression for the correlation length is obtained,

$$\xi^{-2}=\kappa^2\,\frac{(1+\Delta\Gamma_2/\kappa^2)}{R}\quad. \tag{A14}$$

By inserting the value of L used at any match point the match point κ^2 can be related to ξ^{-2}. For example, at the h/M match point,

$$\xi^{-2}=\kappa^2\,\frac{\left[1+q\frac{\hat{u}p}{2}\left(1-\frac{\hat{u}p}{2}\right)-\frac{(\hat{u}p)^2}{4}\,q(1-q/2)(f+1)\right]}{\left\{1+\frac{\hat{u}pq}{12}\left(1-\frac{\epsilon}{2}\right)+\frac{(\hat{u}p)^2}{18}\left[-3+\frac{q}{2}(1-4I)+\frac{q^2}{2}\left(\frac{11}{4}+I\right)\right]\right\}}\;. \tag{A15}$$

These series imply

$$\beta=-\epsilon u+3u^2B_0-\tfrac{17}{3}u^3\,,\qquad \eta=\frac{u^2}{6}\,,\qquad 2-1/\nu-\eta=uB_0-u^2\,. \tag{A16}$$

APPENDIX B: NON-ISING PERTURBATION SERIES

The effects of adding the interactions O_3 and O_5 to the Hamiltonian can be divided into two parts. First, when performing the loop expansion for fixed M the Ising Hamiltonian defines effective two-, three-, and four-point couplings (cf. Wallace and Zia[32]). In terms of a shifted field

$$\int \tfrac{1}{2}\kappa^2\varphi^2+\tfrac{1}{2}(\nabla\varphi)^2+\frac{uM\Lambda^\epsilon}{3!}\,\varphi^3+\frac{u\Lambda^\epsilon\varphi^4}{4!}\quad, \tag{B1}$$

with $\kappa^2=t+u\Lambda^\epsilon M^2/2$. The presence of the $v_i O_i$ shift

$$\frac{u\Lambda^\epsilon}{4!}\to\frac{u\Lambda^\epsilon}{4!}\,(1+v_5M)\;,$$

$$\frac{uM\Lambda^\epsilon}{3!}\to\frac{uM\Lambda^\epsilon}{3!}\,(1+\tfrac{1}{2}v_5M)\,, \tag{B2}$$

$$-\nabla^2+\kappa^2\to(-\nabla^2)\left(1+2\,\frac{v_3}{3}M\right)+\kappa^2+\frac{v_5uM^3\Lambda^\epsilon}{3!}\;.$$

These shifts show that the $v_i\Theta_i$ insertions are $O(v_iM)$ smaller than the Ising terms. The perturbation series for the Ising case is modified by the inclusion of these factors. The linear effects are easy to work out: For the Helmholtz potential,

$$\Delta A_i=\Theta_i(\Delta A)\;,$$

$$\Theta_3=-\frac{2}{3}\,\frac{\kappa^2}{u\Lambda^\epsilon}\,\frac{\partial}{\partial M}-\frac{4}{3}\,M\left(u\,\frac{\partial}{\partial u}-t\,\frac{\partial}{\partial w}\right), \tag{B3}$$

$$\Theta_5=\frac{w}{6u\Lambda^\epsilon}\,\frac{\partial}{\partial M}-M\left(\frac{w}{3}\,\frac{\partial}{\partial w}-u\,\frac{\partial}{\partial u}\right),$$

where ΔA is the fluctuation part of the Ising-free energy [Eq. (A1)]. In Eq. (B3) $w=u\Lambda^\epsilon M^2$.

The second contribution is from the new cubic and quintic interactions. To two loops the quintic term has only the mean-field contribution $v_5u\Lambda^\epsilon M^5/5!$ Therefore,

$$A_5=\frac{uM^5\Lambda^\epsilon}{5!}+\frac{M^2}{6}\,(\Delta h)$$

$$+\frac{uM\kappa^2}{8}\left(\kappa^2(L+1)^2+\frac{2}{3}\,w(L^2-f)\right), \tag{B4}$$

where Δh is given by Eq. (A3).

O_3 has no mean-field term but does contribute to the two-loop diagram shown in Fig. 1. Its value,

$$-\tfrac{1}{6}\,uv_3M\left(\frac{(L+1)^2}{4}+\tfrac{3}{8}(L^2-f)\right)\kappa^4\Lambda^{-\epsilon}\quad,$$

is added to the result of (B3) to give

$$A_3=-\frac{2}{3}\,\frac{\kappa^2}{u\Lambda^\epsilon}\,(\Delta h)-\frac{uM\kappa^2}{6\Lambda^\epsilon}\left(\kappa^2\left[\,2(L+1)^2+\tfrac{1}{2}(L^2-f)\right]\right.$$

$$\left.+\tfrac{3}{2}w(L^2-f)\right)\,. \tag{B5}$$

Combining Eqs. (B3)–(B5) with Eqs. (A2) and (A3),

$$\frac{tM^3}{3!}+\frac{t(\Delta h)}{u\Lambda^\epsilon}+A_3+\frac{10}{3}A_5=\frac{1}{3}h\,\frac{\partial A}{\partial t}+O(\epsilon^3)\;, \tag{B6}$$

confirming the mixing of fields to two-loop order. The other eigencombination $\overline{A}_5=A_5+S_5(u)A_3$ is

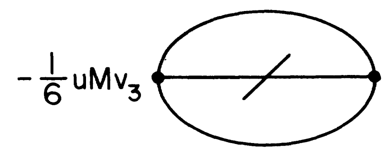

FIG. 1. The sole contribution to the A_i at two-loop order. The slash on the propagator line indicates an extra factor of $(k^2)\Lambda$.

$$\bar{A}_5 = \frac{uM^5\Lambda^\epsilon}{5!} + \frac{\left(\frac{w}{6} - \frac{2}{3}S_5\kappa^2\right)}{u\Lambda^\epsilon}\Delta h + \frac{uM\kappa^2}{8}\left[\kappa^2(L+1)^2 + \tfrac{2}{3}w(L^2-f)\right]\Lambda^{-\epsilon}$$
$$= \frac{uM^5\Lambda^\epsilon}{5!} + \frac{M^2}{6}\Delta h - \tfrac{1}{3}S_5 M(L+1)(\kappa^2)^2\Lambda^{-\epsilon} + \frac{uM\kappa^2}{8}\left[\kappa^2(L+1)^2 + \tfrac{2}{3}w(L^2-f)\right]\Lambda^{-\epsilon}\,, \quad \text{(B7)}$$

where the fact that S_5 is $O(u,\epsilon)$ has been used. The match point for $\bar{A}_5$ is therefore

$$e^{-\epsilon L/2} = \kappa^\epsilon B_0\left[1 - \frac{\epsilon}{4}\hat{u}p\left(3(f-1) + \frac{q}{2}(f+1)\right)\right]. \quad \text{(B8)}$$

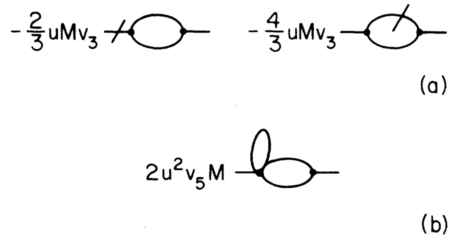

FIG. 2. Diagrams for $\Gamma_2(k)$: the contribution to $R = \Gamma_2(0)\xi^2$ is given by taking $\partial/\partial k^2$ at $k=0$. The one-loop 0_3 insertion is shown in (a) and the two-loop insertion of 0_5 in (b).

Note that this differs only at $O(\epsilon^2)$ from the h/M match point. The series for $\bar{h}_5$ is obtained by differentiation:

$$\bar{h}_5 = \frac{uM^4\Lambda^\epsilon}{4!} + \frac{M\Delta h}{3} + \frac{M^2\Delta\Gamma_2}{6} - \frac{1}{3}S_5(\kappa^2)^2\Lambda^{-\epsilon}[(L+1) + q(2L+3)]$$
$$+ \frac{u}{8}(\kappa^2)^2\Lambda^{-\epsilon}\left\{(L+1)^2 + 2q(L^2-f) + q\left[2(L+1)(L+2) + \frac{2q}{3}(L^2 - f + 2L)\right]\right\}. \quad \text{(B9)}$$

Again the match point for $\bar{h}_5$ is somewhat clumsy; to lowest order, $L = -(3+2q)/(3+q)$.

The ratio $R = \Gamma_2\xi^2$ can be divided into $R_I + v_i R_i$; again $R_i = \Theta_i R_i + R_i^{\text{self}}$. To the order needed

$$R_3^{\text{self}} = \tfrac{2}{3}M\left[1 + u\left(\frac{L+2}{2}\right) - \frac{u}{6}\right], \quad \text{(B10)}$$

$$R_5^{\text{self}} = u^2 M\left(\frac{(L+1)}{12}\right), \quad \text{(B11)}$$

corresponding to the diagrams in Fig. 2.

APPENDIX C: HIGHER-ORDER EQUATION OF MOTION RESULTS

In Sec. II the equivalence of the $\bar{0}_3$ operator to field mixing was shown to lowest order. Defining

$$V \equiv \bar{0}_3 = \tfrac{1}{2}\int \varphi^2(x) h_\varphi(x)\,, \quad \text{(C1)}$$

then the addition of vV to the Hamiltonian gives the following change in the Gibbs functional:

$$\Delta G = v\langle V\rangle - \frac{v^2}{2}\langle (V - \langle V\rangle)^2\rangle\,. \quad \text{(C2)}$$

Applying $\delta/\delta t(x_3)\delta/\delta\varphi(x_1)$ to the functional integral defining G gives

$$\langle \tfrac{1}{2}\varphi^2(x_3)\Delta(x_1) - \delta(x_1 - x_3)\varphi(x_3)\rangle = 0\,, \quad \text{(C3)}$$

with $\Delta(x) \equiv h_\varphi(x) - h(x)$ which shows $\langle V\rangle = \int h(x)\partial G/\partial t(x) + \Lambda^d M$. Consider inserting $[\delta/\delta\varphi(x_2)][\delta/\delta\varphi(x_1)]$ in the integrand:

$$\langle \Delta(x_1)\Delta(x_2) - \Gamma_\varphi(x_1)\delta(x_1 - x_2)\rangle = 0\,, \quad \text{(C4)}$$

with $\Gamma_\varphi = t(x) - \nabla_\Lambda^2 + u\Lambda^\epsilon\varphi^2(x)/2$. Integrating Eq. (C4) over x_1 and x_2 gives

$$\left\langle\left(\int h_\varphi(x) - h(x)\right)^2\right\rangle = \int \Gamma_\varphi(x) = t + u\Lambda^\epsilon\partial G/\partial t\,, \quad \text{(C5)}$$

a result that can be obtained by examining the Hamiltonian. Applying $[\delta/\delta t(x_3)][\delta/\delta t(x_4)]$ to Eq. (C4),

$$\Big\langle \frac{\Delta(x_1)\Delta(x_2)}{4}\varphi^2(x_3)\varphi^2(x_4) - \frac{\varphi^2(x_3)}{2}\frac{\varphi^2(x_4)}{2}\Gamma_\varphi(x_1)\delta(x_1 - x_2)$$
$$- \frac{\Delta(x_1)}{2}[\varphi(x_3)\varphi^2(x_4)\delta(x_2 - x_3) + \varphi(x_4)\varphi^2(x_3)\delta(x_2 - x_4)] - \frac{\Delta(x_2)}{2}[\varphi(x_3)\varphi^2(x_4)\delta(x_1 - x_3) + \varphi(x_4)\varphi^2(x_3)\delta(x_1 - x_4)]$$
$$+ \varphi(x_3)\varphi(x_4)[\delta(x_2 - x_3)\delta(x_1 - x_4) + \delta(x_1 - x_3)\delta(x_2 - x_4)] + \frac{\delta(x_1 - x_2)}{2}[\delta(x_1 - x_3)\varphi^2(x_4) + \delta(x_1 - x_4)\varphi^2(x_3)]\Big\rangle = 0\,.$$

(C6)

This is simplified by considering the sequence of derivatives $\delta/\delta t(x_4)\ \delta/\delta h(x_3)\delta/\delta\varphi(x_1)$,

$$\left\langle -\frac{\varphi^2(x_4)}{2}\varphi(x_3)\Delta(x_1)+\tfrac{1}{2}\varphi^2(x_4)\delta(x_1-x_3)+\varphi(x_1)\varphi(x_3)\delta(x_1-x_4)\right\rangle=0\,, \tag{C7}$$

and the sequence $\delta/\delta t(x_3)\delta/\delta t(x_4)\delta/\delta\varphi(x_1)$:

$$\left\langle -\frac{\varphi^2(x_4)\varphi^2(x_3)\Delta(x_1)}{4}+\frac{\varphi^2(x_4)\varphi(x_3)\delta(x_1-x_3)}{2}+\frac{\varphi(x_4)\varphi^2(x_3)}{2}\delta(x_1-x_4)\right\rangle=0\,. \tag{C8}$$

Combining these with (C6),

$$\begin{aligned}\left\langle\frac{\varphi^2(x_3)\varphi^2(x_4)}{4}h_\varphi(x_1)h_\varphi(x_2)\right\rangle=&\tfrac{1}{4}\langle\varphi^2(x_3)\varphi^2(x_4)h(x_1)h(x_2)\rangle+\tfrac{1}{4}\langle\varphi^2(x_3)\varphi^2(x_4)\Gamma_\varphi(x_1)\delta(x_1-x_2)\rangle\\&+\langle\{\varphi(x_3)\varphi(x_4)[\delta(x_1-x_4)\delta(x_2-x_3)+\delta(x_2-x_4)\delta(x_1-x_3)]\}\rangle\\&+\tfrac{1}{2}\delta(x_1-x_2)\langle\delta(x_1-x_3)\varphi^2(x_4)+\delta(x_1-x_4)\varphi^2(x_3)\rangle\\&+\tfrac{1}{2}\langle h(x_1)[\varphi^2(x_4)\varphi(x_3)\delta(x_1-x_3)+\varphi^2(x_3)\varphi(x_4)\delta(x_1-x_4)]\rangle\\&+\tfrac{1}{2}\langle h(x_2)[\varphi^2(x_4)\varphi(x_3)\delta(x_2-x_3)+\varphi^2(x_3)\varphi(x_4)\delta(x_2-x_4)]\rangle\,.\end{aligned} \tag{C9}$$

Letting $x_3\to x_1$, $x_4\to x_2$ and integrating over x_1 and x_2,

$$\begin{aligned}\sigma_V^2&\equiv\langle(V-\langle V\rangle)^2\rangle\\&=-\int h(x_1)h(x_2)\frac{\delta^2G}{\delta t(x_1)\delta t(x_2)}+2\Lambda^d\int h(x_2)\frac{\delta^2G}{\delta t(x_2)\delta h(x_1)}-\Lambda^{2d}\iint\frac{\delta^2G}{\delta h(x_1)\delta h(x_2)}+4\Lambda^d\int\frac{\delta G}{\delta t(x)}\\&\quad+\tfrac{1}{4}\left\langle\int\varphi^2(x)\Gamma_\varphi(x)\varphi^2(x)\right\rangle+\left\langle\int h(x)\varphi^3(x)\right\rangle\,.\end{aligned} \tag{C10}$$

The first three terms are exactly what would be expected if the linear analysis were exact $G(t,h)\to G(t+vh,h-v\Lambda^d)$. The fourth term is a shift in t so that $G(t,h)\to G(t+vh-2\Lambda^d v^2,h-v\Lambda^d)$. It is the last two terms which break the simple mixing, the complete $O(v^2)$ result being

$$\begin{aligned}G\to&\ G[t(x)+vh(x)-2\Lambda^d v^2,h(x)-v\Lambda^d]\\&-\frac{v^2}{8}\left\langle\int\varphi^2(x)\Gamma_\varphi(x)\varphi^2(x)\right\rangle-\frac{v^2}{2}\left\langle\int h(x)\varphi^3(x)\right\rangle\,.\end{aligned} \tag{C11}$$

The first disruptive term is a combination of φ^6 and related operators. The second could be evaluated by the classical equation of motion, expressed in terms of φ^6 operators, or removed by an $h(x)$ dependent shift in $\varphi(x)$.

There is a simple way to obtain the result of (C11). Transform the field nonlinearly[33]

$$\varphi(x)\to\bar\varphi(x)-v\frac{\bar\varphi^2(x)}{2}\,. \tag{C12}$$

The old order parameter $M=\langle\varphi\rangle$ is a combination of the new spin and energy densities. The Hamiltonian becomes to $O(v^2)$,

$$\begin{aligned}H=&\int[\tfrac{1}{2}\bar t(x)\bar\varphi^2(x)+\tfrac{1}{2}|\nabla\bar\varphi|^2_\Lambda+\tfrac{1}{4}u\Lambda^\epsilon\bar\varphi^4(x)-h(x)\bar\varphi]\\&-\tfrac{1}{8}v^2\int\bar\varphi^2(x)\Gamma_{\bar\varphi}(x)\bar\varphi^2(x)-\tfrac{1}{2}v^2\int h_{\bar\varphi}(x)\bar\varphi^3(x)\,,\end{aligned} \tag{C13}$$

with $\bar t(x)=t(x)+vh(x)$.

The expectation value of these terms must be combined with the Jacobian of the transformation (C12). This adds a term

$$-\Lambda^d\ln[1-v\bar\varphi(x)]=\Lambda^d\left(\int v\bar\varphi(x)+\frac{v^2}{2}\bar\varphi^2(x)\right) \tag{C14}$$

to the Hamiltonian which, combined with Eq. (C7), is responsible for the Λ^d terms in Eq. (C11).

The change of variable method given in (C12)–(C14) can be extended to any Hamiltonian $H=\mathcal{H}-\int h(x)\varphi(x)$ to which an interaction of the form $\int h_\varphi(x)\psi(x,\varphi)$ is added; ψ is any operator and $h_\varphi(x)\equiv\delta\mathcal{H}/\delta\varphi(x)$. Then to first order in ψ, one may use the equations of motions or make the change of variable

$$\varphi=\bar\varphi-\psi(x,\bar\varphi)\,, \tag{C15}$$

and obtain

$$\left\langle\int h_\varphi(x)\psi(x)\right\rangle=\left\langle\int h(x)\psi(x)\right\rangle+\left\langle\int\frac{\delta\psi(x)}{\delta\varphi(x)}\right\rangle. \tag{C16}$$

If $\psi(x)$ depends locally on $\varphi(x)$ and its derivatives, the second term (which comes from the Jacobian of the transformation) is proportional to Λ^d and therefore may usually be absorbed into changes in the field, critical temperature, coupling constant, etc.

This result is intimately related to the operators classified as redundant by Wegner.[34] In Wegner's differential generator format, an operator is termed redundant if it can be written (in the present notation) as

$$\int\left(\psi(x)\,\frac{\delta H}{\delta\varphi(x)}-\frac{\delta\psi(x)}{\delta\varphi(x)}\right), \qquad \text{(C17)}$$

where the second term is again the Jacobian of a transformation corresponding to (C15). Wegner shows that such an operator does not contribute to the free energy at first order. The first order contribution is, of course, just the expectation value of the operator and its vanishing is just (C16).

However, it is an error to consider such operators as having no physical significance. In the present case, and presumably others, the interaction added to the Hamiltonian is not the full redundant operator given in (C17); only the operator $\int h_\varphi(x)\psi(x)$ is involved and therefore there are contributions to the free energy, even in first order, given by Eq. (C16). For the asymmetric LGW Hamiltonian, the physical consequence is not at all trivial: the fields are mixed in the temperature-like variable.

The results obtained by functional derivatives for correlation functions such as Eq. (C9) may be recovered from Eq. (C16) by choosing a nonlocal $\psi(x)$:

$$\psi(x_1)=\int f(x_1,x_2,x_3,x_4)h_\phi(x_2)\phi^2(x_3)\phi^2(x_4)\,. \qquad \text{(C17)}$$

Inserting this into Eq. (C16) gives an expression of the form

$$\int f(x_1,x_2,x_3,x_4)[\langle h_\phi(x_1)h_\phi(x_2)\phi^2(x_3)\phi^2(x_4)\rangle\cdots]=0\,.$$

Since f is arbitrary the bracketed expectation values must be zero for all (x_1,x_2,x_3,x_4), yielding Eq. (C9). In the same way, any other relationship obtained from the equation of motion or higher-order partition-function invariances can be extracted from Eq. (C16) with a suitable ψ.

By iterating Eq. (C16) one obtains

$$\left\langle\int h_\phi^n(x)\psi(x)\right\rangle=\left\langle\int h^n(x)\psi(x)\right\rangle+\cdots\,, \qquad \text{(C18)}$$

where the undisplayed terms represent the Jacobian terms. Equation (C18) shows that any analytic h dependence (compatible with the possible symmetry of the Hamiltonian) may be introduced into any coupling constant. With $\psi\equiv1$, a mechanism for providing the h-analytic regular part of the Gibbs free energy is shown to reside in the higher-order operators h_ϕ^n. Equation (C18) also shows that the operator $\int h_\phi^n\psi$ has a definite anomalous dimension if ψ has, given by $d\psi-n\eta/2$. More conventionally, the coupling constant dependence is removed from the leading power at φ. For ϕ^4 theory, define $h'_\phi\equiv\varphi^3(x)/6+(t-\nabla^2)\varphi(x)/u\Lambda^\epsilon$. The anomalous dimension of $\int(h'_\phi)^n\psi$ is then $d\psi+n(\epsilon-\eta/2)$. This can be a useful check for calculations of anomalous dimensions of nontrivial composite operators.[12-14] Finally, Eq. (C16) can be generalized to m-component fields $\phi_j(x)$. Then with $h_\phi^j=\delta\mathcal{H}/\delta\phi_j(x)$,

$$\left\langle\int h_\phi^j(x)\psi_j(x)\right\rangle=\left\langle\int h^j(x)\psi_j\right\rangle=\left\langle\int\delta\psi_j/\delta\phi_j(x)\right\rangle. \qquad \text{(C19)}$$

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