The liquid-gas critical point in 3.3 dimensions*

Oriol T. Valls and J. A. Hertz

The James Franck Institute and The Department of Physics, The University of Chicago, Chicago, Illinois 60637

(Received 16 March 1977)

Liquid-gas phase transitions are usually assumed to belong to the same universality class as Ising magnets. However, in the liquid-gas case, the free-energy expansion contains odd powers of the order parameter. We show in this work that, even though the odd terms are irrelevant near four dimensions, they become relevant at dimensionality $d_c = (10-5\eta)/3 \approx 3.33$. A new, stable, fixed point may appear. We approximately calculate, to order $\epsilon' = d_c - d$, the difference between the critical exponents for this new fixed point and the Ising critical exponents. This difference turns out to be numerically small. We conclude that, even though in three dimensions the liquid-gas and Ising-magnet phase transition do not belong to the same universality class, the effect on the critical exponents is probably too small to be observed.

I. INTRODUCTION

In the taxonomy of critical-point problems which has been so actively developed in the last decade,¹ liquid-gas transitions are generally placed in the same universality class with those in uniaxial (Ising-like) magnets, since both have scalar order parameters $(n=1)$. In general, experiments have seemed to support this identification: indeed, the similarity between fluid and magnetic critical points was important in suggesting the idea of the universality of critical phenomena in the first place. However, the spins in a magnet possess an exact up-down symmetry (in the absence of an external field) which has no counterpart in the fluid. In the latter case, the order parameter, the deviation $\rho - \rho_c$ from critical density, has an approximate symmetry near the critical point which follows from the analyticity of the Van der Waals coexistence curve at the critical point. However, there is no exact symmetry between liquid and gas phases.

Is this difference in symmetry relevant to critical phenomena in the two kinds of systems, or is the approximate symmetry of the fluid sufficient to place it in the same universality class with the magnet9 This is the first question we try to answer in this paper. Hubbard and Schofield² have already raised this question and answered it for systems near four dimensions, where one can apply Wilson's ϵ expansion.³ They find that the difference between fluids and magnets is irrelevant (in Wilson's sense) and that all critical properties should be the same for the two systems. We find, however, that below a critical dimensionality $d_c = \frac{1}{3}(10-5\eta) \approx 3.3$, the ϵ expansion can break down; a term of odd symmetry becomes relevant, and a new fixed point may become stable, altering the critical exponents of the fluid. These corrections can be calculated as power series in $\epsilon' = d_c - d$; in this paper we calculate the changes in γ and η to order ϵ' .

In the next section we review the formulation of the liquid-gas transition in terms of a Landau-Ginzburg model Hamiltonian and note why it is the presence in this Hamiltonian of a term of fifth order in the order parameter that makes this case potentially different from its magnetic counterpart. In Sec. III we outline the application of the renormalization group to this problem and show that the fifth-order term becomes relevant below the special dimensionality d_c mentioned above. We will see that below d_c , a new stable fixed point, with new critical exponents, may occur. Section IV contains an approximate calculation of this fixed point and the corresponding changes in critical exponents. The calculation requires knowing the four-point vertices of the symmetric (magnetic) theory; these are obtained from the ordinary ϵ (=4 – d) expansion. In the final section we comment on the results.

II. MEAN-FIELD THEORY AND THE LANDAU-GINZBURG DESCRIPTION

Landau-Ginzburg theory provides a description of fluctuations around a particular mean-field theory. Accordingly, we recall a few features of the Van der Waals (mean-field) theory of a liquidgas system, which is analogous to the Weiss mean-field theory for a magnet. Very close to the critical point, where one can make power-series expansions, the two theories are manifestly equivalent (except for scale factors) since the leading terms in both expansions have the same form. However, at a finite deviation from criticality, the Van der Waals problem does not admit an invariance under the change $\rho - \rho_c$ \rightarrow $- (\rho - \rho_c);$ the symmetry is confined to the first two terms in the Taylor series. One might call the approximate symmetry a dynamically generated one; it exists only because we are near the critical point.

Thus the Landau-Ginzburg effective Hamiltonian

18 2367 04 1978 The American Physical Society

of the fluid problem will differ from that of the magnet in that it need not contain only terms even in the order parameter; odd powers are permitted as mell. So let us examine an effective Hamiltonian of the form V_4 V_3

$$
H(\Psi) = h\Psi + \frac{1}{2}r\Psi^2 + \frac{1}{3}v_3\Psi^3 + \frac{1}{4}v_4\Psi^4 + \frac{1}{5}v_5\Psi^5 + \dots \,, \qquad (2.1)
$$

ignoring all gradient coupling, etc., as in Landau mean-field theory. The linear term $h\Psi$ must be set to zero to have a critical point. (This occurs in the magnet as well.) We want the critical point to happen when r passes through zero, so that H changes from a single-well to a double-well structure. But if $v_2 \neq 0$, this will not happen; *H* will have an inflection point at $\Psi = 0$ when $r = 0$. This describes a first-order transition, not a critical point. In physical language, we are not at the right density. We must define a new Ψ , shifted from the old one by a value chosen so that when H is expanded in terms of the new Ψ , the coefficient of the cubic term vanishes.

Thus the first odd-symmetric term that remains is the quintic. Since we want the integral of e^{-H} to be finite, we also need a positive v_6 (or some higher even-power term), but this will not enter into the calculation of any critical properties. Our initial effective Hamiltonian is then

$$
H[\Psi] = \int d^d x \left[\frac{1}{2} \gamma \Psi^2(x) + \frac{1}{2} (\nabla \Psi)^2 + \frac{1}{4} v_4 \Psi^4(x) + \frac{1}{5} v_5 \Psi^5(x) \right].
$$
 (2.2)

We have added the usual Landau $(\nabla \Psi)^2$ term, but omitted nonlinear gradient terms like $\Psi(\nabla\Psi)^2$ or $\Psi^3(\nabla\Psi)^2$. In the next section we apply the renormalization group to this model. The question we will seek to answer is whether the $v₅$ term, or any other new term that it generates under the renormalization group, is relevant in three dimensions.

III. RENORMALIZATION GROUP FOR THE FLUID

We can renormalize this problem in the standard way.² First the functional integral is carried out over the large-q components of Ψ , $\Lambda e^{-t} < q \leq \Lambda$, where Λ is the cutoff in the theory. This changes the values of the coefficients r , v_4 , and v_5 , and, indeed, gives them some momentum dependence. The momenta and fields are then rescaled so that the cutoff is again Λ and the $(\nabla \Psi)^2$ term looks like it did in the original problem. Finally (and this step is necessary only for the asymmetric problem) we shift Ψ at each point by a constant chosen so that the cubic term

$$
H_3 = \frac{1}{3\sqrt{N}} \sum_{q_1 q_2} v_3(q_1, q_2, -q_1 - q_2) \Psi_{q_1} \Psi_{q_2} \Psi_{-q_1 - q_2}
$$
 (3.1)

vanishes at $q_1 = q_2 = 0$. Note that we can only do

FIG. 1. Contributions to $\partial v_2/\partial l$. A slashed line means its momentum lies in the shell $e^{-t} < k < 1$.

this in the uniform limit; a q -dependent $v₃$ will remain the renormalized H and cannot be made to vanish. The first such surviving terms are interactions of the form $\Psi(\nabla\Psi)^2$. The differential renormalization-group equations obtained thereby contain distinct terms from each of the three steps in the renormalization procedure. Those which arise from the integration of the shell Ψ 's admit a diagrammatic representation. For example, these contributions to the change. in the quadratic coefficient $v_2(k)$ are shown in Fig. 1 and have the form $(\Lambda = 1, l$ infinitesimal)

$$
\frac{\partial v_2^{(k)}}{\partial l}\Big|_{\text{int}} = \frac{1}{4} \int \frac{d\Omega_d}{(2\pi)^d} \frac{12 \text{ terms in } v_4}{v_2(\vec{1})} - \frac{1}{18} \int \frac{d\Omega_d}{(2\pi)^d} \frac{36 \text{ terms in } v_3 v_3}{v_2^2(\vec{1})} . \tag{3.2}
$$

The shift $\Psi(x) - \Psi(x) + al$ or $\Psi''(x) - \Psi''(x) + n a \Psi^{n-1}(x)$ leads to a change

$$
\frac{\partial v_n(k_1, \ldots, k_n)}{\partial l} \Big|_{\text{shift}}
$$

=
$$
\frac{na}{n+1} \left[v_{n+1}(0, k_1, \ldots, k_n) + v_{n+1}(k_1, 0, k_2, \ldots, k_n) + \ldots + v_{n+1}(k_1, k_2, \ldots, k_n, 0) \right].
$$
 (3.3)

The constant a is chosen so that the total $\partial v_a(0, 0, 0)$ / ∂l vanishes. For this discussion, the terms which come from rescaling are the most important. They have the simple linear form^{3,4}

$$
\frac{\partial v_n(k_1,\ldots,k_n)}{\partial l}\Big|_{\text{rescaling}} = \left(n(1-\frac{1}{2}\eta) - (\frac{1}{2}n-1)d - \sum_{i=1}^n \vec{k}_i \cdot \vec{\nabla} k_i\right) v(k_1,\ldots,k_n),\tag{3.4}
$$

and from them we can ascertain the relevance or irrelevance of a given interaction v_n . If $v(k_n, \ldots, k_n)$ is finite at all $k_i = 0$, it is relevant if the coefficient $n(1-\frac{1}{2}\eta) - (\frac{1}{2}n-1)d$ is positive, irrelevant if it is negative, and marginal if it vanishes.

Thus as we lower the dimensionality from some high value, one more interaction after another becomes relevant. If we ignore η for the moment, we find the cubic term to be relevant below $d=6$. the quartic one becomes relevant below $d=4$, the quintic at $d = \frac{10}{3}$, and the sixth-order one at $d = 3$.

If, as in the present problem, the v_3 term has been eliminated at zero wave vector, the presence of the $\vec{k} \cdot \vec{\nabla}_{k}$, term in (3.4) renders the remaining $v₃$ term irrelevant above $d=2$, assuming that the lowest-order terms are quadratic in k_i . A finite positive η lowers the critical dimensionality slightly for each interaction, so in the physically interesting three-dimensional case, just one new interaction (v_n) not present in the magnetic problem near $d=4$ is relevant.

The foregoing suggests that we try to solve the renormalization-group equations near $d_a = \frac{1}{3}(10-5\eta)$, where v_5 becomes relevant, to lowest nontrivial order in $\epsilon' = d_c - d$, by analogy with the now-standard procedure near $d = 4$ in the symmetric problem. If we find a new stable fixed point with $v_{\rm s}^*$ proportional to some power of ϵ' , we would then be able to extract the changes in critical exponents from their values in the symmetric theory as power-series expansions in ϵ' by perturbing the group equations around this new fixed point.

While this program remains possible in principle, we have chosen to do our calculation usingWilson's diagrammatic perturbation-theory matching method' instead. The reasons for abandoning the renormalization group as the means of doing the calculation are:

(1) In order to do any calculation, we have to guess the form of the new fixed point, and it is not obvious how to do this correctly. The simplest assumptions we have tried (e.g., v_4 and v_5 finite at $k_i = 0$, v_3 quadratic in k_i and therefore irrelevant) do not lead to sensible results. Indeed, we are not allowed to assume that the fixed-point interactions $v_n^*(k_1, \ldots, k_n)$ are analytic in the k_i . We found in fact a form of the fixed point which seemed to make sense and $v_3 \propto (k_i)^{4/3-2\eta/3}$. This made it exactly equally as relevant as v_5 , which had a constant term $O(k_i^0)$. It also turned out to be necessary to have the quartic term v_4 a singular function of its argument.

(2} The group equations become very messy, partly because of the necessity of keeping the v_o interactions at finite k . In addition, one needs to look at the equations for higher-order vertices (e.g., v_7) in order to stabilize the growth of v_5 from the rescaling term (3.4) when ϵ '>0. (These also have singular k dependence.) It then becomes very difficult to follow the path of the system in parameter space and find the new fixed point.

We therefore turn in the next section to the matching method instead. The renormalization group has, however, allowed us to ascertain the critical dimensionality d_c below which a v_5 term is relevant. The next question to be answered is whether the new relevant interaction leads to modified critical behavior.

IV. NEW FIXED POINT AND CRITICAL EXPONENTS

The method that we follow in this section is a straightforward extension of the matching metho of Wilson. We will assume that immediately below $d_c \approx \frac{10}{3}$ the fixed point (and its exponents) differs little from the Ising fixed point. That is, we will assume that the fixed-point value of the four-point interaction v_4^* for $d < d_c$ is the same as the Ising value (i.e., as given by the ϵ expansion) plus a correction which vanishes at $d = d_{c}$, and that the interactions of odd order have fixed-point values proportional to some power of ϵ' . Our objective is to find the corrections of order ϵ' to the critical exponents.

We write, accordingly,

$$
v_5^* = v_5^* (\epsilon'), \quad v_4^* = v_4^{*1} + v_4^{*1} (\epsilon'), \tag{4.1}
$$

where v_4^{*I} is the Ising value. We will show in this section that

$$
v_5^{*2} \propto \epsilon', \quad v_4^{*'}(\epsilon') \propto \epsilon' \,. \tag{4.2}
$$

We review now the matching procedure. We want to choose special values of the interaction parameters v_i (called v_i^0) so that the perturbation series for $k^2 G(k)$ (G is the propagator) exponentiates to match the critical behavior k^{η} . In the symtes to match the critical behavior k^n . In the metric problem, the value of v_4^0 is found by matching perturbation theory to the scaling form of the four-point vertex function in the long-wavelength limit. The value of $v_{\rm s}^0$ will be determined in an analogous fashion in this work by examining the five-point vertex function, which, as $k \rightarrow 0$, is given by^{3,5,}

$$
\Gamma_5 \propto \xi^{3d/2 - 5 + 5\eta/2}, \qquad (4.3)
$$

where ξ is the correlation length. We have

$$
\xi \propto r^{-(2-\eta)}, \quad G_0(k) = 1/(r+k^2).
$$
 (4.4)

Hence

$$
\Gamma_5 \propto r^{3\epsilon'/4-5\eta/4} \ . \tag{4.5}
$$

We assume

$$
\eta = \eta^I + \eta' \epsilon' \tag{4.6}
$$

The expansion of Eq. (4.5) in powers of ϵ' is to be matched with the perturbation expansion for Γ_{5} , and thus the value of v_5^0 is to be deduced.

Two parenthetical comments: (1) The reader will recall^{3,5,6} that the special values of the couplings v_i^0 are not exactly equal to the fixed-point values v_i^* . However, to the order in ϵ' to which we work, they are the same, so we will not make the distinction explicitly hereafter. (2) In the symmetric problem it was necessary to fix only the interaction v_4 by this procedure. In the asymmetric problem, we will find it necessary to choose

properly the whole set of interactions v_i , $1 \le i \le 5$ $(i=2$ is a trivial case). Thus the technical details are more involved, although the idea remains: to fix the parameters in H so that perturbation theory matches scaling theory.

We have to develop, therefore, the perturbation expansions for Γ_5 and for the self-energy Σ defined by

$$
G^{-1}(k) = r + k^2 + \Sigma(k) - \Sigma(0).
$$
 (4.7)

Even with the limitation, imposed at the beginning, of keeping to order ϵ' only, the evaluation of the diagrams appearing in the perturbation expansion is extremely cumbersome. That forces us to restrict ourselves to the following two classes of diagrams.

(1) Diagrams containing odd interactions only. To compute the exponents to order ϵ' , this will mean two vertices in the self-energy diagrams, three in the $\Gamma_{\rm s}$ diagrams. The diagrams in this class will be calculated exactly.

(2) Diagrams containing the above numbers of odd vertices plus one four-point vertex which is evaluated to zeroth order in ϵ' . These diagrams will be calculated approximately.

Diagrams containing v_4 will not be needed except to cancel divergent terms to produce the proper logarithmic singularities.

Two further points are worth noticing: First, since we include at the most one interaction, we may consistently use the expression for v_4^I only to order ϵ , and, since $\eta \propto \epsilon^2$, we take $d_c = \frac{10}{3}$. Second, this approximation is the simplest possible; one cannot simplify further by considering class-1 diagrams only, since that would amount to working with a Hamiltonian with no even terms, which could have a first-order phase transition only.

We proceed now to the calculation of the diagrams in class 1. First, we compute those that appear in the calculation of η , that is, contribute to $\Sigma(k) - \Sigma(0)$. The contribution ought to be proportional to k^2 ln k , because

$$
G(k, r=0) = 1/k^{2-\eta}, \quad k^{-\eta} = 1 - \eta \ln k + \dots \qquad (4.8)
$$

These diagrams are those in Figs. 2(a) and 2(b). Let us first calculate diagram 2(a):

$$
\Sigma_{2(a)}(k) = 24(v_5^0)^2 \int d^d x \ e^{-i\vec{k} \cdot \vec{x}} G^4(x, 0) \,. \tag{4.9}
$$

As shown in Appendix A,

$$
G(x, 0) = A/x^{d-2}, A = \Gamma(\frac{1}{2}d - 1)/4\pi^{d/2}, \qquad (4.10)
$$

where Γ is the gamma function.

We can find $\Sigma(k) - \Sigma(0)$ by expanding the exponential in (4.9). The first term does not depend on k and the term we want is that proportional to k^2 . The angular integral is then equal to $\Omega_d/2d$

FIG. 2. Self-energy diagrams. (a), (b), (f), and (i): diagrams of order v_5^2 . (c): diagrams of order v_3^2 and v_5v_3 . (d): effective vertex \overline{v}_3 . (e): equivalent to (b)+(c). (g): result after removing worst divergence in (f). (h): compensating four-point vertex. (j): result after removing worst divergence in (i). (k): diagram with compensating field v_1 that cancels (j).

 $(\Omega_d$ is the area of a unit sphere in d dimensions), and we obtain

$$
\Sigma_{2(a)}(k,0) - \Sigma_{2(a)}(0,0) = 24(v_5^0)^2 A^4(\Omega_d/2d)k^2 \ln k \tag{4.11}
$$

We next turn our attention to diagram 2(b). The loops are a cutoff- dependent constant and the central part diverges as $k^{-2/3}$:

$$
\Sigma_{2(b)}(k,0) \propto k^{-2/3} \ . \tag{4.12}
$$

We can cancel this disagreeable divergence, however, by choosing a k -dependent three-point interaction $v_3(k_1, k_2, -k_1, -k_2)$ of a magnitude such that $v_3(0, 0, 0)$ just cancels the loop term in Fig. 2(d). This defines an effective three-point interaction $\overline{v}_3(k_i)$. We then no longer need consider diagrams with single loops attached to $v₅$ vertices. Furthermore, we can take the k dependence of v_3 to be anything we like; we choose

$$
\overline{v}_3 \propto k_1^{4/3} \tag{4.13}
$$

in agreement with the condition $\overline{v}_3(0) = 0$ and consistent with Eq. (3.3) for v_3 :

$$
\frac{4}{3}v_3 = k\frac{d}{dk}v_3 + \ldots
$$

Thus diagrams $2(b)$ and $2(c)$ sum up to $2(e)$,

$$
\Sigma_{2(e)}(k,0) - \Sigma_{2(e)}(0,0) \propto k^2 , \qquad (4.14)
$$

and hence do not contribute to η . There are no other k -dependent self-energy diagrams of class 1.

We next compute the contribution of the class-1 diagrams to $\Sigma(k=0, r) - \Sigma(0, 0)$. These contributions are needed to find the exponent γ , since one has

$$
r-\Sigma(0,r)+\Sigma(0,0)\propto r^{1/\gamma} \ . \qquad (4.15)
$$

First, the contribution from $\Sigma_{2(a)}$ is found by using the expression (see Appendix A)

$$
G(x, r) = (2^{1/3} A / x^{4/3}) (x \sqrt{r})^{2/3} K_{2/3}(\sqrt{r} x).
$$
 (4.16a)

That is,

 $G(x, r) = (A/x^{4/3})[1 - c(rx)^{4/3} + \frac{3}{4}rx^2 + \dots],$ (4.16b)

where c is some constant. From this expression we obtain a term in $r \ln r$:

$$
\Sigma_{2(a)}(0,\gamma) - \Sigma_{2(a)}(0,0) = -24(v_5^0)^2 A^4 \Omega_d \frac{3}{2} \gamma \ln \gamma .
$$
\n(4.17)

Diagram 2(b) makes a divergent contribution to Σ of the form

$$
\Sigma_{2(b)}(0,r) \propto c r^{-1/3} + c' r^{1/3}, \qquad (4.18)
$$

since the bubble diverges as r ^{-1/3} and the loops have the form $c_1 + c_2 r^{2/3}$. But just as we did for the corresponding contribution to $\Sigma(k, 0)$ [Eq. (4.12)], we can cancel this divergent term with a three-point interaction, since the $k \rightarrow 0$, $r \rightarrow 0$ limit of v_3 just cancels the constant part of the him of ν_3 just cancels the constant part of the loop gives and loop. The remaining $r^{2/3}$ part of the loop gives and $r^{2/3}$ dependence to \overline{v}_3 , so that the sum of all diagrams with the divergent bubble $[2(b), 2(c)]$ is Fig. 2(e), which is simply proportional to r . Thus it makes no contribution to γ .

The next diagram of $O(v_5^2)$ which contributes to Σ is Fig. 2(f). Since it has a single loop on the upper $v₅$ vertex, we know that its most divergent piece mill be canceled by a diagram with a threepoint vertex there, without a loop. The resulting contribution, Fig. $2(g)$, makes a contribution to $\Sigma(0, r) - \Sigma(0, 0)$ whose leading term is [by using the expression (4.16)] proportional to $r^{2/3}$. The *total* $r^{2/3}$ contribution [from 2(g) and 2(a)] may be canceled, however, by properly choosing v_4' , represented in Fig. 2(h) by a black square. At $r \rightarrow 0$, v_4 is constant.

The final $v_{\rm s}^2$ diagram which contributes to $\Sigma(r)$ is Fig. 2(i), which goes like $1/r$ from the single propagator line. We eIiminate the bottom loop and one of the top ones by adding the corresponding $v₃$ diagrams; this gives Fig. 2(j), whose leading divergent term is proportional to $r^{1/3}$. Finally, we eliminate this term by introducing an "external field" $v_1 \propto r^{2/3}$. Then Fig. 2(k) can be made to cancel Fig. 2(j) st this order, and the next most divergent term in Fig. 2(j) is of order r , which does not contribute to γ .

One can easily check that the new interactions we have introduced do not lead to any more terms proportional to r lnr or r^* ($x<1$). Thus the total contribution from class-1 diagrams to $\Sigma(0, r)$ $-\Sigma(0, 0)$ is given by Eq. (4.17).

We next consider the contribution of class-1 diagrams to Γ_5 . Within the limitations explained after Eq. (4.7) , the expression (4.5) may be rewritten as

$$
\Gamma_5 \propto 1 + \left(\frac{3}{4} - \frac{5}{4}\eta'\right) \epsilon' \ln r + \dots \tag{4.19}
$$

The first contribution to Γ_5 in the perturbation expansion is v_5 . For the term of order ϵ' , we need now to compute the $v_5^{\;3}$ diagrams which behave as lnr. The only diagrams to be considered are those in Figs. $3(a)$ and $3(b)$. Diagram $3(c)$ will be canceled (see below), so that its $r^{-1/3}$ divergence will not appear.

Diagram 3(a) is easily evaluated, since it is equal to

$$
\Gamma_{3(a)}^5 = -864(v_5^0)^3 \int \frac{d^4k}{(2\pi)^4} \Pi^2(k) G(k) , \qquad (4.20)
$$

where the polarization Π is defined in

re the polarization Π is defined in
\n
$$
\Pi(k) = \int \frac{d^d p}{(2\pi)^d} G(p+k)G(p).
$$
\n(4.21)

In Appendix A we show that, at $r = 0$,

$$
\Pi(k, 0) = B/k^{4-d}, \quad B = 3A^2 2^{2/3} \pi^{5/3}.
$$
 (4.22)

One then finds

then finds

$$
\Gamma_{3(a)}^{5} = -864(v_{5}^{0})^{3} \frac{27}{8} \frac{A^{4} \pi^{5/3}}{\Gamma(\frac{2}{3})} \ln r.
$$
 (4.23)

The calculation of the contribution of the $\ln r$ term from diagram 3(b) is easy, since it is proportional to the derivative with respect to r of the self-energy diagram 2(a). One obtains also from it a divergent term proportional to $r^{-1/3}$. This term and diagram 3(c) are canceled by diagram 3(d). This cancellation is clearly the same as that involved in the self-energy diagrams $2(a)$, $2(g)$, and $2(h)$. The $\ln r$ term from $3(b)$ is thus given by

$$
\Gamma_{3(b)}^{5} = +384(v_{5}^{0})^{3} \frac{9}{8} \frac{A^{4} \pi^{5/3}}{\Gamma(\frac{2}{3})} \ln r.
$$
 (4.24)

This completes the calculation of the diagrams in class 1. We proceed now with those in class 2.

FIG. 3. Class-1 diagrams for Γ_5 . (a) and (b) are logarithmically divergent; (d) compensates the $r^{-1/3}$ divergence in (c).

 ${\bf 18}$

FIG. 4. Relevant class-2 self-energy diagrams.

 (b)

As indicated above, it is not possible to compute them exactly. The approximation used is in the expression for the four-point vertex Γ_4 for which we have, from the ϵ expansion (see Appendix B),

$$
\Gamma_4(k_i) = u_0 k_1^{\epsilon/3} k_2^{\epsilon/3} k_3^{\epsilon/3}, \qquad (4.25)
$$

where

$$
u_0 = \frac{8}{9} \pi^2 \frac{2}{3},\tag{4.26}
$$

and k_1 , k_2 , and k_3 are the momentum transfers in the three channels Γ_4 has. In order to be able to do the angular integrals involved, we will in many cases approximate Γ_4 by changing the k dependence from one channel to another.

The diagrams that turn out to give net contributions to the relevant parts of Σ and Γ_5 (i.e., the k^2 lnk and $r \text{ ln } r$ terms in Σ and the $\text{ ln } r$ term in Γ_{ϵ}) are listed in Figs. 4 and 5, respectively. Their approximate calculation is described in Appendix C and their values and combinatorial factors are listed in Table I. Other diagrams whose divergences are canceled by compensating interactions

FIG. 5. Relevant class-2 Γ_5 diagrams.

[like $2(b)$ and $3(c)$ in class 1] are omitted, as the cancellations proceed in a way, that is a straightforward generalization of that of class 1. If we define the quantities P , P' , and Q as follows:

TABLE I. Values of diagrams.

Diagram	Approximation method	Value (logarithmic part)	Combinatorial coefficient
2(a)	exact	$P(r=0)$ or $P'(q=0)$	$24 = M$
3(a)	exact	(definition) 0	$864 = N$
3(b)	exact	$-Q'$ (definition)	384
4(a)	approximation 1	u_0BP or u_0BP'	18M
4(b)	approximation 1	u_0BP or u_0BP'	12M
5(a)	approximation 1	u_0BQ	6N
5(b)	exact	$0.128u_0Q$	6N
5(c)	approximation 1	u_0BQ	12N
5(d)	approximation 1	u_0BQ	12N
5(e)	approximation 2	$0.0394u_0Q$	12N
5(f)	approximation 2	$0.0394u_0Q$	12N
5(g)	approximation 1	$u_0 B Q$	24N
5(h)	approximation 1	u_0BQ	12N
5(i)	approximation 1	u_0BQ	12N
5(j)	approximation 1	u_0BQ	6N
5(k)	approximation 3	$0.081u_0Q$	48N
5(1)	approximation 1	$-u_0BQ'$	8N
5(m)	approximation 1	$-u_0BQ'$	4N
5(n)	approximation 1	$-u_0BQ'$	8N
5(0)	approximation 1	$-u_0BQ'$	8N/3
5(p)	approximation 2	$-0.0394u_0Q'$	8N
5(q)	exact	$-0.128u_0Q'$	4N
5(r)	approximation 1	$-u_0BQ'$	4N/3
5(s)	approximation 1	$-u_0 B Q'$	4N

$$
\Sigma_{2(a)}(k,0) - \Sigma_{2(a)}(0,0) = 24P(v_5^0)^2k^2 \ln k \,, \qquad (4.27)
$$

$$
\Sigma_{2(a)}(0,\tau) - \Sigma_{2(a)}(0,0) = 24P'(v_5^0)^2\tau \ln \tau, \qquad (4.28)
$$

$$
\Gamma_{3(a)}^{5}/\overline{v}_{5}^{0} = -864 Q(v_{5}^{0})^{2} \ln r , \qquad (4.29)
$$

we obtain for the sum of the contributions from class-1 and class-2 diagrams

$$
\Gamma^5 / \overline{v}_5^0 = 1 + 98.54 \times 864 Q(v_5^0)^2 \ln r, \qquad (4.30)
$$

$$
\Sigma(k, 0) - \Sigma(0, 0) = -13.22 \times 24 P(v_5^0)^2 k^2 \ln k, \qquad (4.31)
$$

$$
\Sigma(0,\boldsymbol{r}) - \Sigma(0,0) = + 13.22 \times 24 P' (v_5^0)^2 r \ln r \,. \tag{4.32}
$$

The correction to the Ising exponents of order ϵ' can now be found from the formulas (4.7), (4.8), and (4.15).

First, from Eqs. (4.30) and (4.19) we obtain

$$
(v_5^0)^2 = \frac{\frac{3}{4} - \frac{5}{4} \eta'}{98.54 \times 864} \epsilon' \ . \tag{4.33}
$$

Using (4.31) , (4.7) , and (4.33) , we obtain by using

$$
P/Q = \frac{4}{30}, \tag{4.34}
$$

which is easily obtained from Eqs. (4.11), (4.23), and (4.24),

$$
\eta' = 3.7 \times 10^{-4} \tag{4.35}
$$

At $\epsilon' = \frac{1}{3}$ this would give a correction to the Ising exponent

$$
\delta \eta = 1.2 \times 10^{-4} \tag{4.36}
$$

The correction $\delta\gamma$ to the exponent γ is obtained using (4.32) , (4.7) , and (4.15) . We use the result

$$
P'/Q = \frac{4}{3},\tag{4.37}
$$

and then we find that

$$
\delta \gamma = \gamma - \gamma_{\text{Ising}} = -3.7 \times 10^{-3} \epsilon' \,. \tag{4.38}
$$

At $\epsilon' = \frac{1}{3}$ (three dimensions),

 $\delta y = - 1.2 \times 10^{-3}$. (4.39)

The other exponents can be obtained from scaling relations.

V. FINAL REMARKS

These changes in critical exponents are very small indeed, about an order of magnitude smaller than current experimental imprecision. Thus they are not in conflict with the most recent relevant experiments, which found no measurable difference between fluid exponents and Ising-model calculations.⁷ The reason the changes turn out so small in this calculation is essentially a matter of combinatorial factors. For example, the expressions for γ' or η' involve the self-energy diagrams of Figs. $2(a)$ and 4 in the numerator and the vertex diagrams $3(a)$, $3(b)$, and 5 in the denominator, and

the combinatorial coefficients for the latter are much larger than those of the former [e.g., 2(a) has a factor of 24 and $3(a)$ a factor of 864]. Thus the ratios P/Q and P'/Q are very small numbers and, hence, so are the changes in exponents. (A similar effect occurs in the ordinary ϵ expansion; this helped make it work as well as it does when ϵ = 1.) Because of these dominant combinatorial effects, we do not think that the smallness of γ' and η' is very sensitive to the approximations we have made in evaluating the class-2 diagrams. Indeed, for the one class-2 diagram that can be evaluated exactly, the error introduced by our approximate procedures is a factor of order 2 . This would not be enough to effect the observability of the exponent corrections even if it occurred in every diagram.

The major approximation made in this work has been our taking v_4^I to order ϵ , which has allowed us to consider a limited number of diagrams only. Since $\epsilon > \frac{2}{3}$, in principle our approximation is quite questionable. However, it is well known that perturbation expansion in ϵ gives surprisingly satisfactory results for $\epsilon = 1$ (the usual case) or even ϵ = 2 with only one or two terms. It is our assumption that this holds also for the asymmetric case. Put another way, we have established to order ϵ the existence of a different fixed point with v_{5}^{*} = $O(\epsilon')$ below dimensionality d, in the liquid-gas system. Thus we can say (to order ϵ) that fluid critical points do belong in a new universality class, distinct from Ising magnets.

We have not addressed directly the question of the stability of the new fixed point within our perturbation calculation. However, our calculation could have been phrased in terms of a renormalization-group recursion relation of the form

 $v_5^{n+1} = b^{5-3d/2} [v_5^{(n)} + C v_5^{(n)}(1 - A v_4^*) \ln b]$ (5.1)

where **b** is the rescaling factor $(A - A/b)$, and C and AC are products of solid angle and combinatorial factors associated with the diagrams of Figs. 3 and 5, respectively. We find a fixed point, since $Av^*_{\alpha} > 1$. Its stability is manifest from the linearized recursion relation; the situation is completely analogous to that in the Wilson-Fisher problem.

Upon examining Eqs. (4.23) and (4.24) we observe that if we did not keep the class-2 contributions to Γ_5 , the net contribution to the coefficient of lnr in (4.19) would be negative, and $(v_5^0)^2$ would be negative. This would mean an imaginary v_5^0 , which is unphysical. Such a fixed point can not be reached via any sequence of renormalization-group transformations beginning from a real effective Hamiltonian. We think this result, which was obtained without any use of the quartic anharmonicity v_4 ,

reflects the fact that a theory without a v_4 is not stable because of the oddness of the v_5 . The class-2 terms in Γ_5 have the opposite net sign froni those of class ¹ (because they have an extra interaction vertex) and are large enough (at $\epsilon = \frac{2}{3}$, at least) to more than compensate for the class-1 ones and change the sign of $(v_5^0)^2$ in Eq. (4.33), making the new fixed point real.

Finally, it is tempting to speculate that while in three dimensions, the effects we have discussed are very small, they might be measurable in two. Our calculations are not relevant to such a system because many more interactions are relevant in two dimensions. [Terms up through v_{16} are relevant in the two-dimensional Ising model, for example, as can be inferred from Eq. (3.4).] The ϵ' expansion is meaningful only between $d = d_c$ and $d=3(1-\frac{1}{2}\eta)$, where v_6 becomes relevant. A twodimensional calculation would have to take a totally different approach. Experimental investigation is also called for.

APPENDIX A

We calculate $G(x, 0)$, $G(x, r)$, and $D(q)$. First $G(x, 0)$:

$$
G(x, 0) = \frac{1}{(2\pi)^d} \int d^d k \, e^{i\vec{k} \cdot \vec{x}} \frac{1}{k^2}
$$

=
$$
\frac{\Omega_{d-1}}{(2\pi)^d} \int_0^\Lambda dk \, k^{d-3} \int \sin^{d-2}\theta \, e^{ikx\cos\theta} d\theta,
$$
 (A1)

where Λ is some cutoff. The angular integral can be found in Ref. 8 (No. 3.387-2):

$$
\int \sin^{d-2}\theta \ e^{ikx\cos\theta} d\theta
$$

= $\pi \left(\frac{2}{kx}\right)^{d/2-1} \Gamma\left(\frac{d-1}{2}\right) J_{d/2-1}(kx), \quad (A2)$

where J is a Bessel function, Γ the gamma function. Then

$$
G(x) = \frac{1}{(2\pi)^d} \Omega_{d-1} \sqrt{\pi} 2^{d/2-1} \Gamma\left(\frac{d-1}{2}\right)
$$

$$
\times \int_0^{\Lambda} dy \, y^{d/2-2} J_{d/2-1}(y) . \tag{A3}
$$

The integral over y is given by (Ref. 9, Sec. V.14.1)

$$
I = \int_0^{\Delta x} dy y^{p-1} J_p(y)
$$

= $(2p-2) y J_p(y) S_{p-2,p-1}(y) - y J_{p-1}(y) S_{p-1,p}(y) \Big|_0^{\Delta x}$, (A4)

where S is a Lommel function. By judicious use of the asymptotic forms for J and S at $y \rightarrow 0$ and $y \rightarrow \infty$ one finds (Ref. 8, No. 8.576, and Ref. 9, Sec. $7.5.5)$

$$
I = 2^{d/2-2} \Gamma(\frac{1}{2}d - 1) [1 - F(\Lambda x)], \qquad (A5)
$$

where $F(y) \rightarrow 0$ as $y \rightarrow \infty$. This formula holds for $4 > d > 2$.

Using

$$
\Omega_d = 2\pi^{d/2} / \Gamma(\frac{1}{2}d) , \qquad (A6)
$$

we then have

$$
G(x, 0) = (A/x^{d-2})[1 - F(\Lambda x)],
$$
 (A7)

$$
A = (1/4\pi^{d/2})\Gamma(\frac{1}{2}d - 1), \qquad (A8)
$$

as quoted in the text.

 $G(x, r)$, on the other hand, can be found only in the limit $\Lambda \rightarrow \infty$. The integral over y [cf. (A3)] is then given by

$$
I(r) = \int_0^\infty dy \, \frac{y^{d/2}}{y^2 + r x^2} \, J_{d/2-1}(y) \,, \tag{A9}
$$

which can be seen to be equal to (Ref. 8, No. 6.566-2)

$$
I(\gamma) = (\chi \sqrt{\gamma})^{d-2} K_{d/2-1}(\chi \sqrt{\gamma}) \quad (2 < d < 5).
$$
 (A10)

 K is a hyperbolic Bessel function. From Eq. (A10), Eq. (4.16) in the text is easily obtained at $d = \frac{10}{3}$.

We finally give a brief account of the calculation of $\Pi(k, 0)$ using the techniques in this appendix. A complete discussion of $\Pi(k, r)$ is to be found in Ref. 10.

$$
\Pi(k) = \int G^2(x)e^{i\vec{k}\cdot\vec{x}} d^dx.
$$
 (A11)

Put $G(x) = A/x^{d-2}$. Then

$$
\Pi(k) = A^2 \Omega_{d-1} 2^{d/2-1} \Gamma \left(\frac{d-1}{2} \right) \sqrt{\pi} k^{d-4}
$$

$$
\times \int_{0}^{\infty} \frac{dy}{y^{3d/2-4}} J_{d/2-1}(y) . \tag{A12}
$$

Using now the expression (Ref. 9, Sec. 7.14.1)

$$
\int_0^\infty y^\mu J_\nu(y) dy
$$

= $(\mu + \nu - 1) y J_\nu(y) S_{\mu - 1, \nu - 1}(y) - y J_{\nu - 1}(y) S_{\mu\nu}(y) \Big|_0^\infty$,
(A3) (A13)

and, again, using the asymptotic properties of the Bessel and Lommel functions, we find that the 'integral over y in Eq. (A12) is $\frac{3}{2}$ at $d = \frac{10}{3}$, and we obtain Eq. (4.22).

APPENDIX B: Γ_4 FROM THE ϵ EXPANSION

Here we calculate the four-point vertex Γ_4 which occurs in the class-2 diagrams by the ordinary ϵ

$$
\Gamma_4(k_1k_2k_3) = u_0 \left(1 + \frac{3u_0}{8\pi^2} \ln k_1 + \frac{3u_0}{8\pi^2} \ln k_2 + \frac{3u_0}{8\pi^2} \ln k_3 + O(u^2) \right)
$$
 (B1)

where the k_i are the momenta in the three channels. The value of u_0 is dictated^{5,6} by the matching of the corresponding expansion for Γ_4 at all $k_i = 0$ and r finite to the form dictated by scaling:

$$
u_0 = \frac{8}{9} \pi^2 \epsilon \tag{B2}
$$

We exponentiate (B1) in the following fashion:

$$
\Gamma_4(k_1k_2k_3) = u_0[(1 + \frac{1}{3}\epsilon \ln k_1)(1 + \frac{1}{3}\epsilon \ln k_2)
$$

×(1 + $\frac{1}{3}\epsilon \ln k_3$) + O(ϵ^2)]
→ u₀k₁^{ε/3}k₂^{ε/3}k₃^{ε/3}. (B3)

APPENDIX C: CLASS-2 DIAGRAMS

In this section we describe the approximate calculation of the diagrams for Σ and $\Gamma_{\rm s}$ which contains a Γ_4 vertex. Because Γ_4 depends on the momenta in all three channels, we cannot evaluate these diagrams exactly in one ease. Accordingly, we approximate Γ_4 by changing its k_i dependence in a way that makes the diagram simply related to one of the class-1 diagrams that can be computed exactly, but which preserves the correct degree of homogeneity in Γ_4 . That is, we make replacements like

$$
\Gamma_4(k_1k_2k_3) = u_0k_1^{\epsilon/3} k_2^{\epsilon/3} k_3^{\epsilon/3} - u_0k_1^{\epsilon}.
$$
 (C1)

In a certain sense, this is till correct to $O(\epsilon)$, since

$$
k_1^{\epsilon/3} k_2^{\epsilon/3} k_3^{\epsilon/3} = k_1^{\epsilon} \left(\frac{k_2}{k_1}\right)^{\epsilon/3} \left(\frac{k_2}{k_1}\right)^{\epsilon/3}
$$

= $k_1^{\epsilon} \left(1 + \frac{1}{3} \epsilon \ln \frac{k_2 k_3}{k_1^2} + O(\epsilon^2)\right)$. (C2)

We call the replacement $(C1)$ approximation 1. In enables us to evaluate most of the diagrams in Fig. 4 and 5.

To see how it works, start with Fig. 4(a). It can be thought of as generated from Fig. $2(a)$ by tying any two of the internal G lines together with the four-point vertex. The part of the diagram involving these lines is

$$
\int_{k, k'} G(k)G(k+p)\Gamma_4(p, k-k', k+k'+q)G(k')G(k'+q).
$$
\n(C3)

If we use the full expression (4.25) for Γ , this integral is very difficult at $d = \frac{10}{3}$, and we do not know how to do it. If we use approximation 1 and let $\Gamma = u_0 p^{\epsilon}$ ($\epsilon = \frac{2}{3}$), however, it factors simply into separate integrals over k and k', giving $u_0\Pi^2$ (p)p^e. But we know (4.22), $\Pi(p) = B/p^e$, so this part of Fig. 4(a) is just $Bu_0\Pi(p)$. Consequently, diagram 4(a) is just a factor Bu_0 times diagram 2(a).

Approximation 1 works in exactly the same way on diagrams $4(b)$, $5(a)$, $5(c)$, $5(d)$, $5(g) - 5(o)$, $5(r)$, and 5(s). We have indicated by small arrows on the figures the channel into which we have moved all the k dependence of Γ_4 . That is, when the arrow appears between two lines of momenta $p₁(in)$ and $p_2(\text{out})$, we approximate Γ_4 by $u_0 | p_1 - p_2 |$ ^e. Notice that our approximation is a lower bound on the exact value of the diagrams $[cf. Eq. (C2)]$. Almost the same procedure works on diagrams 5(e), $5(f)$, and $5(p)$. Here, however, the channel to which we transfer all the k dependence is one with $k_i = 0$, so we do the calculation at finite r , using Γ we do the carculation at finite r, using $u_0 r^{e/2}$. The adjacent internal part of the diagram involved then looks like $-\frac{1}{2}\partial\Pi(p,r)/\partial r$ for some internal momentum p . Using Ma's expansion for II,¹⁰ we find that this derivative is proportional to $r^{-\epsilon/2}$, which cancels the $r^{\epsilon/2}$ in Γ , leaving just a constant times the class-1 diagram. We call this approximation 2. Again, this procedure gives a lower bound on the true value of the diagram, since we take $r \div 0$.

Figure 5(k) is the only troublesome one. The relevant part of it involves

$$
\int_{k, k'} G(k)G(k+q)G(k'-k)\Gamma(k, k-k', k')G(k')G(k'+q).
$$
\n(C4)

[The rest of it is just $\Pi(q)$, and the product of (C4) and $\Pi(q)$ is integrated over q.] We were not able to reduce it to a simple form by approximations ¹ or 2. However, approximation 3,

$$
\Gamma = u_0 |k' - k|^{2} k^{-2/3} k'^{2/3}, \qquad (C5)
$$

reduces (C4) to the product of two independent integrals of the form

$$
\int \frac{d^d k}{(2\pi)^d} \frac{1}{k^{8/3}(\bar{k} + \bar{q})^2},
$$
 (C6)

which with the change of variable $p = \overline{k}q$ becomes

$$
\frac{1}{q^{4/3}} \frac{\Omega_{7/3}}{(2\pi)^{10/3}} \int \frac{dp \, p^{-1/3} \sin^{4/3}\theta \, d\theta}{(p+1)^2} \,. \tag{C7}
$$

Thus the entire diagram is proportional to an integral over q of $\Pi(q)$ times $q^{-8/3}$, i.e., $q^{-10/3}$, which is logarithmically divergent just like the class-1 diagram 3(a). So the present diagram is just a constant times diagram 3(a), with the

constant determined by the value of the integral in $(C7)$. It can be evaluated with the help of formulas 3.252-12 and 3.631-3 of Ref. 8 as $\pi^2/\sqrt{3}$, so (combinatorial factors aside) diagram 5(k} is a factor

$$
u_0 \left(\frac{\Omega_{7/3}}{(2\pi)^{10/3}}\right)^2 \frac{\pi^4}{3B} = 0.081 u_0
$$
 (C8)

times diagram 3(a).

Finally, diagrams 5(b) and 5(q) can be evaluated exactly; they are just bubbles with zero external

- *Work supported by NSF Grant Nos. DMR 75-13343 and 76-21298, the Alfred P. Sloan Foundation, the Louis Block Fund, and the NSF-MRL program at the University of Chicago.
- ¹M. E. Fisher, Rev. Mod. Phys. 46, 597 (1974).
- $2J.$ Hubbard and P. Schofield, Phys. Lett. A $40, 245$ (1972) .
- 3 K. Wilson and J. Kogut, Phys. Rep. 12C, 75 (1974).
- 4 F. J. Wegner and A. Houghton, Phys. Rev. A 8, 401 (1973).

momenta and a Γ_4 at one end, attached (at the other end) to the class-1 diagrams 3(a) and 3(b). The extra part is just

$$
\int \frac{d^d k}{(2\pi)^d} \Gamma(0, k, -k) G^2(k)
$$

$$
= \frac{\Omega_{10/3} u_0 \gamma^{1/9}}{(2\pi)^{10/3}} \int \frac{dk \ k^{25/9}}{(\gamma + k^2)^2}
$$

$$
= \frac{u_0 \Omega_{10/3}}{(2\pi)^{10/3}} \times \frac{1}{2} \Gamma(\frac{17}{9}) \Gamma(\frac{1}{9}) = 0.128 u_0. \quad (C9)
$$

- $5K. G.$ Wilson, Phys. Rev. Lett. 28, 548 (1972). 6S. K. Ma, Modern Theory of Critical Phenomena (Benjamin, New York, 1976), Chap. 9.
- ${}^{7}R$. Hocken and M. R. Moldover, Phys. Rev. Lett. 37, 29 (1976).
- ⁸I. S. Gradshteyn and I. W. Ryzhik, Table of Integrals, Series and Products (Academic, New York, 1965).
- ⁹Bateman Manuscript Project, Higher Transcendental Functions (McGraw-Hill, New York, 1953), Vol. 2. ¹⁰S. K. Ma, Phys. Rev. A $\frac{7}{1}$, 2172 (1973).