Calculation of the Critical Exponents by a Renormalization of the Ornstein-Zernike Equation

Q. Zhang and J. P. Badiali

Laboratoire Structure et Réactivité aux Interfaces, Université Pierre et Marie Curie, 4 Place Jussieu,
75230 Paris CEDEX 05, France

(Received 11 February 1991)

We calculate the critical exponents at the liquid-vapor critical point by using the classical ingredients of the liquid-state theory. Two coupling constants are defined at a microscopic level. The closure of the Ornstein-Zernike equation is given by the Callan-Symanzik equation from which we determine the position of the fixed point. The role of the three-body direct correlation function is emphasized. A comparison between this work and the standard theory of critical phenomena based on the Landau-Ginzburg-Wilson Hamiltonian is presented.

PACS numbers: 61.20.Gy, 05.70.−a

Experimental results show that the universality class of a fluid is the same as that of the Ising model [1,2] although the liquid does not have the same symmetry class as the ferromagnetism. This suggests that the existence of a three-body correlation function does not change the values of the critical exponents. The main goal of this Letter is to prove this point starting from the liquid-state theory.

The structure of a liquid formed by molecules interacting via a radial pair potential is characterized by the total correlation function $h(r_{12})$ which determines the probability of finding two molecules 1 and 2 separated by a distance r_{12} [3]. In addition to $h(r_{12})$, we define $c(r_{12})$, the direct correlation function (DCF), via the Ornstein-Zernike (OZ) equation:

$$h(r_{12})=c(r_{12})+\int h(r_{13})c(r_{32})d\mathbf{r}_3\,, \tag{1}$$

where $d\mathbf{r}_3$ means an integration over the spatial coordinates of 3. For convenience, the density number ρ is included in the definition of $h(r_{12})$ and $c(r_{12})$. In order to calculate $h(r_{12})$ we must add to Eq. (1) a closure relation which is an approximate relation between $h(r_{12})$ and $c(r_{12})$. Now, we know that the usual closures are inefficient in the critical region. Recently, Reatto and co-workers [4] proposed a new approach which combines the ingredients of the liquid-state theory and some aspects of the renormalization-group theory. In this Letter, we show that the calculation of the critical exponents at the liquid-vapor phase transition can be performed directly from the OZ equation by using the methods of quantum field theory [5,6].

The first theory of critical phenomena assumed that $c(r_{12})$ is a short-range function compared to $h(r_{12})$ and that all the moments of $c(r_{12})$ are well defined. Fisher [7] showed that only the first part of this assumption is exact. Therefore, each correlation function f ($=h$ or c) must be written $f=f^S+f^L$. The function f^L gives the long-range behavior of f while f^S vanishes when r_{12} is greater than a few molecular diameters and remains a smooth function of the thermodynamical parameters (ρ and T, for example). When this splitting is introduced in Eq. (1) we can write

$$h^L(r_{12})-\int h^L(r_{13})c^L(r_{32})d\mathbf{r}_3-\int h^L(r_{13})c^S(r_{32})d\mathbf{r}_3=H(r_{12})\,, \tag{2}$$

where $H(r_{12})$ is short ranged compared to the left-hand side of Eq. (2). Since $c^S(r_{32})$ is really short ranged we can expand $h^L(r_{13})$ as in the OZ theory [7], and we get

$$K\Delta h^L(r_{12})-Mh^L(r_{12})+\int[h^L(r_{13})-h^L(r_{12})]c^L(r_{32})d\mathbf{r}_3=H'(r_{12})\,, \tag{3}$$

with $M=[1-\int c(r)d\mathbf{r}]$ and $K=(1/2d)\int r^2c^S(r)d\mathbf{r}$ (d is the number of dimensions). $H'(r_{12})$, which has the same range as $H(r_{12})$, is negligible when r_{12} is greater than a given length, say λ_0. Instead of solving Eq. (3) with the condition $(r_{12}/\lambda_0)\gg 1$, we formally set $\lambda_0=0$. After this shrinking, we consider $h^L(r_{12})$ given by

$$-\Delta h^L(r_{12})+m^2h^L(r_{12})-\int[h^L(r_{13})-h^L(r_{12})]c^L(r_{32})d\mathbf{r}_3=\delta(r_{12})\,. \tag{4}$$

Hereafter $h^L(r_{12})$ differs from the one considered in Eq. (3) by a multiplicative constant, $c^L(r)$ is divided by the constant K, and $m^2=M/K$. These constants are dimensionless in the critical region. From statistical mechanics [3] we know that $m^2=(\rho k_BT\chi_TK)^{-1}$, where χ_T is the isothermal compressibility. In Fourier space we write Eq. (4) as $h^L(k)\Gamma^L(k)=1$, where

$$\Gamma^L(k)=k^2+m^2+[c^L(k=0)-c^L(k)] \tag{5}$$

is the two-point vertex function [5]. $\Gamma^L(k)$ is only determined by $c^L(k)$, which we must calculate by a perturbation theory. Here the reference system corresponds to an approximation on $c(r_{12})$. This function, noted $c_\Lambda(r_{12})$, is defined as usually [3] but its calculation is restricted to the molecules enclosed in a sphere $S(1,\lambda)$ of radius λ, finite but very large, centered on 1. $c_\Lambda(r_{12})$ coincides with $c(r_{12})$ if λ goes to infinity. From $c_\Lambda(r_{12})$ we get

m_Λ and Γ_Λ. These quantities verify an equation similar to Eq. (5). Moreover, we assume that $c_\Lambda(r_{12}) \sim (r_{12})^{-(d+\sigma)}$ with $\sigma > 2$; then $c_\Lambda(k) - c_\Lambda(k=0)$ is an increasing function of Λ that we can neglect if we focus on $k \ll 1/\lambda$. It can be shown [8] that this restriction on $c_\Lambda(r_{12})$ is just the condition which avoids the existence of long-range interactions [9]. Now, the long-range behavior of Γ_Λ is simply $\Gamma_\Lambda(k) = k^2 + m_\Lambda^2$ from which m_Λ can be dimensioned and m_Λ is of order $\Lambda \sim 1/\lambda$. By arguments of continuity we can show that $m_\Lambda^2 > 0$ [8]. For calculating $c^L(k)$ we start from its diagrammatic definition and we use a topological reduction [10] which allows us to introduce directly $h_\Lambda(k)$ in the perturbation theory.

As an example of our strategy we first add one long-range bond $h_\Lambda(r_{12})$ into the reference system as indicated in Fig. 1. In (a) the hatched part represents the infinite sum of graphs in which the interactions are restricted to $S(1,\lambda)$. It contains $c_\Lambda(r_{12})$ plus $\delta h_\Lambda(r_{12})$, which corresponds to the infinite sum of bonds in which 1 and 2 are connected by graphs containing nodal points. When $h_\Lambda(r_{12})$ is connected in parallel on 1 and 2 the graph is really new compared to those of the reference system although $r_{12} \leq \lambda$. We can prove this point by remembering that the OZ equation can be solved by an iterative procedure in which $h_\Lambda(r_{12})$ appears as the result of an infinite sum of chain graphs in which the bonds are $c_\Lambda(r_{ij})$ [3]. Since the molecules i and j are not necessarily inside $S(1,\lambda)$, the graph (a) and more generally those shown in Fig. 1 are actually new. In (b) and (c) we introduce the triplet DCF $c_\Lambda(1,2,i)$, while in (d) and (e) we take into account the existence of nodal points between 1 and 2. Finally, in (f), (g), and (h) h_Λ is connected to two field points. In (h) we introduce the four-body DCF $c_\Lambda(1,2,3,4)$. The sum of all contributions due to the reference system will be represented by a four-body function $u_{4\Lambda}(1,2,3,4)$ as indicated in Fig. 1. When we increase the number of h_Λ a similar construction can be done. For instance, when 1 and 2 are connected by two h_Λ, the connection can be direct or via $c_\Lambda(1,i,j)$ and the sum of these two possibilities gives rise to $u_{3\Lambda}(1,i,j)$ as shown in Fig. 2. More generally, the perturbation theory requires one to know $\delta h_\Lambda(r_{12})$, a set of n-body DCF, $c_\Lambda(1,2,\ldots,n)$, and their integral $c_{n\Lambda}$ over $n-1$ coordinates. These last quantities can be evaluated at the critical point and moreover we can find their values c_n in the real system.

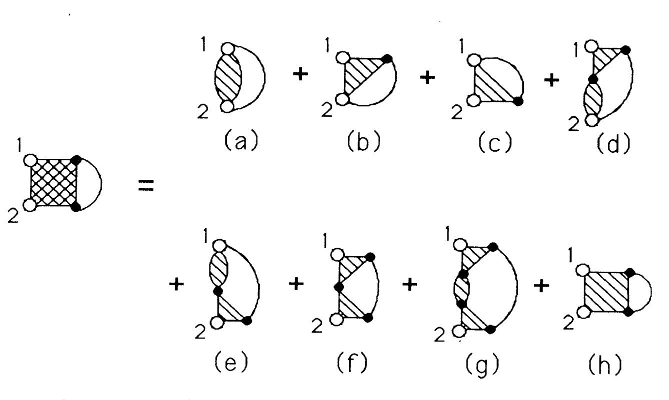

FIG. 1. Introduction of one long-range bond h_Λ into the reference system. h_Λ is represented by a line while the hatched parts in (a)–(h) are defined in the text. On the left-hand side, the hatched part corresponds to the function $u_{4\Lambda}(1,2,3,4)$.

In order to do that we use (i) the relation between the derivative of $c(1,\ldots,n)$ relative to the density ρ and the integral of $c(1,\ldots,n,n+1)$ over the coordinates of $(n+1)$ [11], (ii) the definition of m^2 in terms of χ_T, and (iii) the critical isotherm $p - p_c \sim (\rho - \rho_c)^\delta$ (p is the pressure) [2]. We get immediately $c_n = (-1)^n(n-2)! + a_n(\rho-\rho_c)^{\delta+1-n}$ with $2 \leq n$. The terms of higher order in $\rho - \rho_c$ have been neglected and a_n is a smooth function of ρ and T.

In the reference system, $c_{2\Lambda}$ $[\equiv c_\Lambda(k=0)]$ determines $m_\Lambda^2 = 1 - c_{2\Lambda}$. The dimension of $c_{n\Lambda}$ can be obtained by simple scaling arguments. For each sphere $S(a,\lambda)$ we define a mean density $\rho_\Lambda(a) = [\sum\theta(r_{ia} - \lambda)]/\bar{\omega}(\lambda)$, where the sum runs over all the molecules in the system, $\theta(r)$ is the Heaviside step function, and $\bar{\omega}(\lambda)$ is the volume of $S(a,\lambda)$; we also define the fluctuations in density $\Delta\rho_\Lambda(a) = \rho_\Lambda(a) - \rho_c$. For two spheres $S(1,\lambda)$ and $S(2,\lambda)$, the function $H(1,2) = \langle\Delta\rho_\Lambda(1)\Delta\rho_\Lambda(2)\rangle$, which measures the correlations in the fluctuations of density, has the same spatial variation as $h_\Lambda(r_{12})$ provided $r_{12} \gg \lambda$. If we change λ into $\lambda' = s\lambda$, $\Delta\rho_\Lambda(a)$ becomes $\Delta\rho_{\Lambda'}(a) = (s^{-x})\Delta\rho_\Lambda(a)$, where x $(x > 0)$ takes into account the fact that $\rho_\Lambda(a) - \rho_c$ must decrease when λ increases. However, a change in λ also modifies m_Λ which gives the length scale. Accordingly, the function $H(1,2)$ will be unchanged if we also change r_{12} into $r'_{12} = r_{12}/s$. For $r_{12} \gg \lambda$, $h_\Lambda(r_{12}) = (r_{12})^{-(d-2)}$ and we get $x = (d-2)/2$. Since λ is very large $\rho_\Lambda(a)$ is weakly dependent on a and $\rho_\Lambda(a) \simeq \rho_\Lambda$; finally $\rho_\Lambda - \rho_c \sim \Lambda^{(d-2)/2}$. *The density number ρ_Λ deviates from ρ_c as a consequence of the correlations which persist beyond λ.* From this result and the relation between the DCF we find that $c_{n\Lambda} = (-1)^n(n-2)! + g_{n,0}\Lambda^{-n(d-2)/2+d}$, with $2 \leq n$; $g_{n,0}$ is dimensionless. Clearly, in the perturbation theory we only consider the values of n for which $c_{n\Lambda}$ is finite, i.e., $n \leq 2d/(d-2)$.

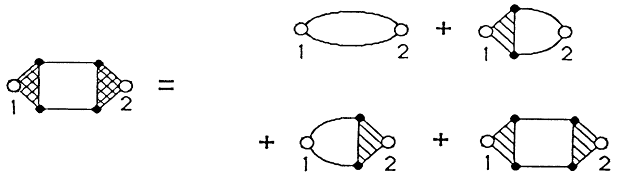

FIG. 2. Introduction of two long-range bonds h_Λ in the perturbation theory. On the left-hand side, the hatched parts correspond to the functions $u_{3\Lambda}(1,i,j)$ and $u_{3\Lambda}(2,i,j)$.

Now, we can calculate the dimension of other quantities defined above. The integral of $u_{3\Lambda}(1,2,3)$ over the coordinates of 2 and 3, noted $u_{3\Lambda}$, is immediately $g_{3,0}\Lambda^{(6-d)/2}$. The dimension of $u_{4\Lambda}$ results from the graphs given in Fig. 1. In $\delta h_\Lambda(r_{12})$, all the points being located inside $S(1,\lambda)$, we assume that its range is smaller than $(r_{12})^{-(d-2)}$; consequently its integral is of the order Λ^y with $y>-2$. After a large cancellation between three- and four-body DCF, the leading term is $g_{4,0}\Lambda^{(4-d)}$. The graph in which 1 and 2 are related by three long-range bonds in parallel introduces a four-body function for which the diagrammatic structure is different from $u_{4\Lambda}(1,2,3,4)$, but we can prove [8] that the leading term is again $g_{4,0}\Lambda^{(4-d)}$. More generally, we can calculate the dimension of $u_{n\Lambda}$. Since $u_{n\Lambda}$ is finite when $n\le 2d/(d-2)$ we introduce a new shrinking in the distances. When focusing on very large distances we formally set $\lambda=0$, and we replace $u_{3\Lambda}(1,2,3)$ and $u_{4\Lambda}(1,2,3,4)$ by new vertices $u_{3\Lambda}$ and $u_{4\Lambda}$ of weight $g_{3,0}\Lambda^{(6-d)/2}$ and $g_{4,0}\Lambda^{(4-d)}$, but now Λ goes to infinity. Now, a graph contains h_Λ bonds and vertices defined at a microscopic level ($g_{3,0}\Lambda^{(6-d)/2}$ and $g_{4,0}\Lambda^{(4-d)}$ are, respectively, the limit of $c_{3\Lambda}+1$ and $c_{4\Lambda}-2$ when Λ goes to zero). $g_{3,0}$ and $g_{4,0}$ play the role of the bare coupling constants in the standard theory. The integration over h_Λ leads to the evaluation of the Feynman integrals for which the calculation is well known [5,6]. To each graph G of $c(1,2,\ldots,n)$ we associate a superficial degree of divergence $\Omega(G)$ which tells us what the behavior of these integrals is for very large values of Λ. We know that [6]

$$\Omega(G)=\sum N_m[m(d-2)/2-d]-n(d-2)/2+d\,, \qquad (6)$$

where N_m is the number of m-point vertices and the sum runs over all values of m. We must retain the graphs for which $\Omega(G)>0$ [6]. The graphs in Fig. 1 represent the first step in the perturbation theory. From its infrared behavior we deduce the critical dimension d_c [6]. Hence, *the existence of a three-body correlation function does not change d_c, which remains $d_c=4$* [8,12]. The condition $n\le 2d_c/(d_c-2)$ implies that we only have to study the DCF for $n=2$, 3, and 4.

Now, the perturbation theory gives $c^L(k)$ in terms of $\Gamma_\Lambda(k)$, $u_{3\Lambda}$, $u_{4\Lambda}$, and $d=4-\varepsilon$. The corresponding vertex function $\Gamma_b(k)$ contains ultraviolet divergences that we absorb in the definition of renormalized quantities (m, u_3, and u_4) and in a scale factor $Z=\Gamma^L(k)/\Gamma_b(k)$. At the critical point the cancellation of m induces some infrared divergences and we must introduce an arbitrary "mass parameter" μ which characterizes the renormalization points [5].

First, $u_{3\Lambda}$ and $u_{4\Lambda}$ must be replaced by the renormalized quantities u_3 and u_4 that we write in terms of dimensionless coupling constant $u_3=g_3\mu^{(2+\varepsilon)/2}$ and $u_4=g_4\mu^\varepsilon$. The analysis of Eq. (6) shows that the insertion of any $u_{3\Lambda}$ in the expansion of u_4 leads to a converging term that we can drop. Then u_4 has formally the same expansion as in the ϕ^4 theory [6]; we have

$$g_4=g_{4\Lambda}\left(\frac{\Lambda}{\mu}\right)^{\varepsilon}+\frac{3}{16\pi^2}\left[g_{4\Lambda}\left(\frac{\Lambda}{\mu}\right)^{\varepsilon}\right]^2\left(\ln\frac{\Lambda}{\mu}+\cdots\right). \qquad (7)$$

Equation (6) also shows that the expansion of u_3 contains one $u_{3\Lambda}$ and an arbitrary number of $u_{4\Lambda}$. It is easy to show that

$$g_3=g_{3\Lambda}\left(\frac{\Lambda}{\mu}\right)^{(2+\varepsilon)/2}+\frac{1}{16\pi^2}g_{3\Lambda}\left(\frac{\Lambda}{\mu}\right)^{(2+\varepsilon)/2}g_{4\Lambda}\left(\frac{\Lambda}{\mu}\right)^{\varepsilon}\left(\ln\frac{\Lambda}{\mu}+\cdots\right). \qquad (8)$$

The expansion of $c^L(k)$ which corresponds to $n=2$ requires us to calculate the same graphs as in the ϕ^4 theory plus some graphs containing $u_{3\Lambda}$. The first one with $u_{3\Lambda}$ is shown in Fig. 2. It has a term diverging as $\ln(\Lambda/\mu)$ which contributes to m ($k=0$); its k dependence, which has a finite limit when Λ goes to infinity, can be included in the definition of Z. Now, g_3 has no explicit contribution to $\Gamma^L(k)$ which keeps the same form as in the ϕ^4 theory. To calculate the fixed point we use the so-called Callan-Symanzik equation which expresses the independence of $\Gamma_b(k)$ on the renormalization point [5]. Here, this equation takes the form [6]

$$\left[\frac{\partial}{\partial\ln\mu}+\beta_3(g_3,g_4,\varepsilon)\frac{\partial}{\partial g_3}+\beta_4(g_4,\varepsilon)\frac{\partial}{\partial g_4}-\gamma(g_3,g_4,\varepsilon)\right]\Gamma^L(k)=0\,. \qquad (9)$$

The functions β_3 and β_4 are defined by $\beta_3=dg_3/d\ln\mu$ and $\beta_4=dg_4/d\ln\mu$, while $\gamma=d\ln Z/d\ln\mu$; in these derivatives $g_{3\Lambda}$, $g_{4\Lambda}$, and Λ are kept fixed. Equation (9) will reproduce the simple scaling behavior if the coupling constants g_3 and g_4 reach the values g_3^* and g_4^* such that any further change in the scale of the momenta does not affect them. This stable fixed point is the solution of the equations $\beta_3(g_3^*,g_4^*,\varepsilon)=0$ and $\beta_4(g_4^*,\varepsilon)=0$. Since g_4 obeys the same equation as in the ϕ^4 theory we have $g_4^*=\frac{16}{3}\pi^2\varepsilon$. From Eq. (8) we get $\beta_3=-g_3[(6-d)/2-(1/16\pi^2)g_4]$ which leads to $g_3^*=0$. Hence, the stable fixed point corresponds to $g_4^*=\frac{16}{3}\pi^2\varepsilon$ and $g_3^*=0$.

By using the classical arguments [5,6] we deduce from Eq. (9) that $\Gamma^L(k)=k^{2-\eta}$ with $\eta=\gamma(g_3^*,g_4^*,\varepsilon)=\gamma(g_4^*,\varepsilon)$. Accordingly, η has the same value as in the ϕ^4 theory, $\eta=\varepsilon^2/54$. Since other critical exponents are calculated at the fixed point for which $g_3^*=0$, we conclude that *the liquid-vapor critical point has the same critical exponents as those of the Ising model.* Thus, in the liquid state ϕ^3 or c_3 does not modify the value of the critical exponents. However, we cannot conclude that c_3 does not participate in the universal critical behavior. In our calculation the functions $u_{3\Lambda}$ and $u_{4\Lambda}$ which introduce the coupling constants are defined at a microscopic level and their dimensions result from $1-c_{2\Lambda}\sim\Lambda^2$ and the relation between the DCF. The existence of $c_{3\Lambda}$ produces some cancellations in $u_{4\Lambda}$ which lead to $u_{4\Lambda}=g_{4\Lambda}\Lambda^{4-d}$. Such a result cannot be obtained in the standard theory where the various coefficients which appear in the Hamiltonian are considered as independent phenomenological quantities. We may elucidate the role of c_3 by considering the system at $d_c=4$ for which $g_3^*=g_4^*=0$. Then, as in the mean-field approach, an analytical expansion in terms of $\rho-\rho_c$ can be expected for all thermodynamics quantities. From the results given above, $n<2d_c/(d_c-2)$ in order to get a finite value for $c_{n\Lambda}$, while c_n finite requires $n<\delta+1$. At $d=d_c$ the reference system must be identical to the real one; this leads to $\delta=(d_c+2)/(d_c-2)=3$ as expected [2]. From the relation between c_2 and χ_T we get $(1-c_2)_{\rho,T_c}\sim(\rho-\rho_c)^2\sim\xi_1^{-2}$, where ξ_1 is the correlation length. From the relation between c_2 and c_3 we get $(c_2+c_3)_{\rho,T_c}\sim\rho-\rho_c\sim\xi_1^{-1}$. These results show the general dependence of c_2 and c_3 upon the correlation length. At a given value of ρ_c it is assumed [2,6] that the correlation length ξ_2 varies as $(T-T_c)^{-1/2}$, leading to $(1-c_2)_{\rho_c,T}\sim T-T_c$ and $(c_2+c_3)_{\rho_c,T}\sim\xi_2^{-1}\sim(T-T_c)^{1/2}$. In addition, from the results established above we know that $(1+c_3)_{\rho_c,T_c}=0$ while $(2+c_4)_{\rho_c,T_c}$ is a constant and then the equation of state can be written as

$$p(\rho,T)-p(\rho_c,T)=a_1(T-T_c)(\rho-\rho_c)+a_2(T-T_c)^{1/2}(\rho-\rho_c)^2+a_3(\rho-\rho_c)^3, \tag{10}$$

where the coefficients a_1, a_2, and a_3 are only functions of ρ_c and T_c. The second term on the right-hand side of (10) which is determined by c_3 does not exist in the expansion proposed by Fisher [7]; it also disappears in the standard ϕ^4 theory due to symmetry arguments. From Eq. (10) we can calculate the critical exponent β. Its value is the classical one $\beta=\frac{1}{2}$ but all three terms in (10) have the same importance in the calculation. Thus, at $d_c=4$ the DCF and their relations play a similar role as in the case $d<4$ where the fluctuations must be considered and the full calculation is needed.

In this Letter, new results have been obtained at two different levels. First, we have shown that the critical exponents can be calculated from the ingredients of the liquid-state theory without any explicit reference to the Landau-Ginzburg-Wilson Hamiltonian. Here, it is the DCF and its relations which play the main role. The closure of the OZ equation is then given by the Callan-Symanzik equation. This represents a new approach which clarifies some aspects of the standard theory. The calculations presented here can be easily extended to more general situations as for instance the case of mixtures [8] or continuum percolation [12]. Second, we have analyzed the role played by the three-body correlation function which is ignored in the standard theory. We have shown that this function participates in the critical behavior without changing the values of the critical exponents which remain those of the Ising model.

---

[1] M. Rovere, D. W. Hermann, and K. Binder, Europhys. Lett. **6**, 585 (1988).

[2] See, for instance, K. G. Wilson and J. B. Kogut, Phys. Rep. **12C**, 75 (1974); S. K. Ma, *Modern Theory of Critical Phenomena* (Benjamin, New York, 1976).

[3] See, for instance, J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, New York, 1976).

[4] A. Parola and L. Reatto, Phys. Rev. A **31**, 3309 (1975); A. Parola, A. Meroni, and L. Reatto, Phys. Rev. Lett. **62**, 2981 (1989).

[5] E. Brezin, J. C. Le Guillou, and J. Zinn-Justin, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and M. S. Green (Academic, New York, 1976), Vol. 6, p. 125.

[6] D. Amit, *Field Theory, Renormalization Group and Critical Phenomena* (World Scientific, Singapore, 1984).

[7] M. Fisher, J. Math. Phys. **5**, 944 (1964).

[8] Q. Zhang and J. P. Badiali (to be published).

[9] A. Aharony, in *Phase Transitions and Critical Phenomena* (Ref. [5]), p. 357.

[10] H. C. Andersen, in *Modern Theoretical Chemistry, Statistical Mechanics* (Plenum, New York, 1977), Vol. 5, p. 1.

[11] R. J. Baxter, J. Chem. Phys. **41**, 553 (1964).

[12] It can be shown that the same kind of theory leads to $d_c=6$ in the case of the continuum percolation [D. Di Caprio, Q. Zhang, and J. P. Badiali (to be published)].