EXTENSION OF THE ORNSTEIN-ZERNIKE THEORY II [†]

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ABSTRACT

A study is made of the terms in an expansion of the direct correlation function at the critical point. If homogeneity of long-range correlations is assumed, we find that the terms involving m-point correlation functions, $m > 2$, do not dominate the terms that depend only on pair-correlation effects. For a system with a short-range pair potential, we have previously shown that this result yields, in the usual notation, $2-\eta = \min[2, d(\delta-1)/(\delta+1)]$, d=dimensionality. It is argued that for a pair potential $V(\underset{\sim}{r}) \sim -r^{-d-\sigma}$, for $r \to \infty$, we should expect no change in this relation for $\sigma > \min[2,\tilde{s}]$, where $\tilde{s}$ is an exponent appearing in our analysis; $\tilde{s} = 7/4$ for $d=2$ and $s \approx 2$ for $d=3$. For smaller σ the problem is more complex and our analysis is only suggestive; it indicated that when $\sigma < \tilde{s}$ one should be prepared to find a marked difference in the behavior of critical exponents between the $\sigma < d/2$ and $\sigma > d/2$ cases. For the latter we again find $2-\eta = \min[2, d(\delta-1)/(\delta+1)]$. We find $2-\eta=\sigma$ in both cases.

1. INTRODUCTION

In a previous work[1] herein referred to as I, we derived a relationship between the critical exponent δ that describes the shape of the critical isotherm and the exponent η that describes the decay of the pair correlation function $\hat{h}(12)$ at the critical point as $r_{12} \to \infty$. The derivation was based upon the use of a functional expansion for $c(12)$, the direct correlation function. In addition to $V(12)$, the pair potential, the expansion involves $\hat{h}(12)$ and $c(12)$ itself [more precisely, $h(12) = \hat{h}(12) - n(1)\delta(12)$ and $\hat{c}(12) = c(12) - n(1)\delta(12)$, where n is the singlet distribution function and δ the delta function, Dirac for a fluid and Kronecker for a lattice system] as well as the functional derivatives of $\hat{c}$ with respect to n. Here and below we use the notation of I except as otherwise indicated. As in I we write a function of $\underset{\sim}{r}_{12}$ sometimes as $f(12)$ and sometimes as $f(\underset{\sim}{r}_{12})$ as convenience dictates, and often we write $\underset{\sim}{r}_2 - \underset{\sim}{r}_1$ simply as $\underset{\sim}{r}$ rather than $\underset{\sim}{r}_{12}$, with $r = |\underset{\sim}{r}|$.

The fundamental postulate used in analysing the expansion of c was the following: near the critical point the correlations between points $\underset{\sim}{r}_1, \underset{\sim}{r}_2, \ldots,$ are homogeneous in κ^{-1} (the correlation length) and r_{ij} (the distances between any pair of the points) for sufficiently large r_{ij}. Specifically it was postulated that on the critical isotherm for small κ, the long-range parts of $\hat{h}$ and $\hat{c}$ are homogeneous[2], as well as the long-range parts of the functions $\hat{c}_m = \delta^{m-2}[\hat{c}(12) - \hat{c}_c(12)]/\delta n(3)\ldots\delta n(m)$, $m > 2$, where the subscript c here and throughout refers to the critical point. From this assumption the relation

$$\hat{c}_c(\underset{\sim}{r}) \sim \hat{h}_c(\underset{\sim}{r})^{\delta}, \quad r \to \infty, \tag{1.1}$$

was obtained for a fluid or lattice gas. In I, our derivation of (1.1) rested upon our conclusion that for $r \to \infty$ the terms in the expansion of $\hat{c}_c(\underset{\sim}{r})$ containing the $\hat{c}_m$, $m > 2$, (i.e. directly manifesting m-point correlation effects for $m > 2$) do not dominate the contributions of the terms that involve only $\hat{c}$ itself and h. Because of space limitations we gave only a heuristic argument suggested by the work of Percus[3] in support of our neglect of the former terms, based upon the slowly varying nature of h_c for large r. We also dealt only with systems for which $V(\underset{\sim}{r})$ is negligibly small (for large r) compared to $\hat{h}_c(\underset{\sim}{r})^{\delta}$.

This paper has two sections beyond the introductory material of sections 1 and 2. In sec. 3 we are concerned with a system in which $V(\underset{\sim}{r})$ is short ranged. For such a system we give a detailed argument, based on the homogeneity of the long-ranged part of $\hat{c}_m$, in support of our conclusion that the terms containing $\hat{c}_m$, $m > 2$, do not dominate the terms that depend only on the behavior of the 2-point functions on the expansion of $\hat{c}_c$.

In section 4 we investigate the effect of a long-ranged $V(\underset{\sim}{r})$ of the form $-r^{-d-\sigma}$ for large r (d=dimensionality, $\sigma > 0$). We conclude that there will be no change in the relationship between δ and η for $\sigma > \min[2,\tilde{s}]$ where $\tilde{s}$ is an exponent appearing in our analysis that is 7/4 for $d=2$ and approximately 2 for $d=3$. For smaller σ the problem is much more complex, and our analysis is only suggestive, requiring as it does several strong additional assumptions. It indicates that when $\sigma < 2$ one should be prepared to find a marked difference in certain critical behavior between the $\sigma < c/2$ and $\sigma > d/2$ cases of the sort that one already finds in the simpler spherical model[4], for which $c_c = -V/kT$ for large r [k = Boltzmann's const. and T = temperature].

Since the appearance of I, Ferer et. al.[5] have concluded that when $d=3$, $\hat{h}(r)$ may not satisfy the strong form of homogeneity postulated in I. We discuss elsewhere[6] the modification in our results to be expected from weakening the homogeneity assumption in a way suggested by their work; here we retain the homogeneity assumption of I but point out some aspects of our work that will be unchanged if it turns out that the assumption of I must be weakened for $d=3$. For $d=2$, there is no evidence of the breakdown of homogeneity.

2. GENERAL RELATIONS AND ASSUMPTIONS

Our starting point in I was the assumption that when $T=T_c$, $\hat{h}(\underset{\sim}{r})$ is a homogeneous function of degree $t-d$ in r and κ^{-1} for r and κ^{-1} both large compared to the particle diameter or distance between lattice sites, which we shall denote as a. Thus we postulate $\hat{h} = \hat{h}^S + \hat{h}^L$, where for $r \gg a$, $\hat{h}=\hat{h}^L$, with $\hat{h}^L$ given by

$$\hat{h}^L \cong f(\kappa r) r^{t-d} = \kappa^{d-t} e(\kappa r), \tag{2.1a}$$

$$\hat{h}_c^L \cong \text{const } r^{t-d}. \tag{2.1b}$$

The precise functional form of $f(x)$ and $e(x)$ will not concern us. In the same spirit[2] we write $\hat{c} = \hat{c}^S + \hat{c}^L$ where for $r \gg a$, $\hat{c}=\hat{c}^L$, with $\hat{c}^L$ given by

$$\hat{c}^L \cong F(\kappa r) r^{-s-d} = \kappa^{s+d} E(\kappa r), \tag{2.2a}$$

$$\hat{c}_c^L \cong \text{const } r^{-s-d}. \tag{2.2b}$$

We use t here to denote what is usually written as $2-\eta$, and the inverse correlation length κ in (2.1) and (2.2) can be defined by the equation

$$\kappa^{-2} = \int r^2 \hat{h}(\underset{\sim}{r})\, d\underset{\sim}{r} \Big/ \int \hat{h}(\underset{\sim}{r})\, d\underset{\sim}{r}. \tag{2.3}$$

From (2.1a) and the suppostion that $\int \hat{h}^S(\underset{\sim}{r}) d\underset{\sim}{r}$ is bounded, we conclude

$$\int \hat{h}(\underset{\sim}{r})\, d\underset{\sim}{r} \sim \kappa^{-t}. \tag{2.4}$$

Eq. (2.4) can in fact be used instead of (2.3) to define κ when $\int r^2 \hat{h}(\underset{\sim}{r})d\underset{\sim}{r}$ does not exist, as in the case of very long-range potentials[7]. The functions $\hat{h}(\underset{\sim}{r})$ and $\hat{c}(\underset{\sim}{r})$ are related to one another in a way easily expressed in terms of their d-dimensional Fourier transforms $\hat{H}(\underset{\sim}{k})$ and $\hat{C}(\underset{\sim}{k})$:

$$\rho \hat{H}(\underset{\sim}{k}) = - \hat{C}(\underset{\sim}{k})^{-1}, \tag{2.5}$$

where ρ is number density and $F(\underset{\sim}{k}) = \int f(\underset{\sim}{r}) e^{i\underset{\sim}{r}\cdot\underset{\sim}{k}} d\underset{\sim}{r}$. Here and throughout the article the integral $\int d\underset{\sim}{r}$ stands for a sum over lattice sites in the lattice-gas case. We note that

$$\rho(d\mu/d\rho) = -\rho\hat{C}(0) = -\rho\int \hat{c}(\underset{\sim}{r})d\underset{\sim}{r} \quad ,$$

where μ is the chemical potential. For a lattice gas with a volume per site of v_o and an occupation variable τ taking the values 0 or 1, the function $\hat{h}$ is given in the notation often used for lattice correlations by

$$(\rho v_o)^2 \hat{h}(r_{ij}) = \langle \tau_i \tau_j \rangle - \langle \tau_i \rangle \langle \tau_j \rangle \quad .$$

Several distinct cases appear in our analysis depending upon the magnitude of $t/2$. To see the way in which they arise we note that at the critical point (2.1b) and (2.2b) imply that there is a p such that

$$\hat{c} \sim \hat{h}^p \text{ for } r >> a \tag{2.6}$$

where

$$\lambda = p(d-t) - d \quad . \tag{2.7}$$

Also consistent with (2.1b) and (2.2b) are the expressions

$$\hat{H}_c(\underset{\sim}{k}) \simeq \text{const}\, k^{-t}, \quad k \to 0; \tag{2.8}$$

and

$$\hat{C}_c(\underset{\sim}{k}) \simeq \text{const}_1 k^{s} + \text{const}_2 k^{2} + \cdots, \quad k \to 0, \tag{2.9}$$

where the term of order k^0 in (2.9) is zero because $\hat{C}_c(\underset{\sim}{k}) = 0$ at $k=0$. Using (2.5) to compare (2.8) and (2.9) we conclude that in general $s \geq t$, and if $\text{const.}_2 \neq 0$, that $t = \min[2,s]$, so if $s < 2$, (2.7) yields $t = s = d(p-1)/(p+1)$. Thus we can write, if $\text{const}_2 \neq 0$,

$$t = \min[\,2,\ d(p-1)/(p+1)\,]. \tag{2.10}$$

On the other hand, if $\text{const}_2 = 0$ we would have $t = s = d(p-1)/(p+1)$ for $s > 2$, as long as s were smaller than the smallest unexhibited power of k in (2.9). In general, we find no reason to assume $\text{const}_2 = 0$, and would expect in fact a whole series of even-power terms in (2.9) with non-zero coefficients that define the spatial moments of $\hat{C}_c^{\,S}$.

The relations (2.3) through (2.10) hold even under the weakened form of homogeneity postulated in ref. [5] since they do not rest upon (2.1a) or (2.2a), but depend only on the (b) parts of (2.1) and (2.2), which are not brought into question by the work of Ferer et. al.

In the special case of $s=2$, (2.2b) implies that at the critical point

$$\hat{C}_c(\underset{\sim}{k}) = \text{const}\, k^2 \ln k + \text{const}_3 k^2 + \ldots, \quad k \to 0,$$

and as a result, (2.1), (2.2) and (2.5) are no longer compatible. However, the asymptotic forms

$$\hat{c}(\underset{\sim}{r}) \simeq F(\kappa r) r^{-d-2} (\ln r)^{(-2-d)/2d}, \quad r \to \infty, \tag{2.11}$$

$$\hat{h}(\underset{\sim}{r}) \simeq f(\kappa r) r^{2-d} (\ln r)^{(2-d)/2d}, \quad r \to \infty, \tag{2.12}$$

are compatible with the critical-point transforms

$$\begin{aligned} \hat{C}_c(\underset{\sim}{k}) &\simeq \text{const}\, k^2 (\ln k)^{(d-2)/2d} + \cdots, \quad k \to 0, \\ \hat{H}_c(\underset{\sim}{k}) &\simeq \text{const}\, k^{-2} (\ln k)^{(2-d)/2d} + \cdots, \quad k \to 0, \end{aligned} \tag{2.13}$$

and hence with (2.5). Eq. (2.6) is satisfied as well with

$$\gamma = (d+2)/(d-2). \tag{2.14}$$

We introduced (2.6) here solely as a consequence of (2.1b) and (2.2b). In the next section however, it will be shown an independent set of considerations lead us to (2.6), with $p = \delta$ [i.e. to Eq. (1.1)] and that for a special value of δ this is true even if (2.1) and (2.2) are not assumed, as long as it is assumed that the chemical potential μ behaves in the simple way near the critical point given by (2.19). The somewhat less restrictive assumption (3.16) leads to a generalization of (2.6)

$$\hat{c} \sim \hat{h}^p (\ln \hat{h})^q. \tag{2.15}$$

If $s=2$, then (2.15), (2.5), and (2.14) are satisfied when $q < 1$ if (2.11) and (2.12) are generalized to

$$\hat{c}(\underset{\sim}{r}) \simeq F(\kappa r) r^{-d-2} (\ln r)^{[q(d-2)-d-2]/2d}, \quad r \to \infty, \tag{2.16}$$

$$\hat{h}_m(r) \simeq f(\kappa r)\, r^{z-d} (\ln r)^{(q+1)(z-d)/zd}, \quad r \to \infty. \tag{2.17}$$

The case $s=2$, $q \leq -1$ requires further analysis reminiscent of the case $p \geq (d+2)/(d-2)$ in (2.6) For $s\neq 2$, different powers of $\ln r$ in $\hat{c}$ and $\hat{h}$ would have to be used to maintain consistency between (2.15) and (2.5), but only in the special case of $s=2$ does there appear any compelling reason for investigating (2.15) in the first place. Similarly for $s\neq 2$, one can modify (2.1) and (2.2) by including, for example, factors of $\ln r$ to certain powers that will be consistent with (2.5) and (2.6), but only for $s=2$ is one forced to go beyond the simple homogeneity assumptions of (2.1) and (2.2) in order to maintain consistency between (2.5) and (2.6).

In addition to (2.5) we shall use a second relation that involves $\hat{h}$ and $\hat{c}$. It is given by the expressions

$$\begin{aligned} C(12) &= -V(12)/kT + R(12), \\ R(12) &= -[\mu_0 - \mu - \rho h(12)\, d\mu/d\rho\,]/kT + \sum_{m\geq 1} S_m, \end{aligned} \tag{2.18}$$

$$S_m(12) = (\rho^m/m!) \int \hat{C}_{m+1}(1,3,\cdots,m+2)_0 \prod_{i=3}^{m+2} \{[h(i2) - h(12)]\, d(i)\}.$$

In (2.18), the subscript zero denotes that the quantity labeled is to be evaluated at the number density $\rho g(12)$ rather than at ρ. It was noted in I that if we assume

$$|\mu - \mu_c| \sim |\rho - \rho_c|^{\delta} \tag{2.19}$$

then $-[\mu_o - \mu - \rho h(12)\, d\mu/d\rho]/kT \sim h(12)^{\delta}$ at the critical point, so that if neither V nor S_m dominates $h(12)^{\delta}$ as $r_{12} \to \infty$ at the critical point, then we shall have (1.1). The relative sizes of S_m, h, and V are the subject of the next two sections.

3. THE GENERAL TERM IN THE EXPANSION OF C

In our analysis, all of which takes place at $T=T_c$, we shall make repeated use of the expressions in this paragraph to express various results as powers of $\hat{h}(\underset{\sim}{r})$ after getting them as powers of κ_0 and to simplify the expressions for the powers of h. If $\kappa \sim |\rho-\rho_c|^{\varepsilon}$ at $T=T_c$, then at $T=T_c$, $\partial^i \kappa^q/\partial\rho^i \sim \kappa^{q-(i/\varepsilon)}$, so that at $T=T_c$, $\rho=\rho_c$, we have $\partial^i \kappa_0^{\,q}/\partial\rho_0 = \kappa_0^{\,q-(i/\varepsilon)}$ and $\kappa_0 \sim r_{12}^{(d-t)\varepsilon} \sim \hat{h}_c(12)^{\varepsilon}$. Furthermore $(d-t)\varepsilon > 2$ (from the Gunton-Buckingham inequality[9] and $t\varepsilon = \delta - 1$) and $d\varepsilon > t\varepsilon+2 = \delta+1$. (We also conjecture that $(d-s)\varepsilon = 2$, even when $s > t$, but we do not use this conjecture here). Here and below we use q to stand for whatever power of h appears in a particular discussion; it does not have a fixed meaning throughout the article.

We consider next the properties of $\hat{c}_m^S$ and $\hat{c}_m^L$, $m > 2$, that we shall postulate, where $\hat{c}_m^E$ for E either S or L is defined by

$$\delta^{m-2}[\hat{c}^E(12)-\hat{c}_c^E(12)]/\delta n(3) \ldots \delta n(m) = \hat{c}_m^E$$

for $m > 2$. We extend this definition to $m=2$ by setting $\hat{c}_2^E = \hat{c}^E(12)-\hat{c}_c^E(12)$.

Since $\hat{c}^S(12) \sim 0$ if $r_{12} >> a$ and since $\hat{c}_m^E(1, \ldots, m)$ is completely symmetrical in the variables $\underset{\sim}{r}_{ij}$, $1 \leq i < j \leq m$, we believe it is reasonable to further postulate that

$$\hat{c}_m^S \sim 0 \text{ if } r_{ij} >> a \text{ for any } r_{ij},\ 1 \leq i < j \leq m. \qquad (3.1)$$

Because we know $\int[\hat{c}(12)-\hat{c}_c(12)]d(2) \sim \kappa^t$ [from (2.4) and (2.5)] as well as

$$\int[\hat{c}^L(12)-\hat{c}_c^L(12)]d(2) \sim \kappa^L, \qquad (3.2)$$

[from (2.2a)] we conclude

$$\int [\hat{c}^S(12) - \hat{c}_c^S(12)]\, d(2) \sim \kappa^{\delta} \text{ where } \delta \geq t. \tag{3.3}$$

Because

$$\int \hat{c}^E_{m+2}(1,\ldots,m+2)\, d(2)\ldots d(m+2) = \partial^m / \partial \rho^m \int [\hat{c}^E(12) - \hat{c}_c^E(12)]\, d(2), \tag{3.4}$$

(3.3) in turn yields

$$\int \hat{c}^S_{m+1}(1,\ldots,m+1)\, d(2)\ldots d(m+1) \sim \kappa^{\delta - [(m-1)/\epsilon]} \text{ at } T=T_c,\ \delta \geq t. \tag{3.5}$$

In keeping with (2.2a), and more generally with the whole notion of homogeneity in κ^{-1} and r_{ij} of long-range correlations near the critical point, we postulate[2]

$$\hat{c}^L_{m+1} \simeq \kappa^p E(\kappa_{ij}), \text{ where } \kappa = \kappa r,\ 1 \leq i,j \leq m+1. \tag{3.6}$$

We can immediately find p, since from (3.1), $\int \hat{c}^L_{m+1} d(2) \ldots d(m+1) \sim \kappa^{D-md}$ while from (3.2) and (3.4)

$$\int \hat{c}^L_{m+1}\, d(2)\ldots d(m+1) \sim \partial^{m-1}\kappa / \partial \rho^{m-1}, \sim \kappa^{s-[(m-1)/\epsilon]}, \tag{3.7}$$

so

$$p = s - [(m-1)/\epsilon] + md, \tag{3.8}$$

and $\int (\hat{c}^L_{m+1})_0 d(1) \ldots d(m) \sim h_c(r)^q$, $q \geq \delta - m$.

Instead of calling the vectors over which we do not integrate (in S_m) $\underset{\sim}{r}_1$ and $\underset{\sim}{r}_2$, it will prove a bit more convenient here to call them $\underset{\sim}{r}_\alpha$ and $\underset{\sim}{r}_\beta$ (and to write $\underset{\sim}{r}$ for $\underset{\sim}{r}_\beta - \underset{\sim}{r}_\alpha$ rather than for $\underset{\sim}{r}_2 - \underset{\sim}{r}_1$). We shall study each S_m by setting $\hat{c}_m = \hat{c}^L_m + \hat{c}^S_m$ and considering separately the integrals $\int \hat{c}^E_{m+1}(\alpha,1,\ldots,m)_0 \pi_{i=1}^m \{[h(i\beta) - h_c(\alpha\beta)]d(i)\}$ with E first taken

as L and then S. Each such integral can itself be written as a sum of terms of the form

$$h_{c_m}(r)^{m-\ell}\int(\hat{c}^{E}_{m+1})(\alpha,1,\ldots,m)_0\left[\pi_{i=1}^{\ell}h_c(i\beta)\right]d(1)\ldots d(m)\,, \qquad (3.9)$$

where $\ell \leq m$. For convenience let us use abbreviated notation to denote the integral of (3.9) as $\int(\hat{c}^{E}_{m+1})_0\pi_\ell h_c\, d[m]$. Since

$$\int(\hat{C}^{E}_{m+1})_0\,\pi_\ell h_c\, d[m] = \partial^{m-\ell}/\partial\rho^{m-\ell}\int(\hat{C}^{E}_{\ell+1})_0\pi_\ell h_c\, d[\ell], \qquad (3.10)$$

we need only evaluate

$$\int(c^{E}_{\ell+1})_0\pi_\ell h_c d[\ell]\,,$$

which will prove to be asymptotically proportional to a power of $h_c(r_m)$ under our assumptions. Then, because

$$h_c^{m-\ell}\left(\partial^{m-\ell}h_c^{\ell}/\partial\rho_0^{m-\ell}\right)\sim h_c^{\ell}, \quad r\to\infty, \qquad (3.11)$$

we can immediately use our evaluation to find (3.9), and hence S_m.

For $r\to\infty$, we argue that

$$\int(\hat{C}^{4}_{\ell+1})_0\,\pi_\ell h_c\, d[\ell]\to\int\hat{C}^{4}_{\ell+1}(\alpha,1,\ldots,\ell)_0\,\pi_{i=1}^{\ell}\left[h_c^{4}(\alpha i)\,d(i)\right]. \qquad (3.12)$$

This follows from the observation that as $r\to\infty$ for $q < (d-t)\varepsilon$, the interval $r^q < r_{\alpha i} < \infty$ becomes equivalent to the interval $0 < \kappa_0 r_{\alpha i} < \infty$. This interval defines the domain of integration of the left-hand side of (3.12); so if we choose $q < (d-t)\varepsilon$ we can write

$$\int(\hat{C}^{4}_{\ell+1})_0\,\pi_\ell h_c\, d[\ell]\simeq\int_{\Omega}(\hat{C}^{4}_{\ell+1})_0\,\pi_\ell h_c\, d[\ell]\,, \qquad (3.13)$$

where Ω is the domain such that $r_{\alpha i}\geq r^q$; $1\leq i\leq\ell$. But as long as $q > 1$ (and we can so choose it) then the right-hand side of (3.13) approaches the right-hand side of (3.12) as $r\to\infty$. Using (3.6), (3.8), and (2.1b), we estimate the right hand side of (3.12) to be $\sim\kappa_0^{s-[(\ell-1)/\varepsilon]+\ell(d-t)}\sim h_c(r_m)^q$, $q = \delta+\ell$ if $s=t$ and $q > \delta+\ell$ if $s > t$. Thus from (3.10) and (3.11) we have

$h_c(\underset{\sim}{r})^{m-\ell}\int(\hat{c}^{L}_{m+1})_0\pi_\ell h_c d[m] \sim h_c(\underset{\sim}{r})^q$, $q \geq \delta+\ell$.

We must finally consider the contributions from expressions of the form $\int(\hat{c}^{S}_{\ell+1})_0\pi_\ell h_c d[\ell]$, which are $\sim h_c(\underset{\sim}{r})^\ell\int(\hat{c}^{S}_{\ell+1})_0 d(2) \ldots d(\ell)$. From (3.5), this expression is $O(h_c^\delta)$. Thus, using (3.10) and (3.11) for E=S we find that $h_c(\underset{\sim}{r})^{m-\ell}\int(\hat{c}^{S}_{m+1})_0\pi_\ell h_c d[m] \sim O(h_c^\delta)$, $r \to \infty$, as well.

Putting our results together, we see that the dominant contribution to S_m comes from interaction of the h's and $\hat{c}^{S}_{m+1}$, rather than $\hat{c}^{L}_{m+1}$. There is no contribution to S_m of order lower than $h_c(\underset{\sim}{r})^\delta$. Thus according to (2.18), if $V(\underset{\sim}{r})$ is negligibly small, $c_c(\underset{\sim}{r})$ itself will be of order $h_c(\underset{\sim}{r})^\delta$ for $r \to \infty$ when homogeneity of the long-range correlations is assumed, and the p in (2.6) and (2.10) must be δ.

There remains to be treated the special but important case of

$$\alpha = d(\delta-1)/(\delta+1) . \tag{3.14}$$

This is not covered by our previous arguments since in this case we would be led to $s=2$ by (2.1b), (2.2b), (2.5), and (1.1), except that when $s=2$, then (2.1b), (2.2b) and (2.5) are no longer compatible, as pointed out in section II. Thus we are forced to modify at least one of our assumptions. The most gentle modification that can be contemplated appears to be the retention of (2.19) and the replacement of (2.1) and (2.2) by (2.11) and (2.12). It is easily checked that (1.1) is still consistent with (2.5), for (2.13), and (2.14) and that in (2.10) $\mu_0-\mu-\rho du/d\rho$ still contributes a term of order h_c^δ to c_c. The remaining question is therefore whether the $(S_m)_c$ still fail to dominate h_c^δ. When the preceding arguments of this section are applied, the ℓn terms in (2.11) - (2.14) will introduce powers of $\ell n\kappa_0$ as well as powers of κ_0 in the analysis of (3.9), and it is necessary to know what ℓn terms appear in the relation between κ and ρ. Assuming

(2.19), we find at $T=T_c$

$$\kappa^2(\ln\kappa)^{1/6} \sim |\rho-\rho_c|^{\delta-1}. \tag{3.15}$$

This comes from comparing $d\mu/d\rho \sim |\rho-\rho_c|^{\delta-1}$ with the result $d\mu/d\rho \sim \kappa^2(\ln\kappa)^{1/6}$, which follows from the use of (2.12) in $[\rho\int\hat{h}(\underset{\sim}{x})d\underset{\sim}{x}]^{-1} = \rho\, d\mu/d\rho$. It follows that the most dominant terms in $(S_m)_c$ are all of order h_c^{δ}. For example $h_c\int\hat{c}^L d\underset{\sim}{r} \sim h_c\kappa_0^2(\kappa_0)^{1/6}$, which from (3.15) is of order h_c^{δ}. The analysis of the general term is more tedious but no more difficult; it is basically because $|\rho-\rho_c|d\kappa/d\rho$ is not of lower order in $\rho-\rho_c$ than κ itself that all terms involving $\hat{c}_m$, $m > 2$, cannot be of lower order than the simple terms involving only $\hat{c}_2$. The situation remains similar if

$$|\mu-\mu_c| \sim |\rho-\rho_c|^{\delta}|\ln|\rho-\rho_c||^{q} \tag{3.16}$$

is assumed instead of (2.19) with (2.15), (2.16) and (2.17) restoring consistency instead of (1.1), (2.13) and (2.14). Here the dominant term in $(S_m)_c$ would be of order $h_c^{\delta}(\ln h_c)^q$.

4. LONG-RANGE POTENTIALS

We turn now to a discussion of the case of a long-range (LR) potential $V \sim -r^{-d-\sigma}$ for $r \to \infty$. In Eq. (2.18) there is now a competition between $-\beta V$ and R_c to consider. We first ask if it is reasonable to assume that R_c still looks like h_c^p as $r \to \infty$ with p equal or very close to δ. We believe so, and using our knowledge of both the Ornstein-Zernike (OZ) case[8] [$R_c = 0$ for large r as in the spherical model[4]] and the short-range (SR) case [$V=0$ for large r] to guide us, we argue as follows: Assuming (2.19) it immediately follows that $[\mu_0-\mu-\rho h d\mu/d\rho]_c$ still looks like h_c^δ, so we can pass on to an analysis of the S_m. It still appears reasonable to postulate that $h_c \sim r^{t-d}$. (In the OZ case this is so with $t = \min[\sigma,2]$; in the Ising case the simplest possibility consistent with known results appears to be

$$t = \min[\sigma, 2, \tilde{t}] \tag{4.1}$$

where a tilda here and below refers to the SR case). We must take care in defining κ in the case of an LR potential -- for small σ, κ defined by (2.3) no longer exists. However we can use (2.4) as a definition of κ for such cases[7]. It is then still as reasonable as in the SR case to assume that for $r >> a$, $\hat{c}-\hat{c}_c$ is homogeneous in $\Lambda = \kappa^{-1}$ and r of degree $-d-s$. The rationale also remains for making the same assumptions on the $\hat{c}_m^S$ and $\hat{c}_m^L$ that we used in the SR case[10] where we found $R_c \sim h_c^p$, with $p=\delta$ when homogeneity of the $\hat{c}_m^L$ was assumed. Even in three dimensions, where homogeneity of the correlations can be questioned, p departs only very slightly from δ, on the basis of Eq. (2.10) and the currently accepted value of $t[\simeq 49/25]$. Thus we conclude that in the LR case as well as the SR case,

$$c_c \doteq -V/kT + O(h_c^p), \tag{4.2}$$

where $p=\delta$ if strict homogeneity of the $\hat{c}_m^L$ is assumed and $p\approx\delta$ otherwise. From (4.2), (2.1b), (2.2b), and (2.5) we have the useful relation

$$d+s = \min[(d-t)p, d+\sigma]. \tag{4.3}$$

Consequences of the above argument are most directly obtained -- and the argument itself is at its most convincing -- for the case $\sigma > \tilde{s}$ since $\sigma > \tilde{s}$ implies that as $r \to \infty$, V can be neglected compared to the R_c that one would have had if V were negligible in the first place. Hence we are led to $p=\tilde{p}$. (For $d=2$, $\tilde{s}=7/4$, while for $d=3$, $\tilde{s}$ appears to be 2 or a bit less.) Thus where $\sigma > \tilde{s}$, we expect no difference between κ and $\tilde{\kappa}$, and assuming $\tilde{p}=\tilde{\delta}$, no difference from the SR result:

$$t = \min[2, d(\delta-1)/(\delta+1)].$$

If $\sigma < \tilde{s}$ the situation is more complex. If we continue to assume that V can be neglected compared to R_c so that exponents have the same values as in the SR case with $d+\sigma > (d+\tilde{t})\tilde{p}$, we arrive at a contradiction, since $(d-\tilde{t})\tilde{p} = d+\tilde{s}$. Hence if $\sigma > \tilde{s}$, it is no longer plausible to postulate that V can be neglected compared to R_c, i.e. that $d+\sigma \geqslant (d-\tilde{t})\tilde{p}$. This suggests that when $\sigma < \tilde{s}$ we start instead with the trial assumption that R_c can be neglected compared to V, i.e. that the presence of R_c in (4.2) will not shift the values of the critical exponents away from their OZ values. On the basis of this starting point we can compare h_c^{δ} and R_c as $r \to \infty$. Letting a dot denote an OZ value, we have $\dot{s}=\sigma$, and Eq. (4.2) now tells us that $(d-t)p > d+\sigma$, so that h_c^p cannot dominate V. Thus our trial assumption is at least self consistent. If we further assume that

$p=\delta$, we have $p=\dot{\delta}$ with $\dot{\delta}=(d+\sigma)/(d-\sigma)$ when $d/2 < \sigma < d$, $\sigma < 2$, and $\dot{\delta}=3$ when $0 < \sigma < d/2$, $\sigma < 2$. From these expressions follow co-dominance of V and R_c for $d/2 < \sigma < d$, if $\sigma < 2$, and strict dominance of V for $0 < \sigma < d/2$, if $\sigma < 2$. When $\sigma > 2$ we expect $2 < \tilde{s}$ only for $d > 4$, for which $\dot{\delta}=3$, so that V will strictly dominate R_c under our trial assumption as long as $\sigma < 3d-6$. But for $d > 4$, we expect precisely $\tilde{s} = 3d-6$ from $d+\tilde{s} = (d-\tilde{t})\tilde{\delta}$, so we conclude that V will strictly dominate R_c for all $2 < \sigma < \tilde{s}$. In summary: if $\sigma < \tilde{s}$, the hypothesis that V leaves s unchanged at $\tilde{s}$ is self-contradictory, whereas the plausible assumption that R_c will not shift s away from $\dot{s}$ satisfactorily leads us back to the consistent conclusion that R_c will not dominate V. The additional postulate that the $\hat{c}_m^L$, $m \geq 2$, are homogeneous further suggests the result $t = \sigma = d(\delta-1)/(\delta+1)$ for $d/2 < \sigma < \min[d,2]$ and $t=\sigma$, $\delta = 3$ for $0 < \sigma < \min[d/2,2]$. For the values $\sigma = d/2$, $\sigma = d$ we would expect log terms to appear in $\mu-\mu_c$ as $\rho-\rho$ and in $h(\underset{\sim}{r})$, as they do in the spherical model. For the value $\sigma = \tilde{s}$, similar complexity could also appear because of the possible confluence of the V and R_c terms at this value.

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References

1. G. Stell, Phys. Rev. Letters, 20, 533 (1968).

2. In keeping with Eq. (2.1) and its obvious generalization to m-point correlations, $m > 2$, is the assumption that the Fourier transforms of these correlation functions are homogeneous functions in κ and k_{ij}, the relevant transform variables, for small κ and small k_{ij}. This observation is our primary motivation for extending the homogeneity postulate from the full correlation functions to the $\hat{c}_m$, $m \geq 2$, through the equations in transform-space that relate them, such as Eq. (2.5).

3. This idea that functional expansions about $\rho g(12)$ rather than ρ are especially appropriate near the critical point was exploited already by J.L. Lebowitz and J.K. Percus, J. Math. Phys. 4, 116, 248 (1963).

4. See G.S. Joyce, Phys. Rev., 146, 349 (1966).

5. M. Ferer, M.A. Moore, and M. Wortis, Phys. Rev. Letters 22, 1382 (1969).

6. G. Stell, A New Relation Among Critical Exponents (to appear).

7. This definition of κ has been used by W. Theumann in considering such potentials (private communication).

8. G. Stell, Some Critical Properties of Ornstein-Zernike Systems (to appear in Phys. Rev.).

9. J.D. Gunton and M.J. Buckingham, Phys. Rev. Letters, 20, 143, (1968).

10. We note that retaining the homogeneity assumption on $\hat{c}_m^L$ is quite a different matter than assuming that $\hat{h}$ and $\hat{c}$ are in general not sensitive to changes in the range of V. We would expect $\hat{h}$ and $\hat{c}$ to look greatly different off the critical point as $r \to \infty$ in the SR and LR cases, with $\hat{h}$ and $\hat{c}$ both experiencing an exponential decay in the SR case, but looking instead like $\hat{h} \approx (\rho d\mu/d\rho)^{-2}(-\beta V)$ and $\hat{c} \approx -\beta V$ as $r \to \infty$ in the LR case. These differences in the LR case do not act in any obvious way to make the $\hat{c}_m^L$ less homogeneous.