

Hierarchical reference theory of fluids and the critical point

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We derive, for a classical fluid, a new and exact hierarchy of integro-differential equations for the free energy and direct correlation functions of successively higher order. This hierarchy gives the evolution of these quantities as the attractive part w of the interaction is turned on by the successive inclusion of the different Fourier components of w , starting from large momenta. The full hierarchy is also written as a unique functional differential equation for the free energy of a nonuniform fluid. This hierarchy is the basis of a unified theory of fluids. Near the critical point and at small momenta, our equations become equivalent to renormalization-group equations and we recover the usual ϵ expansion. A very simple approximation gives, in three dimensions, $\gamma = 2\nu \approx 1.38$. Suitable truncation of the hierarchy reproduces the correct low-density (virial coefficients) and high-density (optimized random-phase) limit.

I. INTRODUCTION

A microscopic theory of fluids in the region of the critical point of the liquid-vapor phase transition should yield both the universal and the nonuniversal quantities asymptotically close to the critical point, the extension of the critical region and the crossover to the distant behavior of the fluid, i.e., a low-density gas or a dense liquid. All these properties should be deducible from knowledge of the law of interatomic forces. Even if we consider only the cases of simple fluids and of static properties, as we do in this paper, this program is far from being accomplished. In fact, we have information only on the universal critical properties because the modern theory of critical phenomena¹ has so far found application to this system only after one of the following two approximations has been introduced. The first is a discretization of space so that the continuous variables, the positions of the particles, are replaced by discrete ones, the population variables of the cells of a lattice. The second assumes that an operation of coarse graining has been performed, leading to a phenomenological local free energy. When this is expanded in power series of the deviation of the local density with respect to its average value, a Landau-Ginzburg-Wilson (LGW) functional is obtained. A more general and formally exact expansion of the partition function of a fluid in cumulants has been used² as the starting point for application of renormalization-group (RG) techniques. This, however, has not been developed beyond the stage of a formal analysis. We notice also that recently³ a real-space RG approach has been attempted for fluids.

It is generally believed that neither of the two previous approximations modifies the universality class of the system, that of a system with a one-component order parameter like the Ising model. Even at the level of universal quantities this leaves two problems. First the LGW functional contains, in addition to the usual even terms, the odd ones² due to the absence of the particle-hole symmetry in real fluids. Only at the level of the ϵ expansion ($\epsilon = 4 - d$, where d is the spatial dimensionality), i.e.,

within perturbation theory, is it known that these odd terms give irrelevant contributions to the critical behavior.⁴ The role of these terms in a three-dimensional system is not known. Second, the correlation functions of a fluid have a very strong constraint at short distance due to the repulsive part of the interatomic interaction: All correlation functions essentially vanish over a finite domain at short distance corresponding to the overlap of the cores of the particles. Within the previous two approximations this condition is lost so that one is not able to control that this short-distance constraint is interfering in any way with the building up of the critical correlations. The good agreement⁵ between experimental results in certain fluid systems and the RG prediction based on the LGW functional suggests that the universality class of a fluid is indeed that of the Ising model, but one would like to prove this theoretically.

This situation explains why in recent years several of the theories of liquid state⁶ have been reconsidered with the purpose of clarifying the kind of critical behavior which they give, but none of them has been found acceptable. Within the integral equation approach for the radial distribution function (rdf) $g(r)$ it is now known that all the most popular integral equations fail badly near the critical point. The Born-Green equation in three dimensions does not have a real critical point with divergence, for instance, of the isothermal compressibility (K_T).⁷ The Percus-Yevick equation has classical (van der Waals-like) critical exponents but the scaling function is nonclassical and nonuniversal, giving a complete asymmetry between the liquid and the vapor side of the critical point.⁸ This is contrary to the observed behavior of fluids. It is not known if the hypernetted-chain equation has a real critical point, but numerical computations⁹ do not give a power-law behavior for K_T . The other approach to liquids, the perturbative one with respect to a reference fluid, does not fare better in this respect. For instance, the optimized random-phase approximation (ORPA) and the EXP approximation, both excellent theories of dense liquids, give a piecewise analytic free energy, and the critical exponents

are equal to those of the spherical model.¹⁰ For instance, the exponent γ for K_T is $\gamma=2$ in place of the experimental value $\gamma=1.2-1.25$ and of the classical value $\gamma=1$.

In this paper we develop a new theory¹¹ of fluids with the specific purpose of being able to give a full treatment of the critical region. The densities of the coexisting liquid and vapor phases take very rapidly, as we cool the system below the critical temperature T_c , values typical of a dense liquid and, respectively, of a low-density gas. This implies that any such theory must be a global theory of the fluid state: In addition to the critical region it must also give an accurate description of a low-density gas and of a liquid under triple-point conditions.

Our theory is based on two notions. The first is the notion of a reference fluid.⁶ Present-day liquid-state theory is not yet able to give a really accurate description of the properties of a very dense fluid starting from the interatomic potential alone, here assumed to have a pairwise form: $V = \frac{1}{2} \sum_{i \neq j} v(i, j)$. What the theory is able to do is to compute how the thermal and the correlation functions of a suitable reference fluid, typically the hard-sphere fluid, become modified when $v(r)$ takes its actual form. In this approach the properties of the reference fluid are assumed to be known quantities, for instance, from simulation. In a similar way we split the pair interaction

$$v(r) = v_R(r) + w(r) \quad (1)$$

into a reference part $v_R(r)$, which contains the strong repulsive part of $v(r)$, and a residual part $w(r)$. The attractive part of the forces is contained in $w(r)$ but for the present purpose we do not need to specify this separation more than to assume that $w(r)$ has a well-defined Fourier transform $\bar{w}(k)$. In addition, we assume that the properties of the reference fluid are known.

The second notion derives from the renormalization-group theory of critical phenomena: One constructs an infinite sequence of approximations to the properties of the system in such a way that there is a gradual turning on of fluctuations, starting from those of shorter wavelengths.¹ In RG theory this is accomplished either by partial integration over fluctuations of large wavelength or by block averaging. In an analogous way we build a sequence of approximations characterized by a parameter Q of dimension of a wave vector which spans the entire interval $0-\infty$. The effect of the Fourier components $\bar{w}(k)$ with $k < Q$ on density fluctuations is taken into account in the random-phase approximation (RPA),⁶ i.e., in the noninteracting approximation between components with different wave vectors. On the other hand, for $k \geq Q$ the full effect of $\bar{w}(k)$ is taken into account. When $Q = \infty$ we have the reference system with the added effects of $w(r)$ in RPA. When $Q = 0$ the full effect of $w(r)$ is recovered.

This program turns out to be equivalent to establishing the relation between the properties of the reference system and those of the fully interacting one, not in one step as it is usually done but through the intermediary of a sequence of systems characterized by the interaction

$$v_Q(r) = v_R(r) + w_Q(r), \quad (2)$$

where w_Q is given in k space by

$$\bar{w}_Q(k) = \int d^d r w_Q(r) e^{ik \cdot r} = \begin{cases} \bar{w}(k) & \text{for } k \geq Q \\ 0 & \text{for } k < Q. \end{cases} \quad (3)$$

In addition, for any value of Q , the remaining part of the interaction, $w(r) - w_Q(r)$, is taken into account in RPA. The idea of relating reference and fully interacting systems through the intermediary of a sequence of systems was proposed by one of us some time ago¹² but the sequence then proposed is not effective in controlling the turning on of critical fluctuations on separate length scales. On the contrary, we will show that the present scheme is successful in this, like the RG approach. However, unlike the RG approach, we do not proceed by partial integration over degrees of freedom but we give a description of the partially coupled system over all of its length scales. This permits us to keep track at every stage of the effects of the hard core part of $v(r)$.

Our approach, which we call a *hierarchical reference theory* of fluids, can be considered as a generalization of the reference theory of fluids. We do not have just one reference system, the one characterized by v_R , but a full sequence, each system with interaction v_Q being the reference system for the one with interaction v_{Q-dQ} where dQ is an infinitesimal increment. In this way we obtain a differential generator for the free energy A_Q and for the correlation functions of the Q system. This generator is exact. The use of RPA for part of the fluctuations is only a convenient intermediate step for the construction of the generator in order to avoid some discontinuities due to the sharp cutoff which we use.

The contents of the paper are as follows. The basic perturbative expansion is introduced in Sec. II and some mathematical details are contained in Appendix A. The hierarchy of equations for the evolution of the free energy and the correlation functions is obtained in Sec. III. This hierarchy in the critical region is discussed in the context of the ϵ expansion in Sec. IV and the region far from the critical point is treated in Sec. V. In Sec. VI we introduce a primitive model for which the hierarchy truncates at the first equation, and the resulting critical behavior is computed. Section VII contains a discussion of our theory. In Appendix B we write the evolution equation for the free energy in the form of a unique functional differential equation for a nonuniform system. By expanding this differential generator around the uniform state the full hierarchy is recovered. Specific aspects of the theory due to the presence of a hard core in the interatomic interaction and the extension of the method of "optimization" of the perturbation to our hierarchy have already been briefly treated¹¹ and a full discussion will be presented separately.

II. PERTURBATIVE EXPANSION

We consider a system of particles interacting through a spherically symmetric pair potential $v(r)$ which is divided into the sum of two terms as in (1) with $v_R(r)$ containing any singular contribution of $v(r)$. In preparation for the development of Sec. III, we set up a suitable perturbative expansion of the free energy in the power of the nonsingular part of the potential: $w(r) = v(r) - v_R(r)$. Similar pro-

grams have already been accomplished by many authors, especially in the context of the high-temperature expansion.⁶ For our purpose it has been useful to develop an expansion of the Helmholtz free energy A in the grand canonical ensemble (resembling that obtained by Stell in Ref. 13). We use the "hatted" direct correlation functions defined by

$$\hat{c}_n(1, \dots, n) = \frac{\delta^n(-\beta A)}{\delta\rho(1) \cdots \delta\rho(n)} \quad (\beta = 1/k_B T), \quad (4)$$

where $\rho(r)$ is the local density of the system considered as inhomogeneous. \hat{c}_n differs from the ordinary direct correlation function $c_n(1, \dots, n)$ by the ideal gas term. The explicit relation is¹³

$$\hat{c}_n(1, \dots, n) = c_n(1, \dots, n) + \frac{(-1)^{n-1}(n-2)!}{[\rho(1)]^{n-1}} \prod_{2 \leq S \leq n} \delta(1, S), \quad (5)$$

where $\delta(i, j)$ is the three-dimensional Dirac delta function of argument $\mathbf{r}_i - \mathbf{r}_j$. It is also useful to introduce a two-body correlation function $\hat{F}(1, 2)$ by means of the Ornstein-Zernike (OZ) relation

$$-\beta A = -\beta A^R - \frac{1}{2} \int d(1) \rho(1) \phi(1, 1) + \frac{1}{2} \int d(1) d(2) \rho(1) \rho(2) \phi(1, 2)$$

$$+ \frac{1}{2} \text{---}\overset{\frown}{\text{---}} + \frac{1}{4} \text{---}\square\text{---} + \frac{1}{4} \text{---}\text{---}\text{---}\text{---} + \frac{1}{8} \text{---}\text{---}\text{---}\text{---} + O(\phi^3), \quad (9)$$

where A^R is the free energy of the reference system. If the reference potential is the hard-sphere one

$$v_{\text{hs}}(r) = \begin{cases} +\infty, & r < \sigma \\ 0, & r > \sigma \end{cases} \quad (10)$$

we recover the usual high-temperature expansion.⁶

In the expansion (9) we can perform a simple resummation of an infinite number of diagrams. For instance, the diagrams which do not contain any hypervertex [that is, $\hat{c}_n(1, \dots, n)$ with $n > 2$] can be summed up giving the well-known RPA contribution to the free energy. For a homogeneous system this reads⁶

$$\frac{-\beta A_{\text{RPA}}}{V} = \frac{-\beta A^R}{V} - \frac{\rho}{2} \phi(0) + \frac{\rho^2}{2} \int d^d r \phi(r) - \frac{1}{2} \int \frac{d^d k}{(2\pi)^d} \ln[1 - \tilde{\phi}(k) \check{F}^R(k)], \quad (11)$$

where V is the volume of the system,

$$\tilde{\phi}(k) = \int d^d r e^{ik \cdot r} \phi(r), \quad (12)$$

and we have introduced the convention of reversing "hats" when the Fourier transform is performed on \hat{F} or, more in general, on \hat{c}_n . In the remaining diagrams a similar resummation over the chains of ϕ and \check{F}^R bonds can be performed and in this way $\tilde{\phi}(k)$ is eliminated in favor of the renormalized potential

$$\int d(3) \hat{F}(1, 3) \hat{c}_2(3, 2) = -\delta(1, 2). \quad (6)$$

From Eqs. (5) and (6) it is easy to obtain the expression of $\hat{F}(1, 2)$ in terms of usual quantities:

$$\hat{F}(1, 2) = \rho(1) \rho(2) h(1, 2) + \rho(1) \delta(1, 2), \quad (7)$$

$$h(1, 2) = g(1, 2) - 1,$$

where $g(1, 2)$ is the radial distribution function.

The perturbative expansion of the free energy $A[\rho(r)]$ can be expressed in terms of the reference correlation functions $\hat{F}^R(1, 2)$ and $\hat{c}_n^R(1, \dots, n)$. Letting

$$\begin{aligned} \text{---}\triangle\text{---} &= \hat{c}_3^R(1, 2, 3), & \text{---}\square\text{---} &= \hat{c}_4^R(1, 2, 3, 4), \\ \text{---}\text{---} &= \hat{F}^R(1, 2), & \text{---}\text{---}\text{---} &= \phi(1, 2) = -\beta w(1, 2), \end{aligned} \quad (8)$$

$$\text{---}\text{---}\text{---} = \hat{F}^R(1, 2), \quad \text{---}\text{---}\text{---} = \phi(1, 2) = -\beta w(1, 2),$$

we can list the first few diagrams in this expansion with their symmetry numbers (for details see Appendix A):

$$\tilde{\varphi}(k) = \frac{\tilde{\phi}(k)}{1 - \check{F}^R(k) \tilde{\phi}(k)}. \quad (13)$$

Letting

$$\text{---}\text{---}\text{---} = (2\pi)^{-d} \int d^d k [\check{F}^R(k)]^2 \times \tilde{\varphi}(k) e^{-ik \cdot (\mathbf{r}_1 - \mathbf{r}_2)} \quad (14)$$

the expression (9) becomes (see Appendix A)

$$-\beta(A - A_{\text{RPA}}) = \frac{1}{4} \text{---}\text{---}\text{---} + \frac{1}{8} \text{---}\text{---}\text{---} + O(\varphi^3). \quad (15)$$

The perturbative expansion (15) ordered in powers of the renormalized potential $\tilde{\varphi}(k)$ gives rise to the γ ordering introduced by Lebowitz *et al.*¹⁴ when $w(r)$ has the form $w(r) = \gamma^d f(r\gamma)$.

Before concluding this section it is important to point out that from the expansion for the free energy (9) written in the general case of a nonhomogeneous system we can obtain analogous expansions for the direct correlation functions by subsequent functional differentiations as given by (4). In order to perform the differentiation explicitly we note that

$$\frac{\delta \hat{c}_j^R(1, \dots, j)}{\delta \rho(j+1)} = \hat{c}_{j+1}^R(1, \dots, j, j+1), \quad (16)$$

$$\frac{\delta \hat{F}^R(1,2)}{\delta \rho(3)} = \text{Diagram: A triangle with vertices 1, 2, 3. Vertex 1 is on the left, 2 on the right, and 3 at the top. Lines connect 1-2, 1-3, and 2-3.} \quad (17)$$

For example, the first few terms of the expansion of the two-particle direct correlation function read

$$\hat{c}(1,2) = \hat{c}^R(1,2) + \text{Diagram: A horizontal line with open circles at 1 and 2, and a dashed line above it.} + \frac{1}{2} \text{Diagram: A square with vertices 1, 2, 3, 4. Vertices 1 and 2 are at the bottom, 3 and 4 at the top. Solid lines connect 1-2, 1-3, 2-4, 3-4. Dashed lines connect 1-4 and 2-3.} + O(\phi^2) \quad (18)$$

or, in terms of the renormalized potential $\tilde{\varphi}(k)$,

$$\hat{c}(1,2) - \hat{c}_{\text{RPA}}(1,2) = \frac{1}{2} \text{Diagram: A square with vertices 1, 2, 3, 4. Vertices 1 and 2 are at the bottom, 3 and 4 at the top. Solid lines connect 1-2, 1-3, 2-4, 3-4. A wavy line connects 3 and 4.} + \text{Diagram: A triangle with vertices 1, 2, 3. Vertex 1 is on the left, 2 on the right, and 3 at the top. Solid lines connect 1-2, 1-3, 2-3. A wavy line connects 1 and 2.} + O(\tilde{\varphi}^2), \quad (19)$$

where

$$\hat{c}_{\text{RPA}}(1,2) = \hat{c}^R(1,2) + \phi(1,2). \quad (20)$$

Here, as usual, a black dot represents an integrated coordinate and an open dot a root print.

III. THE BASIC HIERARCHY

The perturbative expansions just obtained [(18), (19)] are not suitable for direct analysis of correlations in the critical region. For example, it is known that both a high-temperature expansion and γ ordering to lowest order give a classical description of critical phenomena. The failure of perturbative approaches at the critical point arises from their poor accuracy in the treatment of density fluctuations. In fact, the region of long-range correlations is characterized by a strong coupling between fluctuations of different wavelengths, and a realistic theory of critical phenomena must take into account this coupling. Using a suggestion from the renormalization-group approach we can achieve this goal by means of a gradual introduction of correlations over different scales of length: We define a sequence of approximations to the free energy (A_Q) and correlation functions $\check{c}_n^Q(\mathbf{k}_1, \dots, \mathbf{k}_n)$, $n \geq 2$, characterized by a Q vector ($0 \leq Q \leq \infty$) such that the effect of coupled density fluctuations is taken into account only over the momentum range $k \geq Q$. We can accomplish this by truncating the integration range in each term of the expansions [(15), (19)] whenever a $\tilde{\varphi}(k)$ bond appears. We can give a physical interpretation to this operation. A_Q and \check{c}_n^Q are the quantities relative not to the actual attractive interaction $\phi(k)$ but to a "truncated" one $\phi_Q(k)$ coinciding with $\phi(k)$ only for short wavelengths:

$$\tilde{\phi}_Q(k) = -\beta \tilde{w}_Q(k) = \begin{cases} \tilde{\phi}(k) & \text{for } k \geq Q \\ 0 & \text{for } k < Q. \end{cases} \quad (21)$$

Notice that this cutoff at Q is present only in the interaction: $\check{c}_n^Q(\mathbf{k}_1, \dots, \mathbf{k}_n)$ are defined over the full range of k . The essential effect of the truncation (21) is that of depressing the density fluctuations with $k < Q$.

Now it is possible to analyze the effect of an infinitesimal variation δQ of the parameter Q expressing the properties of the system interacting through $w_{Q-\delta Q}$ in terms of the correlation functions of the system with potential w_Q . We use the expansions [(15), (19)] with a reference potential given by $v_Q(r)$, Eq. (12), and a perturbation $\delta w_Q(r)$ defined by

$$-\beta \delta \tilde{w}_Q(k) = \delta \tilde{\phi}_Q(k) = \tilde{\phi}_{Q-\delta Q}(k) - \tilde{\phi}_Q(k) = \begin{cases} \tilde{\phi}(k) & \text{for } Q - \delta Q \leq k < Q \\ 0, & \text{elsewhere.} \end{cases} \quad (22)$$

Taking into account that $\delta \tilde{\phi}_Q(k)$ is a nonzero function only over an infinitesimal domain, we note that the variation of the free energy and correlation functions linear in δQ derives from graphs with only one $\tilde{\varphi}$ bond [Eq. (13)]. For correlation functions this is true only if these are evaluated for nonzero external momenta. In the limit $\delta Q \rightarrow 0$ we get a set of differential equations for the "evolution" of the free energy and correlation functions corresponding to an infinitesimal change of the parameter Q .

If we proceed in this way, however, the terms linear in $\tilde{\phi}_Q$ in the expansions of A_Q and \check{c}_n^Q give rise to singular contributions in the differential equations because of the discontinuity of $\tilde{\phi}_Q(k)$ at $k=Q$. In order to work with more regular quantities we define two new functions \mathcal{A}_Q and $\check{\mathcal{C}}_Q(k)$ which are free from this singularity and are related to A_Q and $\check{c}_n^Q(k)$ by

$$\mathcal{A}_Q = -\beta A_Q - \frac{\rho V}{2} [\phi(0) - \phi_Q(0)] + \frac{\rho^2 V}{2} \int d^d r [\phi(r) - \phi_Q(r)], \quad (23)$$

$$\check{\mathcal{C}}_Q(k) = \check{c}_2^Q(k) + \tilde{\phi}(k) - \tilde{\phi}_Q(k). \quad (24)$$

It is also possible to give a physical interpretation to this new function $\check{\mathcal{C}}_Q(k)$. $\check{\mathcal{C}}_Q(k)$ differs from $\check{c}_2^Q(k)$ only for $0 \leq k < Q$ precisely by the quantity $\tilde{\phi}(k)$ which is the RPA contribution of the attractive interaction to the direct correlation function. Therefore, $\check{\mathcal{C}}_Q(k)$ is the direct correlation function for the full $w(r)$ in an approximation in which the effects of $\tilde{w}(k)$ for $k < Q$ are taken into account in RPA, whereas for $k \geq Q$ $\tilde{w}(k)$ is fully taken into account. Clearly, when $Q \rightarrow 0$ both \mathcal{A}_Q and $\check{\mathcal{C}}_Q(k)$ become the free energy and the direct correlation function of the fully interacting system.

The construction of the evolution equations starting from (15) and (19) and from similar equations for the higher order \check{c}_n^Q is rather straightforward (see Appendix B). It is more convenient to write these equations in Fourier space, and the first four read

$$-\frac{d\mathcal{A}_Q}{dQ} = \frac{V}{2} \int_{|r|=Q} \frac{d\Omega_p}{(2\pi)^d} \ln[1 + \check{\mathcal{F}}_Q(p)\check{\phi}(p)], \quad (25)$$

$$-\frac{d\check{\mathcal{C}}_Q(k)}{dQ} = \frac{1}{2} \left[\text{Diagram 1} + \text{Diagram 2} \right], \quad (26)$$

$$-\frac{d\check{\mathcal{C}}_3^Q(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3)}{dQ} = \text{Diagram 1} + 2 \text{ PERMS} + \text{Diagram 2} + 2 \text{ PERMS} + \frac{1}{2} \text{Diagram 3}, \quad (27)$$

$$\begin{aligned} -\frac{d\check{\mathcal{C}}_4^Q(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_4)}{dQ} = & \text{Diagram 1} + 2 \text{ PERMS} + \text{Diagram 2} + 11 \text{ PERMS} \\ & + \text{Diagram 3} + 5 \text{ PERMS} \\ & + \text{Diagram 4} + 11 \text{ PERMS} + \text{Diagram 5} + 3 \text{ PERMS} + \frac{1}{2} \text{Diagram 6}. \end{aligned} \quad (28)$$

where "permutations" indicates the nonequivalent graphs obtained by permutations of the momentum labels. Higher-order direct correlation functions satisfy similar equations. Here we have defined

$$\check{\mathcal{F}}_Q(k) = -[\check{\mathcal{C}}_Q(k)]^{-1}, \quad (29)$$

$$\text{Diagram 1} = \frac{[\check{\mathcal{F}}_Q(k)]^2 \check{\phi}(k)}{1 + \check{\mathcal{F}}_Q(k)\check{\phi}(k)}, \quad (30)$$

$$\text{Diagram 2} = \check{F}_Q(k) = \begin{cases} \check{\mathcal{F}}_Q(k) & \text{for } k \geq Q \\ \frac{\check{\mathcal{F}}_Q(k)}{1 + \check{\mathcal{F}}_Q(k)\check{\phi}(k)} & \text{for } k < Q, \end{cases} \quad (31)$$

$$\text{Diagram 3} = \check{\mathcal{C}}_3^Q(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3), \quad (32)$$

$$\text{Diagram 4} = \check{\mathcal{C}}_4^Q(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_4), \quad (33)$$

and an n -sided polygon stands for $\check{\mathcal{C}}_n^Q$. Every integration over a wavy bond is limited to the surface of the sphere $p=Q$. Conservation of momentum is understood for the wave vectors relative to each correlation function.

Equations (26)–(28) are meaningful only when every straight bond carries a momentum different from the one of the wavy bond. This implies that the external momenta are nonzero but the value at zero momentum can be obtained by taking the limit $k \rightarrow 0$. One can also explicitly derive the equations for these zero momentum components, for instance, $d\check{\mathcal{C}}_Q(0)/dQ$, and the result coincides with that given by the limiting procedure.

It is important to stress that Eqs. (25) and (28) are exact. We have chosen to show the evolution equations for \mathcal{A}_Q and $\check{\mathcal{C}}_Q(k)$ (and not those for A_Q and \check{c}_2^Q) because these modified functions have no discontinuity in correspondence to Q and they approach the physical quantities $A_{Q=0}$ and $\check{c}_2^{Q=0}$, when Q tends to zero, in a smooth way. So the introduction of the RPA contribution in (23) and (24) is only an intermediate step which does not affect the final results.

The free energy \mathcal{A}_Q is expressed in terms of the direct correlation function at the level Q , and in general the equation for $\check{\mathcal{C}}_m^Q$ contains the unknown quantities $\check{\mathcal{C}}_{m+1}^Q$ and $\check{\mathcal{C}}_{m+2}^Q$. Therefore, Eqs. (25)–(28) are the first ones of an infinite hierarchy of equations. In order to obtain useful expressions it is necessary to close this hierarchy by introducing some suitable approximation relating $\check{\mathcal{C}}_{m+1}^Q$ and $\check{\mathcal{C}}_{m+2}^Q$ to $\check{\mathcal{C}}_m^Q$ at some finite value of m . Examples of this kind of closure will be discussed later. The full hierarchy (25)–(28) can be written also in a compact form as a single functional differential equation for the free energy $\mathcal{A}_Q[\rho(r)]$ for a nonuniform system. This equation is derived in Appendix B.

An interesting feature of this hierarchy is that the dependence on the specific form of the repulsive interaction is confined in the boundary conditions which must be

imposed on Eqs. (25)–(28). In fact, the limiting values of the direct correlation functions for $Q \rightarrow \infty$ must coincide with the reference correlation functions. For the two-point function (24) this limit corresponds to the reference correlation function modified by the RPA contribution due to the attractive part of the interaction. When the repulsive part of the interaction v_R contains a hard core part (10), it is well known that RPA is not uniquely defined.¹⁵ In this case, in fact, the exact partition function does not depend on the values of $w(r)$ for $r < \sigma$ so that $w(r)$ can be chosen arbitrarily in this range. On the contrary, when an approximation like RPA is used, the result depends on the values of $w(r)$ for $r < \sigma$ also because the corresponding $g(r)$ does not vanish for $r < \sigma$. Exploiting this arbitrariness, RPA can also be made accurate for systems with a hard core by using the RPA relation (20) only for $r > \sigma$, whereas $w(r)$ for $r < \sigma$ is chosen so that $g(r) = 0$ for $r < \sigma$. This constitutes the so-called optimized random-phase approximation¹⁵ which is also equivalent to the self-consistent lowest-order γ approximation.¹⁶ Due to the physical interpretation of \mathcal{C}_Q we can similarly use as the boundary condition at $Q = \infty$ ORPA in place of RPA. In this case $\phi(r) = -\beta w(r)$ represents this “optimized” potential in place of the bare one. In the following we will speak generically of RPA as a boundary condition at $Q = \infty$ but it must be noted that in the presence of a hard core this really is ORPA.

It is known that a fluid in RPA has a critical point where the isothermal compressibility diverges. This fact apparently generates a singularity in the boundary conditions of our problem. In fact, for a given density there is a temperature where the function \mathcal{F}_∞ has a pole at $k = 0$ and it would seem that in this region our equations lose their meaning. However, the danger comes only from the wavy bond lines (a straight bond merely reproduces the reference structure factor as $Q \rightarrow \infty$) and these are evaluated only on the momentum shell $k = Q$, i.e., at large wave vectors where $\mathcal{F}_Q(k)$ is regular. As Q becomes smaller during the integration procedure it is $\mathcal{F}_Q(k)$ which appears, and the RPA singularity will presumably move toward the line of physical singularities, i.e., the true spinodal line.

Finally, it is worth pointing out that the same arguments which led us to write down the hierarchy [(25)–(28)] can be restated for other Hamiltonians. For example, the lattice-gas model can be treated in the same way and the structure of the set of differential equations remains unaltered with the obvious change in the range of integration in momentum space which is restricted to the first Brillouin zone. As a consequence, the parameter Q now labels a one-parameter family of surfaces which spans the whole allowed range of variation of the momenta, and the angular integrations appearing in (25)–(28) become integrations over the surface labeled by Q . Using the lattice-gas-Ising model isomorphism our hierarchy can be easily written down also for a spin system.

IV. THE HIERARCHY IN THE CRITICAL REGION AND THE ϵ EXPANSION

We analyze now the hierarchy of differential equations (25)–(28) near the critical point assuming that the pair interaction is a short-range function. This region of the phase diagram is characterized by the presence of long-range correlations and, as a consequence, by the growing of the structure factor at long wavelength: $S(k) = \rho^{-1} \check{\mathcal{F}}_{Q=0}(k) \gg 1$ for $k \rightarrow 0$. Due to the physical meaning of $\check{\mathcal{F}}_Q(k)$ it is reasonable to assume that this function in the limit $Q \rightarrow 0$ approaches smoothly $\check{\mathcal{F}}_{Q=0}(k)$ so that

$$\rho^{-1} \check{\mathcal{F}}_Q(k) \gg 1 \quad (34)$$

in a neighborhood of $k = 0$ and $Q = 0$. In this region, then, we can simplify the integrands in our hierarchy dropping the term unity with respect to $\phi(k) \check{\mathcal{F}}_Q(k)$ in the denominator of (30) because the wavy bond is always evaluated on the momentum shell $k = Q$. Similarly, we can neglect $\check{F}^Q(k)$ for $k < Q$ because from (31) it follows that $\check{F}^Q(k)$ in this region is a finite quantity so that the contribution coming from the integration over $k < Q$ is negligible in comparison with the contribution from the range $k \geq Q$. Therefore, in the critical region and for small values of k and of the parameter Q the expressions of the bonds appearing in the diagrams (26)–(28) can be approximated by

$$\begin{array}{c} k \\ \text{wavy bond} \end{array} \rightarrow \check{\mathcal{F}}_Q(k), \quad \begin{array}{c} k \\ \text{straight bond} \end{array} \rightarrow \begin{cases} \check{\mathcal{F}}_Q(k) & \text{for } k \geq Q \\ 0 & \text{for } k < Q \end{cases} \quad (35)$$

Now we can rewrite the hierarchy so simplified in a more elegant way by eliminating the explicit appearance of the parameter Q . Assuming that an exponent η exists such that at the critical point the quantity

$$\lim_{Q \rightarrow 0} Q^{-2+\eta} [\check{\mathcal{C}}_Q(xQ) - \check{\mathcal{C}}_Q(0)] \quad (36)$$

has a finite and nonzero limit [this implies that $S(k) \sim k^{-2+\eta}$ at the critical point], we define the functions

$$u_{\frac{1}{2}}^Q(x) = -Q^{-(2-\eta)} \check{\mathcal{C}}_Q(xQ), \quad (37)$$

$$u_m^Q(\mathbf{x}_1, \dots, \mathbf{x}_m) = -Q^{m(d-2+\eta)/2-d} \check{\mathcal{C}}_m^Q(\mathbf{x}_1Q, \dots, \mathbf{x}_mQ)$$

$$\left[\text{with } \sum_{i=1}^m \mathbf{x}_i = \mathbf{0} \right]. \quad (38)$$

Then Eqs. (25)–(28) with the approximation (35) can be written in the following suggestive graphical form:

$$\mathcal{D}_2 u_{\frac{1}{2}}^Q(x) = \frac{1}{2} \begin{array}{c} y \\ \text{wavy bond} \\ x \quad x \end{array} - \begin{array}{c} y \\ \text{straight bond} \\ x \quad x \end{array} \quad (39)$$

$$\mathcal{D}_3 u_3^Q(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) = \left[\text{Diagram 1} + 2 \text{ PERMS} \right] - \left[\text{Diagram 2} + 2 \text{ PERMS} \right] + \frac{1}{2} \left[\text{Diagram 3} \right], \quad (40)$$

$$\mathcal{D}_4 u_4(\mathbf{x}_1, \dots, \mathbf{x}_4) = - \left[\text{Diagram 4} + 2 \text{ PERMS} \right] - \left[\text{Diagram 5} + 11 \text{ PERMS} \right] + \left[\text{Diagram 6} + 11 \text{ PERMS} \right] \\ + \left[\text{Diagram 7} + 5 \text{ PERMS} \right] - \left[\text{Diagram 8} + 3 \text{ PERMS} \right] + \frac{1}{2} \left[\text{Diagram 9} \right], \quad (41)$$

$$\mathcal{D}_n = \frac{-\partial}{\partial \ln Q} + \sum_{i=1}^n \mathbf{x}_i \cdot \nabla_i + \frac{n}{2}(d-2+\eta) - d. \quad (42)$$

Here a line corresponds to $1/u_2^Q(x)$ and a vertex of order n represents $u_n^Q(\mathbf{x}_1, \dots, \mathbf{x}_n)$; in each graph the integration over the variable y is limited to the surface $y=1$ and the arguments of the remaining internal lines must be greater or equal to 1. This *on* and *above* shell restriction is a consequence of (35).

This approximate hierarchy is suitable for an analysis of the critical behavior. Before performing this, however, it is important to notice that the full approximate hierarchy can be written as a unique functional differential equation for the free energy of a nonuniform system in a way which is similar to the case of the exact hierarchy. The details of the derivation are reported in Appendix B. Here we only observe that the differential generator that we obtain for the approximate hierarchy coincides with the one derived by Nicoll and Chang¹⁷ in the context of the RG. Due to this equivalence it can be expected that the critical behavior given by our approach coincides with that given by the RG approach to the LGW functional. This is not necessarily true because the hierarchy [(39)–(41)] is an approximation to the exact one [(26)–(28)] valid only in the critical region and as $Q \rightarrow 0$ and $k \rightarrow 0$ (where k represents collectively the arguments of the correlation functions). However, the boundary conditions for the correlation functions have to be imposed at $Q \rightarrow \infty$ and this is out of the range of validity of the approximate hierarchy. Therefore, even at the critical point we should integrate the full set [(25)–(28)] from $Q = \infty$ to 0 and this is not equivalent to the RG equations. On the other hand, the solution of the exact hierarchy must also be a solution, in the small-momentum regime, of the approximate one so that the determination of the critical behavior can be split in two parts. First, one determines the possible solutions of the approximate hierarchy with some fictitious arbitrary boundary conditions at small but finite momenta. In a second stage one must study the compatibility of this solution by substituting this fictitious boundary condition with the correct one obtained by integrating the exact hierarchy. In this paper we shall consider explicitly only the first part of the problem. If the critical point of a fluid is in the same universality class of Ising-like Hamiltonians as indicated by experi-

ments, this is enough for the determination of universal quantities.

A very simple behavior of this approximate hierarchy is obtained if the scaled functions u_n^Q have a finite limit as $Q \rightarrow 0$, i.e., the equations have a fixed point. This kind of behavior is appropriate for a critical point, and in fact from the definition (37) we know that the isothermal compressibility K_T [proportional to the value of $\mathcal{F}^{Q=0}(0)$] is proportional to $\lim_{Q \rightarrow 0} Q^{-(2-\eta)}/u_2^Q(x=0)$. If u_2^Q goes to a finite limit as $Q \rightarrow 0$ the isothermal compressibility of the actual system ($Q=0$) diverges, thus indicating the presence of a continuous phase transition. Thus we are led to the search of the possible fixed points of the hierarchy (39)–(41) and to the analysis of the equations in a neighborhood of these fixed points. This is the same problem posed in the context of the RG; moreover, due to the previously discussed equivalence of our approximate hierarchy with the differential generator of Nicoll and Chang, we obtain the same results given by RG analysis. We have verified this by an explicit computation starting from (39)–(41). Since the computation follows the standard pattern of RG theory we only discuss the relevant results.

The dimensionality of the system plays a crucial role. As a first step let us consider a system such as the Ising model in zero magnetic field (lattice gas at $\rho = \rho_c = \frac{1}{2}$) that has an internal symmetry such that the odd correlation functions vanish on the critical isocore. If the dimensionality d is larger than 4 only one fixed point exists (the so-called Gaussian one: $u_n^* = 0, n \geq 4$) which is stable and gives rise to mean-field critical exponents. When d is lower than 4 this Gaussian fixed point becomes unstable and a new one appears; this is characterized by nontrivial fixed point functions u_n^* . Following the RG it is possible to expand u_n^* in powers of $\epsilon = 4-d$: At first order in this parameter it turns out that the hierarchy truncates at the level of the equation for u_4^* because u_n^* with $n > 4$ are of higher order in ϵ and so we can find the fixed point functions at order ϵ . The analysis of the behavior of the scaled correlation functions near this fixed point yields¹ the well-known expressions for the critical exponents together with the validity of scaling laws; an analysis of the equa-

tions for u_2^Q and u_4^Q gives also the leading contribution to the exponent η which is of order ϵ^2 . Thus we find

$$\begin{aligned} \gamma &= 1 + \frac{\epsilon}{6} + O(\epsilon^2), \quad \nu = \frac{1}{2} + \frac{\epsilon}{12} + O(\epsilon^2), \\ \eta &= \frac{\epsilon^2}{54} + O(\epsilon^3), \end{aligned} \quad (43)$$

where γ is the exponent for K_T on the critical isocore and ν is that for the correlation length. Invoking the equivalence of our equations with the Nicoll-Chang differential generator for the RG, we can extend these results to every order in ϵ .

The case of a fluid is more complex because the correlation functions of odd order do not vanish. The LGW functional with the terms of odd order included has been analyzed in the context of RG with the ϵ expansion. It has been found that these odd terms are irrelevant at the critical point⁴ and that the value of the critical exponents remains unchanged at least to order ϵ^3 . Again due to the equivalence with the Nicoll-Chang generator the same result is true for our hierarchy, and we conclude that in the framework of the ϵ expansion our approximate equations support the existence of only one stable fixed point, the Ising one. However, in order to conclude that a hypothetical fluid in $d=4-\epsilon$ dimensions has the same critical behavior of the Ising model, one should prove that the evolution of the correlation functions as determined by the exact equations [(25)–(28)] is such that in the small-momentum regime these fall into the domain of attraction of the fixed point given by the ϵ expansion. The extension of this domain is not known within RG theories but there is no evidence for the presence of other (nonperturbative) fixed points.¹ Therefore, it is reasonable to expect that a fluid is in the same universality class of the Ising model, but really convincing evidence must be based on an explicit treatment of the exact hierarchy under some suitable closure. This aspect will be discussed elsewhere.

V. AWAY FROM THE CRITICAL POINT

So far we have shown that our hierarchy of Eqs. (25)–(28) is particularly suitable for a theoretical description of critical phenomena. Now it is important to realize that in a natural way the same set of equations gives rise to the correct virial expansion and to an accurate description of a dense fluid so that our theory can be the basis of an accurate and global description of the fluid state.

At first we note that the behavior of the direct correlation functions at low density is dominated by the ideal gas contribution [see Eq. (5)] and that the c_n term is an analytical function of density in a neighborhood of $\rho=0$. The same is also true for the Q system so that in the expression

$$\check{c}_n^Q(\mathbf{k}_1, \dots, \mathbf{k}_n) = (-1)^{n-1} \frac{(n-2)!}{\rho^{n-1}} + c_n^Q(\mathbf{k}_1, \dots, \mathbf{k}_n) \quad (44)$$

$c_n^Q(1, \dots, n)$ is a regular function at $\rho=0$. Therefore, in order to obtain the leading low-density behavior of the two-particle correlation function we approximate in Eq. (26) \check{c}_2^Q and \check{c}_4^Q by their low-density limit: $\check{c}_2^Q \approx \rho^{-2}$ and

$\check{c}_4^Q \approx -2\rho^{-3}$. Then Eq. (26) is a closed equation for \check{c}_Q^Q which can be solved, and it gives the expression

$$\begin{aligned} c(r) &= \lim_{Q \rightarrow 0} [\check{c}_Q^Q(r) + \rho^{-1} \delta(r)] \\ &= e^{-\beta[v_R(r) + w(r)]} - 1 + O(\rho). \end{aligned} \quad (45)$$

This is the correct low-density limit for the usual OZ direct correlation function. In fact, letting

$$\check{c}_Q^Q(k) = \frac{\alpha^Q(k)}{\rho} + \beta^Q(k) + O(\rho) \quad (46)$$

into (26) and expanding all the terms in powers of ρ , one obtains two coupled equations for α^0 and β^0 :

$$\frac{d\alpha^Q(k)}{dQ} = \int_{|\mathbf{p}|=Q} \frac{d\Omega_p}{(2\pi)^d} \frac{\tilde{\phi}(p)}{[\alpha^Q(p)]^2} \left[1 + \frac{1}{\alpha^Q(|\mathbf{k}+\mathbf{p}|)} \right], \quad (47)$$

$$\begin{aligned} \frac{d\beta^Q(k)}{dQ} &= \int_{|\mathbf{p}|=Q} \frac{d\Omega_p}{(2\pi)^d} \\ &\times \left[\frac{2\beta^Q(p) - \tilde{\phi}(p)}{[\alpha^Q(p)]^3} \left[1 + \frac{1}{\alpha^Q(|\mathbf{k}+\mathbf{p}|)} \right] \right. \\ &\quad \left. + \frac{\tilde{\phi}(p) + \beta^Q(|\mathbf{k}+\mathbf{p}|)}{[\alpha^Q(p)\alpha^Q(|\mathbf{k}+\mathbf{p}|)]^2} \right] \\ &- \int_{\substack{|\mathbf{p}|=Q, \\ |\mathbf{p}+\mathbf{k}| < Q}} \frac{d\Omega_p}{(2\pi)^d} \frac{\tilde{\phi}(p)\phi(|\mathbf{k}+\mathbf{p}|)}{[\alpha^Q(p)\alpha^Q(|\mathbf{k}+\mathbf{p}|)]^2} \end{aligned} \quad (48)$$

with boundary conditions

$$\begin{aligned} \lim_{Q \rightarrow \infty} \alpha^Q(k) &= -1, \\ \lim_{Q \rightarrow \infty} \beta^Q(r) &= e^{-\beta v_R(r)} - 1 + \phi(r). \end{aligned} \quad (49)$$

These equations can be integrated and in r space we get $\alpha^Q(r) = -\delta(r)$ and $\beta^Q(r) = e^{-\beta v_R(r) + \phi_Q(r)} - 1 + \phi(r) - \phi_Q(r)$. From (46), (24), and (44) one finds Eq. (45) for the OZ direct correlation function. When the solution (46) is also inserted into (25) this equation can be integrated and the resulting free energy A gives the correct second virial coefficient for the equation of state.

We have explicitly verified that if we insert in (26) the correct zero density limit of c_3^Q , i.e., $c_3^Q(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \prod_{i,j=1,2,3} \{\exp[-\beta v_Q(r_{ij})] - 1\}$, and the ideal gas value for c_4^Q , the solution of (26) gives the exact virial expansion for the direct correlation function up to first order in ρ . On the other hand, from the structure of Eq. (26) it turns out that this result is general: If the expressions for the three- and four-particle correlation functions are exact to order ρ^{n-1} and ρ^{n-2} , respectively, Eq. (26) is exact to order ρ^n and it can be integrated to give the correct virial expansion for $c(r)$ up to that order. Alternatively, we can obtain $c(r)$ to order ρ^n keeping the equations of the hierarchy up to that for \check{c}_{n+2}^Q and approximating the functions c_m^Q with $m \geq n+3$ appearing in these equations with their ideal gas contribution as given by (44). In this way the

equation for \check{c}_{n+2}^Q has the correct zero density limit and the set of the first $n+1$ coupled equations of the hierarchy (those for \check{c}_Q up to \check{c}_{n+2}^Q) gives, when integrated, the expression for \check{c}_e correct to order ρ^{2+n-e} and in particular $c(r)$ to order ρ^n . This gives the virial coefficients for the equation of state correct up to order $n+1$. We conclude that the construction of a closure of the hierarchy (25)–(28) verifying the correct low-density behavior is straightforward.

We consider now briefly the case of high density in the region of the triple point when the effect of the many-particle correlations on the free energy becomes essentially irrelevant. In fact, both the reference fluid and the Q system for any value of Q are very incompressible so that $\check{F}_Q(k=0)/\rho \ll 1$, and this quantity is very small also at small k where $\check{\phi}(k)$ is significant. All contributions to the evolution equations [(26)–(28)] of the correlation functions contain a factor $\check{\phi}_Q$ which is small so that to lowest order in this quantity $d\check{c}_Q(k)/dQ=0$. Therefore, $\check{c}_{Q=0}(k)=\check{c}_\infty(k)$ but $\check{c}_\infty(k)$ is the direct correlation function of the fluid in ORPA. In terms of the usual Ornstein-Zernike correlation function $c(k)$, this gives $c(k)=\check{c}_{Q=0}(k)+1/\rho=c^R(k)+\check{\phi}(k)$. When we insert this result in the evolution equation for the free energy (25), this equation can be easily integrated giving the usual ORPA contribution (11) to A . ORPA is known to be an excellent approximation for a fluid in the triple-point region,⁶ and we conclude that our hierarchy is well ordered also in the dense regime.

VI. CRITICAL BEHAVIOR FOR A PRIMITIVE APPROXIMATION

In this section we consider a very simple approximation to the hierarchy (25)–(28) which gives a nonclassical critical behavior in three dimensions. The approximation is too drastic to be acceptable for a fluid but the computation is instructive in preparation for more elaborate truncations. The approximations that we make are as follows.

(1) The two-particle direct correlation function is an analytic function of k at $k=0$ even at the critical point (Ornstein-Zernike ansatz), and terms of order higher than k^2 are neglected so that

$$\check{c}_Q(k)=\check{c}_Q(0)-b_Q k^2. \quad (50)$$

(2) The coefficient b_Q is a smooth function of the parameter Q and of the density ρ in the region $Q \rightarrow 0$ and $\rho \sim \rho_c$ so it can be replaced by a constant b .

The first approximation has the obvious consequence that the critical exponent $\eta=0$. This is a rather good approximation in three dimensions where $\eta \sim 0.04$ (but it yields completely wrong results in $d=2$ where $\eta=0.25$). The second assumption neglects the dependence on density of the ratio $S(k=0)/\xi^2$ where $S(k)$ is the usual structure factor and ξ represents the correlation length of the system. $\check{c}_Q(0)$ can be related to the free energy by the equation

$$\check{c}_Q(0)=\frac{\partial^2}{\partial \rho^2}(\mathcal{A}_Q/V) \quad (51)$$

which is a consequence of (4), (23), and (24).

Use of (50), (51), and (29) in (25) gives

$$\frac{\partial}{\partial Q} \left[\frac{\mathcal{A}_Q}{V} \right] = Q^{d-1} \frac{\Omega}{2} \ln \left[-\frac{\partial^2}{\partial \rho^2} \left[\frac{\mathcal{A}_Q}{V} \right] + bQ^2 \right], \quad (52)$$

where Ω is the surface of the unit sphere in d dimension divided by $(2\pi)^d$. Equation (52) is a closed equation for the free energy $\mathcal{A}_Q(\rho)$ and it is meaningful only for small Q because (50) is a small-momentum approximation. Therefore, we do not integrate (52) from $Q=\infty$ as we should but from some small but finite value of Q . Since we are interested here only in the study of the critical singularity which develops just in the $Q \rightarrow 0$ limit and appealing to universality, Eq. (52) allows the determination of universal properties, the critical exponents, and the scaling functions. It is clear, on the other hand, that we do not have anything to say within this approximation on the short-distance behavior of correlations. Note that the dependence of $\mathcal{A}_Q(\rho)$ on temperature is implicit in (52) because it appears only in the boundary condition.

In order to analyze (52) in the critical region it is useful to make a change of variables:

$$x = \sqrt{b/\Omega}(\rho - \rho_c)Q^{-(d-2)/2}, \quad (53)$$

$$H_Q = \frac{1}{\Omega V} [\mathcal{A}_Q(\rho_c) - \mathcal{A}_Q(\rho)] Q^{-d}.$$

In terms of x and H , Eq. (52) becomes

$$-\frac{\partial H_Q}{\partial \ln Q} + \frac{d-2}{2} x \frac{\partial H_Q}{\partial x} - dH_Q - \frac{1}{2} \ln \left[\frac{\frac{\partial^2 H_Q}{\partial x^2} + 1}{\frac{\partial^2 H_Q}{\partial x^2} \Big|_{x=0} + 1} \right] = 0, \quad (54)$$

and this is equivalent to the equation obtained by Nicoll *et al.*¹⁸ by approximating the expression of their renormalization-group differential generator.

As is standard¹ in RG theories, a fixed point solution as $Q \rightarrow 0$ [i.e., $\lim_{Q \rightarrow 0} H_Q = H^*(x)$] signals criticality and an analysis of the behavior of (54) near its fixed point solution $H^*(x)$ gives information about the critical behavior. In fact, from (53) it turns out that the inverse compressibility K_T^{-1} at $\rho = \rho_c$ is proportional to $-(\partial^2 H_Q / \partial x^2) |_{x=0} Q^2$ so that K_T^{-1} vanishes if the derivative remains finite as $Q \rightarrow 0$. Therefore, one has to look for the boundary conditions for H_Q such that H_Q flows to this fixed point. This, implicitly, determines the values T_c and ρ_c of the critical point. For boundary conditions close to the critical ones there will exist an interval of values of the parameter Q where the solution of Eq. (54) is not too distant from the fixed point $H^*(x)$. In this region the evolution of $H_Q(x)$ is determined by the linearized form of Eq. (54) around $H^*(x)$:

$$H_Q(x) \sim H^*(x) + th_1(x)Q^{-\lambda_1}, \quad (55)$$

where λ_1 is its largest eigenvalue, $h_1(x)$ the corresponding eigenfunction, and t a measure of the reduced temperature. In the region of validity of (55) an infinitesimal change of the parameter Q is equivalent to a change of the reduced temperature:

$$-Q \frac{\partial H_Q(x)}{\partial Q} = \frac{\partial H_Q(x)}{\partial t} \lambda_1 t. \quad (56)$$

This relation is conserved by the nonlinear evolution equation (54) so that, near the critical point, it remains valid even as $Q \rightarrow 0$. An immediate consequence of this relation is that $H_Q(x)$ is a function of Q and t only through the quantity Qt^{-1/λ_1} . Moreover, we know that the isothermal compressibility must attain a large but finite value for $Q \rightarrow 0$ and we deduce that in this region $(\partial^2 H_Q / \partial x^2)|_{x=0} \sim Q^{-2}$. The scaling relation (56) implies that

$$K_T^{-1} \approx \left. \frac{\partial^2 H_Q}{\partial x^2} \right|_{x=0} \sim Q^2 \sim t^{2/\lambda_1} \text{ as } Q \rightarrow 0, \quad (57)$$

so that we identify $\gamma = 2/\lambda_1$. Analogously, from (56) we deduce the validity of homogeneity in the critical region

$$K_T \sim t^{-\gamma} f(t^\beta / (\rho - \rho_c)) \quad (58)$$

with the standard relations among critical exponents [the ansatz (50) fixes $\eta = 0$]

$$\gamma = 2\nu, \quad \beta = \gamma / (\delta - 1), \quad \delta = (d + 2) / (d - 2). \quad (59)$$

The second largest eigenvalue of (54) is related to the leading correction to the asymptotic power-law behavior, for instance,

$$K_T(\rho_c, t) \rightarrow K_T^{(0)} t^{-\gamma} (1 + g_0 t^{\omega\nu} + \dots) \text{ as } t \rightarrow 0, \quad (60)$$

where $\omega = -\lambda_2$.

The ϵ expansion associated with (54) has been already studied¹⁸ and it is known that this equation gives the critical exponents correct to linear order in ϵ but not to second order. We have studied Eq. (54) directly in three dimensions by numerical computation of the first two largest eigenvalues. We find

$$\lambda_1 = 1.451 \text{ and } \lambda_2 = -0.581 \quad (61)$$

so that using (57), (59), and (60) we obtain

$$\nu = 0.689, \quad \gamma = 2\nu = 1.378, \quad \delta = 5, \quad \omega\nu = 0.400. \quad (62)$$

As we have already discussed, the approximations which lead to (54) are too poor for a fluid; however, the result (62) has a more general validity. Any closure which implies the Ornstein-Zernike form (50) for small k will give the exponents (62) if the equations have a fixed point at all. The values (62) overestimate the expected ones by about 10%, but considering the roughness of the approximations [(1), (2)] made in this model the results (62) indicate that the set of equations (25)–(28) is a good starting point for an accurate theory of critical behavior. In fact, we cannot forget that the existing theories of fluids give at most classical or mean spherical critical exponents.

VII. DISCUSSION

Since the beginning of the modern theory of critical phenomena the possibility was recognized² of rewriting the partition function of a fluid in a way suitable for RG analysis. This, however, did not develop into a real quantitative theory of the critical point of a fluid because some basic features of the system became obscured in the process and only some formal analysis was performed. We believe that our hierarchical reference theory overcomes this difficulty. We work only with quantities with a well-defined physical meaning, the free energy and the direct correlation functions. We do not perform partial integration over degrees of freedom but we study how these physical quantities evolve when the different Fourier components of the attractive interaction w are turned on. This allows, in principle, studying on the same footing both the short- and the long-range parts of correlation functions. On the other hand, the process which we adopt of turning on the different components of w allows the smooth building up of critical fluctuations on successively larger scales of length in a way very similar to that obtained by RG techniques. Actually the connection with RG theory is very strict because the evolution of correlation functions at *large distances* is governed by equations in which Q , the wave vector which characterizes the turning on of w , turns out to have the role of a momentum cut off exactly as in RG theory. In fact, the approximate hierarchy for this large-distance regime is equivalent to the RG differential generator for the free energy obtained by Nicoll and Chang.¹⁷ It is clear, then, that we recover the usual ϵ expansion when we analyze our equations in a perturbative way around the Gaussian solution at dimensionality four. The hierarchy is well ordered in density since the direct correlation functions are similarly ordered and, in fact, we recover very easily the correct virial expansion of the different quantities. On the other hand, the inclusion of the effect of the attractive interaction in RPA (and in ORPA when a hard core is present) in the starting reference system and the use of a renormalized potential in place of the bare one w gives a new simple ordering in the hierarchy for a system at high density in the region of the triple point. The ordering is in terms of the product $w(k)S^R(k)$ where $S^R(k)$ is the structure factor of the reference system.

These properties of our hierarchy show that this can be the basis of a unified theory of the fluid state. On the other hand, we strictly cannot say yet what is the actual critical behavior of a realistic model of a fluid, for example, the Lennard-Jones system. If we consider the ϵ expansion, for instance, it is not enough to deal with the approximate hierarchy, the one which has the RG structure, but one should solve the exact hierarchy with the correct boundary condition at $Q = \infty$ in order to see if the solution flows toward the fixed point solution obtained from the approximate one. The absence of evidence in RG theory for other fixed points in addition to that of the ϵ expansion and the scaling behavior observed in real fluids suggest that indeed this is the case. Treatment of the exact hierarchy will require the use of a suitable decoupling, and in view of this we have studied a simple model based

on the Ornstein-Zernike ansatz for the direct correlation function. The critical exponents have reasonable values and this induces undertaking the study of similar approximations extended to cover the full range of wave vectors.

Our theory is based on the study of direct correlation functions. When some approximation is introduced in order to truncate the hierarchy it is very difficult to guarantee that the resulting radial distribution function vanishes in the core region of the potential. This appears as a limit of our approach but it can be overcome¹¹ by a suitable generalization of the trick of optimization of the perturbing potential inside the hard core.

Our basic approach is quite general and it can be extended to many other situations. Application to systems of classical spins and to lattice-gas models is straightforward and extension to the case of many-component fluids is possible. The evolution equations also can be written in the case of a nonuniform system as we show in Appendix B and this opens the way to the study of the liquid-vapor interface in the critical region. Our approach is not specific to the critical point and we believe that it will turn out to be useful, for instance, in the study of dense liquids when the pair interaction has contributions on many separate length scales as in the case of some liquid metals.

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APPENDIX A

Here we briefly report some technical details concerning the expansion (9) of the free energy A in powers of a perturbation potential $w(r)$. In order to avoid complications in taking the thermodynamic limit we set up the expansion using the grand-canonical formalism. The grand-canonical partition function of the system in the presence of an external potential $\psi(r)$, is defined as

$$\Xi(\mu, V, T) = \sum_{N \geq 0} \frac{1}{N!} \int d(1) \cdots d(N) \times \prod_{i=1}^N e^{\gamma(i)} \times \exp \left[-\beta \sum_{\substack{i < j \\ i, j=1}}^N v(i, j) \right], \quad (63)$$

$$\gamma(i) = -\beta\psi(i) + \ln z, \quad z = e^{\beta\mu} (2\pi m / \beta h^2)^{3/2}$$

with $v(r) = v_R(r) + w(r)$. From this expression we can obtain the local density $\rho(r)$ of the system by functional differentiation⁶ of $\ln \Xi$ with respect to $\gamma(r)$:

$$\rho(1) = \frac{\delta \ln \Xi}{\delta \gamma(1)}. \quad (64)$$

Similarly, the correlation function (7) can be written as

$$\hat{F}(1, 2) = \frac{\delta^2 \ln \Xi}{\delta \gamma(1) \delta \gamma(2)}. \quad (65)$$

The Helmholtz free energy A is defined as a functional of the density $\rho(r)$ by the Legendre transform

$$-\beta A[\rho] = \ln \Xi - \int d^d r \rho(r) \gamma(r). \quad (66)$$

The successive functional derivatives of $A[\rho]$ with respect to density give the many-particle direct correlation functions (4).

The perturbative expansion of the free energy $A[\rho]$ is most easily expressed in terms of the correlation functions of the reference system $\hat{c}_j^R(1, \dots, j)$ ($j \geq 3$) and $\hat{F}^R(1, 2)$. Using the notations (8) of Sec. II, the expansion in diagrammatic form is

$$-\beta(A - A^R) + \frac{1}{2} \int d(1) \rho(1) \phi(1, 1) - \frac{1}{2} \int d(1) d(2) \rho(1) \rho(2) \phi(1, 2) \quad (67)$$

equals the sum of all connected diagrams consisting of hypervertices $\hat{c}_j^R(1, \dots, j)$ ($j \geq 3$), $\hat{F}^R(1, 2)$ bonds, and $\phi(1, 2)$ bonds, satisfying the following conditions.

- (1) The end point of each ϕ bond is always connected only with the end point of one \hat{F}^R bond.
- (2) The end point of an \hat{F}^R bond may be connected either with a ϕ bond or with a \hat{c}_j^R hypervertex.
- (3) There is at least one ϕ bond in the diagram.
- (4) There is at most one path of \hat{F}^R bonds and \hat{c}_j^R hypervertices between each pair of points in the diagram.
- (5) The diagram remains connected after cutting a single bond.

Each diagram in the expansion must be multiplied by $1/S$ where S is its own symmetry number. S equals the total number of permutations of the labels in the diagram which transform the diagram into another characterized by the same set of connections and therefore topologically equivalent. In (67) we have introduced the arbitrary term $\phi(1, 1)$, which is canceled by one term of the right-hand side (rhs). A similar expansion in terms of c_j^R is found in Ref. 13.

Now it is possible to sum up all the diagrams containing no hypervertices, and this gives the random-phase contribution a_{RPA} to the free energy,

$$-\beta a_{\text{RPA}} = -\frac{1}{2} \int \frac{d^d p}{(2\pi)^d} [\ln(1 - \tilde{F}^R \phi)]_{\mathbf{p}, -\mathbf{p}}, \quad (68)$$

where the logarithm is understood in operatorial sense:

$$[\ln(1 - \Delta)]_{\mathbf{p}, -\mathbf{p}} = -\Delta(\mathbf{p}, -\mathbf{p}) - \frac{1}{2} \int \frac{d^d k}{(2\pi)^d} \Delta(\mathbf{p}, \mathbf{k}) \Delta(-\mathbf{k}, -\mathbf{p}) - \cdots \quad (69)$$

In the case of a homogeneous system (68) is equal to the last term of the rhs of (23). In the remaining diagrams we can perform additional resummations. In fact, from rules (1) and (2) it results that from a given diagram we can

construct an infinity of other admissible diagrams substituting a ϕ bond with a chain of \hat{F}^R and ϕ bonds. We call the φ bond the sum of all these chains. This resummation can be made at each order and the resulting expansion is determined by the same rules (1)–(5) where ϕ bonds are substituted by φ bonds and two supplementary conditions are imposed.

(6) There is at least one hypervertex.

(7) A diagram cannot contain a chain of \hat{F}^R and φ bonds with two or more φ bonds.

The complete expansion of the free energy of an inhomogeneous system is

$$-\beta A = -\beta A^R - \frac{1}{2} \int d(1)\rho(1)\phi(1,1) + \frac{1}{2} \int d(1)d(2)\rho(1)\rho(2)\phi(1,2) - \beta a_{\text{RPA}} + \dots, \quad (70)$$

where ... is the sum of diagrams according to rules (1)–(7). In the case of a homogeneous system it is possible to give the explicit form for the φ bond as

$$\begin{aligned} \tilde{\varphi}(k) &= \tilde{\phi}(k) + \tilde{\phi}(k)\check{F}^R(k)\tilde{\phi}(k) + \dots \\ &= \frac{\tilde{\phi}(k)}{1 - \check{F}^R(k)\tilde{\phi}(k)} \end{aligned} \quad (71)$$

in Fourier space.

APPENDIX B

The expansion (70) of the free energy is valid for an arbitrary reference potential v_R and a general nonsingular perturbation potential $\phi = -\beta w$. Now we specialize the expansion to the case of a reference interaction equal to (2), i.e., the interaction containing both the repulsive part and the short-wavelength portion w_Q of the attractive tail, while the perturbation potential is given by (22): $\delta w_Q = w_{Q-\delta Q} - w_Q$ where δQ is an infinitesimal shift in the parameter Q . In order to obtain a differential equation for the free energy A_Q we need only the change of A_Q linear in δQ . These terms come from the zero- and one-loop (=ring) diagrams of the expansion (70). The zero-loop terms [i.e., those explicitly written in (71)] are automatically included through the definition of the modified free energy for an inhomogeneous system:

$$\begin{aligned} \mathcal{A}_Q[\rho(\mathbf{r})] &= -\beta A_Q[\rho(r)] - \frac{1}{2} \int d^d r \rho(r) [\phi(0) - \phi_Q(0)] \\ &\quad + \frac{1}{2} \int d^d r_1 d^d r_2 \rho(r_1)\rho(r_2) \\ &\quad \times [\phi(\mathbf{r}_1 - \mathbf{r}_2) - \phi_Q(\mathbf{r}_1 - \mathbf{r}_2)]. \end{aligned} \quad (72)$$

The change of \mathcal{A}_Q linear in δQ is obtained from a_{RPA} [see (68)] in the form

$$\begin{aligned} \mathcal{A}_{Q-\delta Q} - \mathcal{A}_Q &= -\frac{1}{2} \int \frac{d^d p}{(2\pi)^d} [\ln(1 + \tilde{\Delta}_Q)]_{\mathbf{p}, -\mathbf{p}} \\ &\quad + O((\delta Q)^2), \end{aligned} \quad (73)$$

where

$$\tilde{\Delta}_Q(\mathbf{p}, \mathbf{k}) = \begin{cases} \check{F}_Q(\mathbf{p}, \mathbf{k})\tilde{\phi}(k) & \text{for } Q - \delta Q \leq k < Q \\ 0 & \text{elsewhere.} \end{cases} \quad (74)$$

As usual, the correlation function $\check{F}_Q(\mathbf{p}, \mathbf{k})$ is the inverse of $\check{c}_Q^2(\mathbf{p}, \mathbf{k})$,

$$-(2\pi)^d \delta(\mathbf{p} + \mathbf{k}) = \int \frac{d^d q}{(2\pi)^d} \check{F}_Q(\mathbf{p}, \mathbf{q}) \check{c}_Q^2(-\mathbf{q}, \mathbf{k}), \quad (75)$$

and $\check{c}_Q^2(\mathbf{p}, \mathbf{k})$ is the Fourier transform of the second functional derivative of the free energy A_Q with respect to the local density $\rho(\mathbf{r})$.

We notice that the limit $\delta Q \rightarrow 0$ in Eq. (73) has to be taken after the computation of the logarithm (69) has been performed. Equation (73) can be written in an alternative way using the modified direct correlation function $\check{\mathcal{C}}_Q(\mathbf{r}_1, \mathbf{r}_2)$ defined in terms of the functional \mathcal{A}_Q by

$$\check{\mathcal{C}}_Q(1,2) = \frac{\delta^2 \mathcal{A}_Q[\rho]}{\delta \rho(1) \delta \rho(2)}. \quad (76)$$

From the definition (72) of \mathcal{A}_Q we obtain the relation between $\check{\mathcal{C}}_Q$ and \check{c}_Q^2 :

$$\begin{aligned} \check{\mathcal{C}}_Q(\mathbf{p}, \mathbf{k}) &= \check{c}_Q^2(\mathbf{p}, \mathbf{k}) \\ &\quad + (2\pi)^d \delta(\mathbf{p} - \mathbf{k}) [\tilde{\phi}(k) - \tilde{\phi}_Q(k)]. \end{aligned} \quad (77)$$

By insertion of (77) and (75) into (73) we obtain after some algebra

$$\mathcal{A}_{Q-\delta Q} - \mathcal{A}_Q = \frac{1}{2} \int \frac{d^d p}{(2\pi)^d} (\ln \chi_Q^2 - \ln \chi_{Q-\delta Q}^2)_{\mathbf{p}, -\mathbf{p}}, \quad (78)$$

where

$$\begin{aligned} \chi_{Q-\delta Q}^2(\mathbf{p}, \mathbf{k}) &= -\check{\mathcal{C}}_{Q-\delta Q}(\mathbf{p}, \mathbf{k}) \\ &\quad + (2\pi)^d \delta(\mathbf{p} + \mathbf{k}) [\tilde{\phi}(k) - \tilde{\phi}_{Q-\delta Q}(k)], \end{aligned} \quad (79)$$

$$\begin{aligned} \chi_Q^2(\mathbf{p}, \mathbf{k}) &= -\check{\mathcal{C}}_Q(\mathbf{p}, \mathbf{k}) \\ &\quad + (2\pi)^d \delta(\mathbf{p} + \mathbf{k}) [\tilde{\phi}(k) - \tilde{\phi}_Q(k)], \end{aligned} \quad (80)$$

and $\delta(0)$ must be interpreted as $(2\pi)^d V$. This equation greatly simplifies in the homogeneous case where

$$\check{\mathcal{C}}_Q(\mathbf{p}, \mathbf{k}) = (2\pi)^d \delta(\mathbf{p} + \mathbf{k}) \check{c}_Q^2(k) \quad (81)$$

so that

$$\begin{aligned} [\ln \chi_Q^2]_{\mathbf{p}, \mathbf{k}} &= (2\pi)^d \delta(\mathbf{p} + \mathbf{k}) \\ &\quad \times \ln[-\check{\mathcal{C}}_Q(k) + \tilde{\phi}(k) - \tilde{\phi}_Q(k)]. \end{aligned} \quad (82)$$

Then we get

$$\mathcal{A}_{Q-\delta Q} - \mathcal{A}_Q = \frac{V}{2} \int_{Q-\delta Q \leq p < Q} \frac{d^d p}{(2\pi)^d} \ln[1 + \check{\mathcal{F}}_Q(p)\tilde{\phi}(p)] \quad (83)$$

and from this we obtain the evolution equation (25).

In order to approximate the exact expression (73) in the critical region it is useful to start from the equivalent form (78) considering the direct correlation function as the sum of its diagonal part plus the nondiagonal one:

$$\check{\mathcal{C}}_Q(\mathbf{p}, \mathbf{k}) = (2\pi)^d \delta(\mathbf{p} + \mathbf{k}) \check{c}_Q^d(k) + \check{\mathcal{C}}_Q^{\text{nd}}(\mathbf{p}, \mathbf{k}). \quad (84)$$

Defining

$$\check{\mathcal{F}}_Q^d(k) = -1/\check{\mathcal{C}}_Q^d(k) \quad (85)$$

and

$$\check{F}_Q^-(k) = \begin{cases} \check{\mathcal{F}}_Q^d(k)/[1+\check{\mathcal{F}}_Q^d(k)\check{\phi}(k)] & \text{for } k < Q - \delta Q \\ \check{\mathcal{F}}_Q^d(k) & \text{for } k \geq Q - \delta Q, \end{cases} \quad (86)$$

$$\check{F}_Q^+(k) = \begin{cases} \check{\mathcal{F}}_Q^d(k)/[1+\check{\mathcal{F}}_Q^d(k)\check{\phi}(k)] & \text{for } k < Q \\ \check{\mathcal{F}}_Q^d(k) & \text{for } k \geq Q, \end{cases}$$

Eq. (78) can be written in the form

$$\mathcal{A}_{Q-\delta Q} - \mathcal{A}_Q = \frac{1}{2} V \int_{Q-\delta Q \leq r < Q} \frac{d^d p}{(2\pi)^d} \ln[1 + \check{\mathcal{F}}_Q^d(p)\check{\phi}(p)] \\ + \frac{1}{2} \int \frac{d^d p}{(2\pi)^d} [\ln(1 - \check{F}_Q^+ \check{\mathcal{C}}_Q^{nd}) \\ - \ln(1 - \check{F}_Q^- \check{\mathcal{C}}_Q^{nd})]_{p, -p}. \quad (87)$$

In analogy with the homogeneous case, the critical region is characterized by the growth of $\check{\mathcal{F}}_Q^d$ so that

$$\frac{\partial \mathcal{A}_Q}{\partial Q} = \frac{1}{2} \int_{|p|=Q} \frac{d\Omega_p}{(2\pi)^d} (\ln \chi^Q)_{p, -p},$$

$$\chi^Q(\mathbf{p}, \mathbf{k}) = -\check{\mathcal{C}}_Q(\mathbf{p}, \mathbf{k}) - \int_{|\mathbf{q}_1| > Q} \frac{d^d q_1}{(2\pi)^d} \int_{|\mathbf{q}_2| > Q} \frac{d^d q_2}{(2\pi)^d} \check{\mathcal{C}}_Q(\mathbf{p}, \mathbf{q}_1) f_Q(-\mathbf{q}_1, \mathbf{q}_2) \check{\mathcal{C}}_Q(-\mathbf{q}_2, \mathbf{k}),$$

where f_Q is defined by

$$-(2\pi)^d \delta(\mathbf{q}_1 + \mathbf{q}_2) \\ = \int_{|\mathbf{k}| > Q} \frac{d^d k}{(2\pi)^d} \check{\mathcal{C}}_Q(\mathbf{q}_1, \mathbf{k}) f_Q(-\mathbf{k}, \mathbf{q}_2). \quad (91)$$

Since [see Eq. (76)]

$$\check{\mathcal{C}}_Q(\mathbf{p}, \mathbf{k}) = (2\pi)^{2d} \frac{\delta^2 \mathcal{A}_Q}{\delta \check{\rho}(-\mathbf{p}) \delta \check{\rho}(-\mathbf{k})} \quad (92)$$

Eqs. (90)–(92) form a closed system of equations. As a rule the limit $\delta Q \rightarrow 0$ associated with \ln_{\pm} must be taken after the explicit computation of the logarithm has been

$$\rho^{-d} \check{\mathcal{F}}_Q^d(k) \gg 1. \quad (88)$$

Thus we can neglect in (87) the term unity in comparison with $\check{\mathcal{F}}_Q^d(k)\check{\phi}(k)$ when $Q \rightarrow 0$ and $K \rightarrow 0$. Moreover, $\check{F}_Q^+(k)$ and $\check{F}_Q^-(k)$ are always bounded quantities for $k < Q$ and $k < Q - \delta Q$, respectively, and the contributions from these momentum ranges can be neglected when $Q \rightarrow 0$. Therefore, Eq. (87) can be simplified near the critical point when $Q \rightarrow 0$ and with straightforward calculations it can be cast into the form

$$\mathcal{A}_{Q-\delta Q} - \mathcal{A}_Q = \frac{1}{2} \int \frac{d^d p}{(2\pi)^d} [\ln_{>}(-\check{\mathcal{C}}_Q) \\ - \ln_{\geq}(-\check{\mathcal{C}}_Q)]_{p, -p}. \quad (89)$$

Here we have introduced the notation $\ln_{>}$ to indicate that in the expansion of the logarithm each integration is limited to the domain $k \geq Q$. Similarly, \ln_{\geq} and $\ln_{=}$ mean that the limitation is $k \geq Q - \delta Q$ and $Q - \delta Q \leq k < Q$, respectively.

Expanding the logarithms in Eq. (89) and then resumming the resulting series in a way similar to that of Ref. 17, we get the following differential equation for the functional \mathcal{A}_Q :

performed. When the functional \mathcal{A}_Q is expanded in Taylor series around a constant value of the local density $\rho(x) = \rho$, Eqs. (90)–(92) give rise to the approximate hierarchy (39)–(41) obtained previously. Moreover, (90)–(92) coincide with the RG differential generator for the free energy derived by Nicoll and Chang for a spin Hamiltonian with the technique of partial integration. Here $\mathcal{A}_Q[\rho]$ given by (72) has the role of the generating functional, the functional derivatives are performed with respect to the local density $\check{\rho}(k)$ in place of the magnetization, and our parameter Q corresponds to the momentum shell of integration of the RG theory.

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