fit, for example, the well-known moment relations,[3] but they must in addition also show the proper behavior of the current-current correlation function as reflected in $\Omega(\kappa)$.

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EXTENSION OF THE ORNSTEIN-ZERNIKE THEORY OF THE CRITICAL REGION*

G. Stell†

Laboratoire de Physique Théorique et Hautes Energies,‡ Orsay, France

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We derive a new relationship between the shape of the critical isotherm and the range of the two-particle correlation function.

In this note we extend some results of Percus and Stell,[1] based on work of Percus[2,3] and of Lebowitz and Percus,[4] to obtain a new relation between the shape of the critical isotherm in the critical region and the range of the total correlation function $h(r)$ at the critical point. In two dimensions the relation coincides with the single expression (13) that Fisher[5] has shown to follow from the work of Widom[6] and of Kadanoff.[7] The relation will also reduce to (13) for $d \geqslant 3$ (d is the number of dimensions) if one assumes that the second moment of $c(\vec{r})$, the direct correlation function, is identically zero at the critical point, but we shall note that there is evidence that it is not.

Our results support the view that the case $d \geqslant 3$ is qualitatively different from the case $d = 2$, with respect to the scaling relations, and they further suggest that $d = 3$ may be on a rather more subtle borderline in this connection than heretofore suspected. They reveal at least one aspect of a mechanism that may invalidate those scaling laws in which d explicitly appears, and suggest that the appearance of the pair potential $V(\vec{r})$ through its second moment is a crucial part of that mechanism.

We use the notation by Fisher,[5] which is defined here by (6) and (7). Assuming a nonzero M_2, where $M_2 = \int c(\vec{r}) r^2 d\vec{r}$, $r = |\vec{r}|$, we find that

$$\eta = 2 - [d(\delta-1)/(\delta+1)] \quad \text{if } 2 > d(\delta-1)/(\delta+1);$$
$$= 0 \quad \text{if } 2 < d(\delta-1)/(\delta+1). \qquad (1a)$$

When $2 = d(\delta-1)/(\delta+1)$, we also find that either the functional form given by (6), and also (9), or that given by (7), consequently (9) and (11), must be modified in order to have consistency among these expressions and (2). Perhaps the simplest and most natural modification follows from retaining (7) and adjusting (6) accordingly; we then find that at the critical point

$$h(\vec{r}) \simeq \frac{A_l}{r^{d-2} (\ln r)^{(d-2)/2d}} \quad \text{for } r \to \infty. \qquad (1b)$$

However, modifications in which ln factors appear in both $h(\vec{r})$ and $\mu - \mu_c$ are also possible. (The subscript c will refer to a critical value wherever used.)

We begin by writing the Ornstein-Zernike[8] integral equation that relates the total correlation function $h(12) = g(12) - 1$ to $c(12)$, where we let 12 stand for $\vec{r}_{12}$. Also letting $d(i)$ stand for $d\vec{r}_i$, we have, for a uniform system of density ρ

$$h(12) = c(12) + \rho \int h(13) c(23) d(3). \qquad (2)$$

Among the various ways[2-4] of writing a second expression relating h to c, perhaps the simplest comes from a functional expansion of $\gamma(1) = \lambda + \beta\mu - \beta\varphi(1)$, where $\lambda = \frac{3}{2}\ln(2\pi m/\beta h^2)$, μ is the chemical potential, β^{-1} is Boltzmann's constant times the absolute temperature, h is Planck's constant, and $\varphi(1)$ is the external field at $\vec{r}_1$. The functional derivative of $\gamma(1)$ with respect to $n(2)$, the one-particle distribution function, is $[\delta(12)/n(1)] - c(12)$ [$\delta(12)$ is the Dirac delta function], which we shall denote as $-\hat{c}(12)$:

$$\frac{\delta\gamma(1)}{\delta n(2)} = \frac{\delta(12)}{n(1)} - c(12) = -\hat{c}(12). \qquad (3)$$

From Eq. (3.4), p. 249, of Ref. 4 we obtain, after some manipulation,

$$c(12)=-\beta V(12)-\beta[\mu_0-\mu-\rho h(12)d\mu/d\rho] +\rho(\Delta\hat{c}*\Delta h)-S(12), \quad (4)$$

where

$$\Delta\hat{c}*\Delta h=\int[\hat{c}_0(13)-\hat{c}(13)]h(23)d(3) -\int[\hat{c}_0(13)-\hat{c}(13)]h(12)d(3); \quad (5a)$$

$$S=\sum_{s\geq 2}S_s,\quad S_s=\frac{\rho^s}{s!}\int\frac{\delta^s\gamma(1)}{\delta n(3)\cdots\delta n(s+2)}\bigg|_0 \times\prod_{i=3}^{s+2}\{[h(i2)-h(12)]d(i)\}; \quad (5b)$$

and the subscript zero denotes that the quantity labeled is to be evaluated at the number density $\rho g(12)$ rather than ρ.

Equation (4) is the basis for the rest of our discussion. We use it because $h(r)$ is a quite slowly varying function of r for large r at the critical point, and in the limit of infinitely slowly varying h, one is left with only $-\beta V$ plus the next term in square brackets involving μ_0. The most obvious way of evaluating the deviation from this limiting relation is to assume that $\rho(\Delta\hat{c}*\Delta h)$ gives the largest contribution, S_2 constitutes the next most important term, etc. However, h is slowly varying only for large r_{12} and has a short-ranged part that can be quite rapidly varying and peaked around the origin, so that we cannot expect this formal ordering scheme to be more than suggestive. Nevertheless, a detailed study that we have made indicates that although $\Delta\hat{c}*\Delta h$ and the S_s do contribute terms of the same order of magnitude as $\beta[\mu_0-\mu-\rho h d\mu/d\rho]$, they in fact yield no terms that dominate it. Here we shall simply take this conclusion as an assumption, referring only briefly to the argument in its support and dwelling instead on its consequences.

We introduce η and δ by assuming that at the critical point

$$h(12)\simeq A_1/r_{12}^{\,d+\eta-2}\quad (r_{12}\to\infty). \quad (6)$$

We also assume that in the critical region the critical isotherm is described by the equation[9]

$$\mu(\rho)-\mu(\rho_c)\simeq A_2|\rho-\rho_c|^\delta\,\mathrm{sgn}\{\rho-\rho_c\}. \quad (7)$$

If (7) is assumed, at the critical point (5) becomes just

$$c(12)\simeq-\beta V(12)-\beta A_2|\rho_c h(12)|^\delta\,\mathrm{sgn}h(12) +\rho_c(\Delta\hat{c}*\Delta h)-S(12)\quad (r_{12}\to\infty). \quad (8)$$

For simplicity we shall only consider $V(12)$'s that fall off fast enough so that the first term in (8) can be neglected as $r_{12}\to\infty$.

In order to complete our analysis of the last two terms of (8) in the critical region, we have assumed further that in that region, c and h can each be written as the sum of a short-ranged part that can be neglected for large r_{12} and a long-ranged part with a dominant term of the form $f(\kappa r)/r^p$, where κ is an inverse correlation length that goes to zero at the critical point:

$$h(12)=h^S(12)+f_a(\kappa r_{12})/r_{12}^{\,d+\eta-2}+\cdots, \quad (9a)$$

$$c(12)=c^S(12)+f_b(\kappa r_{12})/r_{12}^{\,d+s}+\cdots. \quad (9b)$$

Here f_a and f_b are assumed to behave like nonzero constants for $\kappa=0$ and large r_{12}. To illustrate our conclusion that we must anticipate a contribution of $O(h^\delta)$ from the last two terms in (8), we rewrite the last term of (5a) with the aid of (7), to find that at ρ_c and T_c

$$-\rho_c\int[\hat{c}_0(13)-\hat{c}(13)]h(12)d(3) \simeq\delta\beta A_2(\mathrm{sgn}h)|\rho h|^\delta\quad (r_{12}\to\infty). \quad (10)$$

The rest of $\Delta\hat{c}*\Delta h$ can also yield a contribution of $O(h^\delta)$ as a result of the convoluting of the short-ranged part of $\Delta\hat{c}$ with h, and one cannot in general expect exact cancellation between these two $O(h^\delta)$ terms. However, contributions from the convolution of h and the long-ranged part of $\Delta\hat{c}$ appear to be negligible. Similar analysis of the S_s yields further contributions of order h^δ but no terms of lower order; our conclusion is finally that at ρ_c and T_c

$$c(12)\simeq A_3h(12)^\delta\ \text{as}\ r_{12}\to\infty, \quad (11)$$

with A_3 unassessed but assumed to be $\neq 0$ in what follows.

We now use the sort of argument that was initiated by Green[10] and subsequently used and extended by others.[11,12] The precise form of the d-dimensional Fourier transform $\hat{C}(k)$ of the $\hat{c}(12)$ is given by (9b) when $\kappa=0$ depends on the size of s. For small $k = |\vec{k}|$, when $s = 2$,

$$\hat{C}(\vec{k}) = B_l k^2 \ln k + \cdots. \tag{12a}$$

Otherwise,

$$\hat{C}(\vec{k}) = B_2 k^2 + \cdots + B_s k^s + \cdots. \tag{12b}$$

In writing (12) we have made use of the condition that $\hat{C}(0) = 0$ at the critical point. If $s < 2$, (12) reveals that (2), (6), and (11) justify our use of the functional form of (9b), at least at the critical point, and further require that $s = 2-\eta$ and

$$\eta = 2 - d(\delta-1)/(\delta+1), \tag{13}$$

yielding (1a), which is also obtained when $s > 2$ if $B_2 = 0$. On the other hand, if $s > 2$ and $B_2 \neq 0$, then (12) indicates that at the critical point $h(12)$ has the asumptotic form predicted by the Ornstein-Zernike theory, $\eta = 0$. If $s = 2$ and $B_l \neq 0$, (12) reveals that (2), (6), and (11) are not compatible, owing to the ln term in $\hat{C}(\vec{k})$, but the change from (6) to (1b) restores compatibility by suitably modifying (12). With $B_2 = 0$ and $B_l = 0$, however, we would have for all s the same expression (13), which Fisher[5] has shown to follow from the work of both Widom[6] and Kadanoff,[7] and which is also implicit in the work of Domb and Hunter.[13]

When $s > 2$, $B_2 \propto M_2 = \int c(12) r_{12}^2 d(1)$; for all s, the picture that emerges from our work can conveniently be considered in terms of M_2. Assuming (9a), it is easy to show that $M_2 \sim \kappa^{-\eta}$ in the critical region; so η is a direct measure of the finiteness of M_2 at the critical point. For the $d = 2$ Ising model, $\eta = \frac{1}{4}$ and $M_2 = \infty$, owing to the long-ranged tail of $c(12)$. Thus when $d = 2$, any details concerning the contribution of $-\beta V(12)$ to M_2 are masked by this infinity and as a result are irrelevant to us here. For the same model, $d = 3$, η still appears to be >0 according to the exhaustive study of Fisher and Burford,[14] who find $\eta \approx 1/18$. We believe that only the existence of some heretofore unexpected singularity in $h(12)$, such as the occurrence of the $\ln^{1/6} r$ in (1b), could throw any doubt on their very convincing results. Thus for the Ising model, when $d = 3$, it appears that either M_2 is ∞, assuming (6), or h is given by a more complicated expression than (6). Taking (1b) as that expression, however, one still has $M_2 = \infty$, and $-\beta V(12)$ is still hidden. The experimental results[5,7,12] for $d = 3$ are less conclusive but are consistent with $0.2 \geq \eta \geq 0$. Thus, here too, M_2 is probably ∞ but could be finite in some cases. As one goes to $d > 3$, there are only meager clues to serve as a guide, but one reasonable possibility[5] is that M_2 will become finite for some $d > 3$ and will stay finite as d goes to ∞. In any case, if M_2 does become finite for a particular d, for that d the small r_{12} details of $c(12)$ will become important in determining M_2, and since one expects $-\beta V(12)$ to make a major contribution to $c(12)$ for small r_{12}, the value of the second moment of $V(12)$ itself will then emerge as a key quantity in the determination of critical behavior. Finally there is a borderline at which M_2 has a logarithmic divergence when $s = 2$ (simply because $\int r^{-1} dr \sim \ln r$); this gives rise to the term $B_l k^2 \ln k$ in (12a).

Of course, whenever M_2 is not ∞, it may turn out to be 0; we cannot rule this out and it would then mean that $\int V(12) r_{12}^2 d(1)$ does not appear in our considerations after all—a zero M_2 masks $V(12)$ just as effectively as an infinite M_2. Until this point can be clarified by a direct theoretical deduction, the choice between (1) and (13) will have to be made on the basis of their comparative agreement with known results.

For $d = 2$, Eqs. (1) and (13) are identical, and they are consistent with known theoretical results. For $d = 3$, the situation is less clear. Most experimental estimates of δ are consistent with $\delta < 5$ [for which (1) and (13) are again identical] and, when the experimental estimates of η and δ are compared, they are consistent with (1). The Ising results[9] for $d = 3$ of $\delta = 5.2$ and the more recent[15] $\delta = 5.0$, together with the $\eta \approx 1/18$, are in clear disagreement with (13), but the $\delta = 5.0$ can perhaps be reconciled with (1b) if one allows the possibility that (1b) could give rise to an estimate of a small positive η in a Padé-type analysis.[16] For $d \to \infty$, one expects[5] $\delta \to 3$ as well as $\eta \to 0$, in agreement with (1) but not (13).

We finally note that if one includes a factor $(\ln|\rho-\rho_c|)^\lambda$ on the right-hand side of (7), one will again obtain (1b) with a λ-dependent power p of $\ln r_{12}$ rather than $p = (d-2)/2d$; $p = (\lambda+1)(d-2)/2d$. Such a λ could appear to be a small positive power of $|\rho-\rho_c|$ in the same way that p could show up as a small positive power of r_{12}, and then even the estimate $\delta = 5.2$ could perhaps be reconciled with our development. A recent study of experimental results[17] also suggests a value of $\delta = 5$, as does the theoretical work of Ref. 13, indicating that $d=3$ might in general represent the borderline case of $s=2$, accompanied by ln terms in $h(12)$ and possibly in $\mu-\mu_c$ as well.

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†Permanent address: Polytechnic Institute of Brooklyn, Brooklyn, N. Y. 11201.

‡Laboratory associated with Centre National de la Recherche Scientifique (postal address: Laboratoire de Physique Théorique et Hautes Energies, Bât. 211, Faculté des Sciences, 91 Orsay, France).

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