PHYSICAL REVIEW VOLUME 184, NUMBER 1 5 AUGUST 1969

Some Critical Properties of Ornstein-Zernike Systems*

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(Received 24 February 1969)

A study is made of some critical properties of systems that satisfy the Ornstein-Zernike (OZ) condition that the direct correlation function $c(\vec{r})$ behaves like $-(kT)^{-1}$ times the pair potential $V(\vec{r})$ for $\vec{r}$ such that $V(\vec{r}) \ll kT$, even at the critical point. It is pointed out that a number of models of interest that satisfy this condition exist. The relationship (and great difference) between the implication of this condition and the results of the van der Waals-Bragg-Williams-Weiss approach is clarified, and it is noted that in systems satisfying the OZ condition both Widom's homogeneity condition and Kadanoff's scaling hypothesis can be violated, although a self-similarity condition is in general satisfied. The importance of the subtle interplay between small $|\vec{r}|$ and large $|\vec{r}|$ correlations, which is lost in both the mean field and scaling picture, is discussed.

1. INTRODUCTION

In this article we examine some of the critical properties of systems that satisfy the Ornstein-Zernike[1] condition that the direct correlation function $c(\vec{r})$ behaves like $-V(\vec{r})/kT$ [$V(\vec{r})$ = pair potential, k = Boltzmann's constant, and T = temperature] for $r(=|\vec{r}|)$ such that $V(\vec{r})/kT \ll 1$, even at the critical point.[2] We shall call such systems Ornstein-Zernike (OZ) systems. Here we shall investigate only systems with short-range interaction potentials; in another article[3] potentials that fall off like an inverse power of r will be considered. For reasons of technical convenience we shall focus most of our attention upon lattice systems rather than continuum fluids.

Although the two-dimensional Ising model with nearest neighbor $V(\vec{r})$ is not an OZ system, and real three-dimensional fluids do not behave near the critical point like OZ systems either, we feel that there is still much to be learned from a general study of OZ systems. Several models that are exactly soluble prove to be OZ systems; the spherical model[4,5] with any $V(\vec{r})$ is one such model, as is the one-dimensional Ising model with nearest-neighbor interactions in the absence of a magnetic field.[6] Moreover, we have elsewhere[3] found strong evidence that when $V(\vec{r}) \sim r^{-d-\sigma}$ for $r \to \infty$ with d = dimension and $0 < \sigma < d/2$, a fluid or Ising system in any dimension is an OZ system. In addition, a number of important approximations, such as the Percus-Yevick (PY) approximation, satisfy the OZ hypothesis.

Over and above our general goal of gaining more insight into the features that are common to the behavior of all such OZ systems, we have several specific objectives in this article. The first one concerns the relative status of various "classical" assumptions. There appears to be considerable confusion in the current literature, not all of it terminological, concerning the relationship between the OZ hypothesis and the van der Waals-Bragg-Williams-Weiss approach, which we shall refer to as the mean-field approach. In the course of this paper we attempt to clarify this relationship, and to distinguish between the results of the OZ and mean-field assumptions. To illustrate the great difference between them that we find in Secs. 4 and 5, we remark here that under conditions satisfied when $V(\vec{r})$ is of short range, OZ lattice systems undergo no phase transitions for $d < 3$, while the mean-field theories predict such a transition. To give another example, we find that for a $3-d$ OZ lattice system with short-range interactions, certain simple conditions on $c(\vec{r})$ imply that the critical exponent δ used to describe the shape of the critical isotherm must be 5, whereas in the mean-field theory, δ is 3. [For comparison, we note that the assumption of analyticity of the free energy as a function of density ρ and temperature T in the one-phase region around the critical point (T_c, ρ_c) implies only that δ is some odd integer.[7]]

Our second objective is to call attention to the breakdown of both Widom's homogeneity condition[8] and Kadanoff's scaling hypothesis[9] that we find occurring in an OZ system. The breakdown of homogeneity is not serious – first because it occurs only in a certain borderline case and second because it is of such a form that a closely related and useful condition of self-similarity is still preserved even on this borderline. The breakdown of scaling is not a borderline matter, however. For OZ systems it is complete when the dimension is sufficiently high – $d > 4$ for short-ranged potentials. In this connection our work reveals two aspects of critical correlations that are left out of the scaling hypothesis. First we find exquisite sensitivity of thermodynamic properties to a certain interplay between the nature

of the correlations among particles or sites that are close together and the behavior of the correlations among widely separated particles or sites. It is precisely this interplay – the influence of small-r correlation on large-r correlation and vice versa – that is responsible for the difference between the OZ results and the mean-field results. No accomodation for this interplay is made in either the mean field or the scaling theory, and one of our objectives here is to show just how important an ingredient has been left out of a theory when this interplay is disregarded. Another aspect of correlation that we consider provides us with an alternative to Kadanoff's hypothesis[9] that the domain of validity of the scaling theory rapidly shrinks as d increases, but always exists in a neighborhood of the critical point. Kadanoff's idea is appealing and plausible and is supported in spirit – although not in a direct technical way – by the findings of Hemmer, Kac, and Uhlenbeck,[10] who discovered that for a potential parametrized by a range parameter γ, there is an anomalous critical region that shrinks to a point as $\gamma \to 0$ in a one-dimensional system. Since the limit $\gamma \to 0$ is in some respects similar to the limit $d \to \infty$, Kadanoff's view would fit in nicely with this result if there were no evidence of the abrupt disappearance rather than the shrinking of the domain of validity of scaling theory as d increases. In an OZ system, however, we find just such a disappearance as a result of the competition between two terms in the correlation function.

2. FORMAL RELATIONS

The pair correlation function $h(\vec{r})$ and the OZ direct correlation function $c(\vec{r})$ are related to one another by the equation

$$h(\vec{r}) = c(\vec{r}) + \rho \int c(\vec{R} - \vec{r}) h(\vec{R}) d\vec{R} . \tag{2.1}$$

Here ρ is the expected number density of the system, which we assume to be uniform and infinite in volume, and $h(\vec{r}) = g(\vec{r}) - 1$ where $g(\vec{r})$ is the radial distribution function or its lattice-system analog. To make contact with the notation frequently used to describe lattice-gas correlations, we can let τ be the occupation variable which takes the values 0 or 1. Then for a lattice gas in which the volume per site is v_0 we have

$$\begin{aligned} \langle \tau_i \tau_j \rangle &= (\rho v_0)^2 g(r_{ij}) + \rho v_0 \delta_{ij} , \\ \langle \tau_i \tau_j \rangle - \langle \tau_i \rangle \langle \tau_j \rangle &= (\rho v_0)^2 h(r_{ij}) + \rho v_0 \delta_{ij} , \end{aligned} \tag{2.2}$$

where δ_{ij} is the Kronecker delta and ρv_0 is the expected fraction of occupied lattice sites. In the lattice-system case integrals over volume as in (2.1) are to be interpreted as sums over lattice sites, or equivalently, over cells of volume v_0, each cell containing one lattice site. In the case of the spherical model, τ_i can take any value (rather than just 0 or 1) with equal *a priori* probability, but it is still subject to the "spherical" constraint that implies that $\langle [2(\tau_i - \frac{1}{2})^2 \rangle$ must equal one, i.e., that $g(\vec{r}) = 0$ when $\vec{r} = 0$.

For simplicity we shall set $v_0 = 1$ and work only with simple cubic lattices. The Fourier transform of a function $f(\vec{r})$ can then be written

$$\hat{f}(\vec{k}) = \sum_{\vec{r}} f(\vec{r}) e^{i \vec{r} \cdot \vec{k}} , \tag{2.3}$$

where the summation is over all d-dimensional vectors with integer components; $r = (a_1, \ldots, a_d)$. We also have

$$f(\vec{r}) = (2\pi)^{-d} \int \hat{f}(\vec{k}) e^{-i \vec{r} \cdot \vec{k}} d\vec{k} , \tag{2.4}$$

where the integration extends from $-\pi$ to π for each of the d components of the vector $k = (x_1, \ldots, x_d)$.

In the case of the continuum fluid we have instead

$$\hat{f}(k) = \int f(\vec{r}) e^{i \vec{r} \cdot \vec{k}} d\vec{r} , \tag{2.5}$$

and

$$f(\vec{r}) = (2\pi)^{-d} \int \hat{f}(\vec{k}) e^{-i \vec{r} \cdot \vec{k}} d\vec{k} , \tag{2.6}$$

where the integrations in (2.5) and (2.6) extend over all of space. Regardless of whether we are considering (2.3) and (2.4) or (2.5) or (2.6), Eq. (2.1) assumes a particularly simple form in k space

$$\hat{h}(\vec{k}) = \hat{c}(\vec{k}) / [1 - \rho \hat{c}(\vec{k})] , \tag{2.7a}$$

which can also be written

$$1 + \rho \hat{h}(\vec{k}) = [1 - \rho \hat{c}(\vec{k})]^{-1} . \tag{2.7b}$$

We note that in the continuum case the Dirac delta function rather than $\delta_{\vec{r},0}$ is the transform of 1. The functions $\hat{h}(\vec{k})$ and $h(\vec{r})$ are often denoted as $\hat{G}(\vec{k})$ and $G(\vec{r})$ in the literature, and $1 + \rho \hat{h}(\vec{k})$ is sometimes denoted as $S(\vec{k})$ or $\chi(\vec{k})$, while $\rho + \rho^2 \hat{h}(\vec{k})$ has been sometimes written as $\tilde{\mu}_2(\vec{k})$ and $\tilde{F}_2(\vec{k})$. Here we shall use $\hat{\chi}(\vec{k})$ for $1 + \rho \hat{h}(\vec{k})$ and $\chi(\vec{r})$ for its inverse transform.

It is convenient to break up $c(\vec{r})$ into its value c_0 at the origin and the function $c^1(r)$, where

$$\begin{aligned} c^1(\vec{r}) &= c(\vec{r}), \quad \text{for } r \neq 0 \\ &= 0, \quad \text{for } r = 0, \\ c(\vec{r}) &= c^1(\vec{r}) + c_0 \delta_{\vec{r},0} , \end{aligned} \tag{2.8}$$

because we can then write

$$\rho \hat{c}^1(0) \hat{\chi}(\vec{k}) = \left(z - \sum_{\vec{r} \neq 0} \frac{c^1(\vec{r})}{\hat{c}^1(0)} \exp i \vec{r} \cdot \vec{k} \right)^{-1} ,$$

$$= \{z - [\hat{c}^1(\vec{k})/\hat{c}^1(0)]\}^{-1},$$

$$= \left(\xi - \frac{\hat{c}^1(\vec{k}) - \hat{c}^1(0)}{\hat{c}^1(0)}\right)^{-1}, \qquad (2.9)$$

where $\xi + 1 = z = (1 - \rho c_0)/\rho\hat{c}^1(0)$. Since $\chi(0) = 1 - \rho$, $\vec{k}$ integration puts (2.9) into the same form as the saddle-point equation for the spherical model[4,5]; by writing it we have cast the lattice-gas problem into the form of a saddle-point problem even though there is initially no saddle-point determination to be made. Equation (2.9) facilitates contact and comparison with much work that has already been done for the spherical,[4,5] mean-spherical,[11,12] and Gaussian[4] models.

For models that are most closely related to real physical systems,[13] the functions $\hat{c}(0)$ and $\hat{\chi}(0)$ are related to thermodynamical properties through fluctuation relations such that

$$\frac{1}{kT}\frac{dP}{d\rho} = \frac{\rho}{kT}\frac{d\mu}{d\rho} = 1 - \rho\hat{c}(0) = \hat{\chi}(0)^{-1}, \qquad (2.10)$$

where P is the pressure and μ the chemical potential.

In investigating the critical behavior of a system it is convenient to define a set of critical indices or exponents. For example, it appears that we can describe the shape of the critical isotherm near the critical point in terms of the index δ by writing[14]

$$P - P_c \sim \mu - \mu_c \sim |\rho - \rho_c|^{\delta}\,\mathrm{sgn}\,|\rho - \rho_c|; \quad T = T_c, \quad \rho \to \rho_c. \qquad (2.11)$$

The subscript c here and throughout this article refers to values at the critical point.

Similarly along the critical isochore, $T \geq T_c$, we assume

$$\frac{dP}{d\rho} = \rho\frac{d\mu}{d\rho} \sim |T - T_c|^{\gamma}; \quad \rho = \rho_c, \quad T \to T_c. \qquad (2.12)$$

and along the coexistence curve we write

$$|\rho - \rho_c| \sim |T - T_c|^{\beta}; \quad (T, \rho) \to (T_c, \rho_c). \qquad (2.13)$$

The specific heat C_V can be described by the index α for $T \geq T_c$:

$$C_V \sim |T - T_c|^{-\alpha}; \quad T \to T_c, \quad \rho = \rho_c, \qquad (2.14)$$

but sometimes it is useful to assume the more specific form

$$C_V \sim A + B|T - T_c| + \cdots + D|T - T_c|^{-\alpha_s} + \cdots, \qquad (2.15)$$

where the last term is associated with a singular part of C_V, in which either α_s is not an integer or D is not a constant but is a term of order less than any positive power and greater than any negative power of $T - T_c$, such as const $(\ln|T - T_c|)$.

We can also describe the most important features of the correlations by means of exponents. We introduce η by assuming that $h(\vec{r})$ is of the form

$$h(\vec{r}) \sim f(\kappa_1 r)/r^{d-2+\eta}, \quad \text{for } r \gg 1. \qquad (2.16)$$

Here κ_1 is an inverse correlation length, which can be defined for both continuum and lattice systems by setting

$$\kappa_1 = \Lambda^{-1}, \quad \Lambda^2 = \Lambda_2, \qquad (2.17)$$

where Λ_2 is the coefficient of k^2 in the expansion of $\hat{\chi}(\vec{k})^{-1}$ in powers of $k = |\vec{k}|$:

$$1/\hat{\chi}(\vec{k}) = \hat{\chi}(0)^{-1}(1 + \Lambda_2 k^2 - \Lambda_4 k^4 + \cdots).$$

In the case of a simple cubic lattice this means that Λ_2 is the second spherical moment of $\chi(\vec{r})$ over $2d$ times the zeroth moment, $\hat{\chi}(0)$. As noted by Fisher and Burford,[15] for lattice systems Λ_2 is angle-independent but the higher coefficients Λ_4, etc., depend upon k/k.

In the special case of an $h(\vec{r})$ that vanishes faster than any power of r, κ can also be defined by the equation

$$-\kappa = \lim_{r \to \infty} \sup(\ln h(\vec{r})/r). \qquad (2.18)$$

One would expect that near the critical point $\kappa_1 \propto \kappa$ whenever the latter exists and our computations show this is true in an OZ system, in agreement with the work of Fisher and Burford. It is convenient to describe the behavior of κ_1 by defining ν and ϵ such that

$$\kappa_1 \sim |T - T_c|^{\nu}, \quad \text{for } \rho = \rho_c,$$
$$\kappa_1 \sim |\rho - \rho_c|^{\epsilon}, \quad \text{for } T = T_c. \qquad (2.19)$$

From Eq. (2.10), assumption (2.16), and the added assumption that $h(\vec{r})$ remains finite for all r, we can conclude quite generally that

$$(kT)^{-1} dP/d\rho \sim \kappa_1^{2-\eta}, \quad \text{as } \kappa \to 0 \qquad (2.20)$$

so that

$$\gamma = (2 - \eta)\nu, \quad (\delta - 1) = (2 - \eta)\epsilon. \qquad (2.21)$$

As can be seen from the definitions of the critical exponents, the case $T_c = 0$ requires special treatment, since $T - T_c$ and T then behave in the same way as the critical point is approached.

3. OZ ASSUMPTION

OZ reached a number of conclusions concerning correlations in a system in which the interparticle potential $V(\vec{r})$ vanished for all r greater than

some R. Their treatment rests upon a heuristic argument that can not easily be given a precise quantitative form, especially when applied to a model in which there is no R such that $V(\vec{r})=0$ for $r>R$. Nevertheless most of the obscurity in the work of OZ lies in the justification of their basic assumption concerning $c(\vec{r})$ rather than in its interpretation. The assumption itself is consistent with the following statement, which we shall take as our starting point:

> In general, $c(\vec{r})\approx -V(\vec{r})/kT$ for $\vec{r}$ such that $V(\vec{r})\ll kT$; in particular $c(\vec{r})\approx 0$ for $r>R$, if $V(\vec{r})=0$ for $r>R$. (3.1)

This is a strong form of the OZ hypothesis. A weaker assertion is that:

> When $V(\vec{r})=0$ for $r>R$, or when $V(\vec{r})$ is short ranged in the sense that all its spacial moments exist, $c(\vec{r})$ will also be short ranged in the same sense, even at the critical point. (3.2)

This is also consistent with the OZ argument and, as has been pointed out by others, for short ranged $V(\vec{r})$ both forms of the OZ hypothesis impose a very strong set of restrictions on critical behavior. Because of its more specific nature (3.1) is a more convenient form of the OZ hypothesis for us to work with in this paper.

We note that (3.1) does not completely determine $c(\vec{r})$ for $r<R$. In fact, for any potential with a hard core of diameter σ, the structure of Eq. (2.1) is such that[16] the requirement that $g(\vec{r})=0$ inside the core completely determines $c(\vec{r})$ for $r\leqslant\sigma$ when $c(\vec{r})$ is given for $r>\sigma$.

For the lattice gas, the "core" is the result of the exclusion of multiple occupancy of a site, or – to use language that does less violence to the concept of freely moving particles of a fluid – of a cell indexed by the vector $\vec{r}$. It is unlikely that OZ were aware of this restriction on $c(\vec{r})$ for $r\leqslant\sigma$ when $c(\vec{r})$ is given for $r>\sigma$, but nevertheless they were careful to point out that the determination of the precise value of $c(\vec{r})$ for $r<R$ remained for them an unsolved problem.

When treating a potential $V(\vec{r})$ with a core it is often convenient to break $V(\vec{r})$ into a core part plus the rest:

$$V(\vec{r})=q(\vec{r})+w(\vec{r}), \tag{3.3a}$$

where

$$\begin{aligned} q(\vec{r})&=\infty, \quad \text{for } r\leqslant\sigma,\\ &=0, \quad \text{for } r>\sigma;\\ w(\vec{r})&=0, \quad \text{for } r\leqslant\sigma. \end{aligned} \tag{3.3b}$$

In the special case of a nearest-neighbor interaction, (3.1) implies that (2.9) reduces to

$$\rho c_1\hat{\chi}(\vec{k})=[z-2\sum_{j=1}^{d}\cos x_j]^{-1}, \qquad z=(1-\rho c_0)/\rho c_1, \quad \vec{k}=(x_1,\ldots,x_d), \tag{3.4}$$

where c_1 denotes $c(\vec{r})$ at $r=1$.

The inverse transform of the right-hand side of (3.4) has been exhaustively studied and tabulated.[17] When $w(\vec{r})=0$ in (3.3), (3.1) further implies that we have simply

$$\rho\hat{\chi}(\vec{k})=1/(1-\rho c_0), \tag{3.5}$$

but $g(\vec{r})=0$ at $r=0$ implies that $\chi(\vec{r})=1-\rho$ at $r=0$ so that (3.5) yields in the lattice-gas case

$$1-\rho c_0=1/\rho(1-\rho) \quad \text{or} \quad c_0=-1/(1-\rho). \tag{3.6}$$

For completeness we note some simple results for two OZ models of interest. For the nearest-neighbor one-dimensional lattice gas at $\rho=\frac{1}{2}$, Percus[6] found

$$c_0=-2\left[\frac{2+f}{(1+f)^{1/2}}-1\right], \quad c_1=f/(1+f)^{1/2}, \tag{3.7}$$

where $1+f=\exp[-w(1)/kT]$. For $\rho\neq\frac{1}{2}$, $c(\vec{r})$ is still short ranged in the sense of having an exponential decay and thus satisfies (3.1) but not (3.2).

For the spherical model of a lattice gas it can be immediately verified that

$$c(\vec{r})=-V(\vec{r})/kT, \quad \text{for } r\neq 0 \tag{3.8}$$

regardless of the potential or of ρ.

4. MEAN-FIELD ASSUMPTION

For our purposes it is important to be able to characterize the mean-field theory in terms of $c(\vec{r})$. The basis of the mean-field theory is an assumption equivalent to the statement that if the potential of a system is a sum of $q(\vec{r})$ and $w(\vec{r})$ as in (3.3), then the thermodynamic effect of the term $w(\vec{r})$ can be added to that of the $q(\vec{r})$ in the form of an expression involving only $w(\vec{r})$ and the thermodynamics that describe the system when $w(\vec{r})\equiv 0$. The possible presence of a "cross term" manifesting the influence of $q(\vec{r})$ on the change in the thermodynamics when $w(\vec{r})$ is introduced is neglected. As was pointed out by Boltzmann,[18] one expects to come closest to realizing this van der Waals-type assumption when $w(\vec{r})$ is weak and long ranged. Expressing these ideas in terms of $c(\vec{r})$, we might hope to recover the mean-field result by first obtaining the $c(\vec{r})$ for the system in which $w(\vec{r})=0$ and then assuming that the change in $c(\vec{r})$ that comes of adding the $w(\vec{r})$ to $q(\vec{r})$ will depend entirely on $w(\vec{r})$ rather than on both $w(\vec{r})$ and $q(\vec{r})$. On the basis of (3.1) we can further expect to have, for a weak long-range $w(\vec{r})$,

$$c(\vec{r})=c^0(\vec{r})-w(\vec{r})/kT, \tag{4.1}$$

where here and below the superscript zero refers to the quantity that is found for a given ρ and T when $w(\vec{r})\equiv 0$. According to Boltzmann's reasoning, Eq. (4.1) should yield the mean-field result of van der Waals when applied to a fluid, or the Bragg-Williams-Weiss results when applied to

a lattice system. This is easily seen to be the case – when use is made of Eq. (2.10), Eq. (4.1) immediately yields

$$dP/d\rho = (dP/d\rho)^0 + \rho\hat{w}(0), \tag{4.2a}$$

which becomes after integration with respect to ρ

$$P = P^0 + \tfrac{1}{2}\rho^2\hat{w}(0). \tag{4.2b}$$

Equation (4.2) has the form derived by van der Waals, although in his original derivation[19] the constant in the second term of (4.2a) was not clearly identified with $\hat{w}(0)$. However, in the derivation given by Boltzmann[18] this identification is clear.

Van der Waals also considered a method for obtaining successively better and better approximations to P^0 for a hard-sphere system and Boltzmann further developed systematic and exact procedures for accomplishing this, but for computational purposes van der Waals and his contemporaries often used the simple approximation[20] suggested by van der Waals

$$P^0/kT \approx \rho/(1-\rho b)\ , \tag{4.3}$$

where $2b$ is the volume of a d-dimensional sphere with radius σ, $2b = 2\sigma$ for $d=1$, $2b = \frac{4}{3}\pi\sigma^3$ for $d=3$. In the lattice-gas case we can immediately assess $(dP/d\rho)^0$ from (2.10) and (3.6). In all dimensions it is given by

$$(dP/d\rho)^0/kT = 1/(1-\rho), \tag{4.4}$$

which yields the Bragg-Williams-Weiss equation of state when used in (4.2).

Equation (4.2) is applicable only to a system in a single phase and must be supplemented by a further prescription, such as Maxwell's construction, in order to yield a coexistence curve and a two-phase region.

It is a simple matter to verify that if $(dP/d\rho)^0$ is given by either (4.2) or by any reasonable estimate of its continuum analog, including that determined by (4.3), then a critical point at $T_c > 0$ exists for all d, with

$$\delta = 3, \quad \gamma = 1 \tag{4.5}$$

in (2.11) and (2.12), respectively.

It can also be verified in a straightforward way that the use of Maxwell's construction with (4.2) and a reasonable P^0 yields

$$\beta = \tfrac{1}{2} \tag{4.6}$$

in (2.13) while the specific heat proves to be of the form given by (2.14) and (2.15) with

$$\alpha = 0, \quad D = 0. \tag{4.7}$$

Equation (4.1) also completely determines an $h(\vec{r})$ when $c^0(\vec{r})$ is given, and we can thus also obtain η, ν, and ϵ, as we show in the next section. Before passing on to Sec. 5, we note the following two points. Firstly, the mean-field equation of state is insensitive to the form of the potential. As long as $\hat{w}(0)$ exists, it is $\hat{w}(0)$ that determines the nature of the critical behavior in the mean-field approximation, whether $w(\vec{r})$ is zero for large r or not. Secondly, there is no guarantee that $h(\vec{r})+1$ defined by (2.1) and (4.1) will be zero for $r \leq \sigma$. The weaker and longer ranged $w(\vec{r})$ is, the smaller this $h(\vec{r})+1$ is likely to be for $r \leq \sigma$, since in the limit of a $w(\vec{r})$ that is zero at any $\vec{r}$, we would expect $c^0(\vec{r})$ to coincide for $r \leq \sigma$ with the $c(\vec{r})$ that results when $w(\vec{r})$ is added to $q(\vec{r})$. For an arbitrary $w(\vec{r})$, however, we must expect the condition $h(\vec{r}) = -1$ for $r \leq \sigma$ to be violated. The result of this violation is a measure of the importance of the subtle interplay between the correlations over large distances and those over small distances, and we shall find that the effects of this interplay on critical behavior can be immense. We shall study these effects in a lattice system by comparing the use of the mean-field $c(\vec{r})$:

$$c(\vec{r}) = -w(\vec{r})/kT, \quad \text{for } r > 0, \tag{4.8}$$

$$c_0 = -1/(1-\rho), \tag{4.9a}$$

with the use of the same $c(\vec{r})$ for $r > 0$, but with

$$c_0 \text{ such that } h(0) = -1. \tag{4.9b}$$

5. OZ RESULTS FOR A NEAREST-NEIGHBOR POTENTIAL

We note from the form of (2.9) that the T and ρ dependence of $\rho c^1(0)\hat{\chi}(\vec{k})$ is contained entirely in the quantity z when (4.8) is satisfied. We also see from (3.4) that in the nearest-neighbor case, this is true as long as $c(\vec{r}) = 0$ for $r > 1$, even if the stronger assumption that $c_1 = -w/kT$ is not satisfied. In the nearest-neighbor case, (2.17) can be re-expressed as

$$\kappa_1^2 \sim (1 - \rho c_0 - 2d\rho c_1)/\rho c_1, \tag{5.1}$$

and we find that κ_1 exactly satisfies (2.18), since the large r form of the $\rho c_1\chi(\vec{r})$ given by (3.4) is

$$\rho c_1\chi(\vec{r}) \simeq \frac{(\kappa_1 r)^{(d-2)/2} K_{(d-2)/2}(\kappa_1 r)}{(2\pi)^{d/2} r^{d-2}} \tag{5.2}$$

when $K_\nu(x)$ is the Bessel function of imaginary argument, such that as $x \to \infty$,

$$K_\nu(x) \to (\pi/2x)^{1/2} e^{-x}.$$

Comparing this result with (2.18) we see that we can drop the subscript on κ_1. We also note that

$$\eta = 0. \tag{5.3}$$

For fixed r, (either $r \sim 1$ or $r \gg 1$) we find that $\rho c_1\chi(\vec{r})$ always has an asymptotic expansion that can be written as

$$\rho c_1\chi(\vec{r}) = f_0(\vec{r}) + f_1(\vec{r})\kappa^2 + f_2(\vec{r})\kappa^{d-2} + f_3(\vec{r})\kappa^{d-2}\ln\kappa + \cdots, \tag{5.4}$$

where $f_1(\vec{r})$ and $f_2(\vec{r})$ are not zero for $r=0$ or $r=1$ and $f_3(\vec{r})$ is zero when and only when d is odd, for all $\vec{r}$. The unexhibitied terms are always dominated by the presence of at least one of the terms shown. From (2.10), (5.2), and (5.4) we see that $(dP/d\rho)^{-1}$ can $\to\infty$ only if $\kappa\to 0$; thus only if $\kappa\to 0$ can we have a critical point at which $dP/d\rho = 0$. For $d\geq 3$, the right-hand side of (5.4) remains finite as $\kappa\to 0$ and (2.20) and (2.21) immediately follow. For $d=1$ and $d=2$, however, the question is more subtle since for any fixed r, $\rho c_1\chi(\vec{r})$ will go to infinity as $\kappa\to 0$, and only if either c_1 or $h(\vec{r})$ become infinite is consistency maintained in these dimensions. For the lattice gas and similar models the result $h(\vec{r})\to\infty$ for fixed $\vec{r}$ represents unacceptable behavior of $h(\vec{r})$, and for any such model that is an OZ system c_1 must become infinite for $d=1$ and $d=2$ in the nearest-neighbor case. When c_1 is given by a relationship such as (3.7) or (4.8) this means that T must be zero in order for κ to be zero. In this section we have as yet said nothing that involves the difference between (4.9a) and (4.9b), but from the above remarks we must conclude that the mean-field theory, for which $T_c\neq 0$, can only be consistent with the unacceptable result that $h(\vec{r})\to\infty$ for fixed $\vec{r}$ as $\kappa\to 0$. This is a well-known catastrophe that occurs in the mean-field theory. However the OZ theory is in no obvious way inconsistent with alternative possibility that there is no critical point at $T\neq 0$ so that the only possible critical temperature is zero in one or two dimensions. The difference in these alternatives resides wholly in the difference between (4.9a) and (4.9b).

The exceptional behavior of c_1 that occurs in the OZ theory for $d=1$ and $d=2$ entails special analysis and for the remainder of this work we shall restrict our comments to the case of a c_1 that remains finite at the critical point and hence to the case of $d\geq 3$. Since (5.1) precludes the possibility that $c_1\to 0$, we assume that $c_1\sim\kappa^0$ for small κ.

We can determine the behavior of C_V by using (5.4) for $r=1$, since the configurational internal energy is given by

$$U_{\text{conf}} = \tfrac{1}{2}\rho[\hat{w}(0) + \textstyle\sum_{\vec{r}} w(\vec{r})h(\vec{r})]. \tag{5.5}$$

Using (2.19), we see that (5.5) implies for $\rho=\rho_c$ and $T>T_c$

$$C_V \sim O(\Delta T^{2\nu-1}) + O(\Delta T^{(d-2)\nu-1}) + \theta O(\Delta T^{(d-2)\nu-1}\ln\Delta T), \tag{5.6}$$

where we have set $\Delta T = T - T_c$ and where

$$\theta = 1, \text{ for even } d; \quad = 0, \text{ for odd } d. \tag{5.7}$$

We are interested in $\Delta T\to 0$. If $d=3$, the second term is dominant, while if $d=4$, the last term dominates. For $d\geq 5$ the first term dominates. Thus we can identify $\nu-1$ with the $-\alpha$ of (2.14) when $d=3$ and $2\nu-1$ with $-\alpha$ when $d\geq 4$:

$$\nu = 1-\alpha, \quad \text{for } d=3; \qquad \nu = \tfrac{1}{2}(1-\alpha) \quad \text{for } d\geq 4, \tag{5.8}$$

and from (2.21) and (5.3)

$$\gamma = 2(1-\alpha), \quad \text{for } d=3; \qquad \gamma = 1-\alpha, \quad \text{for } d\geq 4. \tag{5.9}$$

Note that for $d=3$ we have another dilemma in the mean-field theory, since the values $\alpha=0$ and $\gamma=1$ noted in Sec. 4 are inconsistent with (5.9).

To determine the value of γ in the OZ theory when (4.9b) rather than (4.9a) is used, we consider (5.4) at $r=0$. We have

$$c_1\rho(1-\rho) = [c_1\rho(1-\rho)]_c + O(\kappa^2) + O(\kappa^{d-2}) + \theta O(\kappa^{d-2}\ln\kappa). \tag{5.10}$$

Letting $\rho-\rho_c=\Delta\rho$, $|\Delta\rho| = M$, and $c_1 - c_{1c} = \Delta c_1$ we find

$$\rho_c^{\,2}(\Delta c_1) - c_{1c}M^2 - \Delta c_1 M^2 = O(\kappa^2) + O(\kappa^{d-2}) + \theta O(\kappa^{d-2}\ln\kappa). \tag{5.11}$$

If we also assume (4.8), then $-\Delta c_1 = \tilde{\beta}w_1 - \tilde{\beta}_c w_1 = w_1\Delta\tilde{\beta}$, where we have written $1/kT$ as $\tilde{\beta}$ to distinguish it from the critical exponent β. We shall treat the case of $-c_1 = \tilde{\beta}w_1$ first, coming back to the more general (2.9) later. We can drop the term $\Delta c_1 M^2$ on the left-hand side of (5.11) as $\kappa\to 0$ and we find

$$-\rho_c^{\,2}w_1\Delta\tilde{\beta} + \tilde{\beta}_c w_1 M^2 = O(\kappa) \quad \text{for } d=3; \quad = O(\kappa^2\ln\kappa), \quad \text{for } d=4; \quad = O(\kappa^2), \quad \text{for } d>4. \tag{5.12}$$

From this we can read off the values of ν, ϵ, δ, and γ:

$$\begin{aligned} &\nu = 1 \text{ for } d=3 && \gamma = 2 \text{ for } d=3\\ &\nu = \tfrac{1}{2} \text{ for } d\geq 4 && \gamma = 1 \text{ for } d\geq 4\\ &\epsilon = 2 \text{ for } d=3 && \delta = 5 \text{ for } d=3\\ &\epsilon = 1 \text{ for } d\geq 4 && \delta = 3 \text{ for } d\geq 4. \end{aligned} \tag{5.13}$$

Note that for $d=3$, both γ and δ are different than in the mean-field theory.

A special remark must be made concerning $d=4$, since one does not find that κ is asymptotically proportional to ΔT or M^2 in that case as $\kappa\to 0$, because of the presence of the $\ln\kappa$ in (5.12). One

still has (2.19) and (5.6) if one defines asymptotic order as indicated in footnote 14, but one will *not* find

$$C_V \propto \text{const} + \ln\Delta T \tag{5.14}$$

as $\Delta T \to 0$ for $\rho = \rho_c$. Instead one finds

$$C_V \propto \text{const} + (1/\ln\Delta T), \tag{5.15}$$

so that C_V remains finite at the critical point for $d = 4$ despite the appearance of the $\ln\kappa$.

Because of the $\ln\kappa$ we do not have homogeneity of κ as a function of $\Delta\tilde{\beta}$ or ΔT and M^2 for $d = 4$, as we do for $d \neq 4$, but we still have self-similarity of curves of constant κ in the $(\Delta\tilde{\beta}, M^2)$ or $(\Delta T, M^2)$ planes. This suggests that the conjectured homogeneity of κ, which we have noted elsewhere[21] is equivalent to the homogeneity condition conjectured by Widom,[8] should be weakened to a conjecture concerning the self-similarity of curves of constant κ (and hence of constant compressibility or susceptibility).

From (5.8) and (5.13) we find $\alpha = 0$ for all $d \geq 3$. Furthermore, by matching terms in (2.15) and (5.6) we find that when $d \geq 3$,

$$m\nu - 1 = 0, \tag{5.16}$$

where m = minimum of $d-2$ and 2, in agreement with (5.13), and that whenever a singular term in (2.15) appears,

$$(d-m)\nu - 1 = -\alpha_s. \tag{5.17}$$

For $d = 3$, no singularity appears. For odd $d > 4$, α_s is an integer plus $\frac{1}{2}$ while for even $d \geq 4$, α_s is an integer but the term $\text{const}\,\Delta T^{-\alpha_s}\ln\Delta T$ always appears. We can summarize the relation between α_s and ν by eliminating m in (5.16) and (5.17) to get

$$\alpha_s = 2 - d\nu, \tag{5.18}$$

where an integer α_s signifies that no singularity appears unless the condition for the presence of a $\ln\Delta T$ term

$$d - 2 = 2j, \quad j = 1, \ldots, \tag{5.19}$$

is also satisfied.

From our discussion we can see at this point that some of the scaling relations that involve dimensionality explicitly are not satisfied when (4.8) and (4.9b) are assumed. For example we see from (5.3) and (5.13) that the relation

$$\eta = 2 - d(\delta - 1)/(\delta + 1)$$

is not satisfied for $d > 4$ whereas we see that the relation derived by us previously (for a non-OZ system),[22]

$$\eta = \text{maximum of } 0 \text{ and } 2 - d(\delta - 1)/(\delta + 1),$$

remains trivially valid. On the other hand (5.18) is consistent with the results of scaling theory, although scaling theory does not appear to give a clear means of deciding between $\alpha = 0$ and $\alpha = 2 - d\nu$ when $\alpha_s < 0$.

We have still to investigate the critical exponent β under the assumptions (4.8) and (4.9b). For $d > 4$, the determination of β is straightforward, since the expression for

$$\kappa \sim (\rho_c^{\,2} w_1 \Delta\tilde{\beta} - \tilde{\beta}_c w_1 M^2)^{1/2}, \tag{5.20}$$

which follows from (5.12), and the related expression for the chemical potential,

$$\frac{\mu(\rho, T) - \mu(\rho_c, T)}{\rho - \rho_c} = \frac{1}{\rho - \rho_c}\int_{\rho_c}^{\rho} \frac{d\mu(n, T)}{dn}\,dn \sim \frac{1}{\rho - \rho_c}\int_{\rho_c}^{\rho} \kappa^2(n, T)\,dn, \tag{5.21}$$

can be used for $T < T_c$ to determine a coexistence curve by means of Maxwell's rule or the condition that

$$\mu(\rho_c + M, T) = \mu(\rho_c - M, T).$$

We have

$$\frac{\mu(\rho, T) - \mu(\rho_c, T)}{\Delta\rho} \sim \frac{\tilde{\beta}_c |w_1|}{3} M^2 + \rho_c^{\,2} w_1 \Delta\tilde{\beta}, \tag{5.22}$$

so the coexistence curve is given by the equation

$$\tfrac{1}{3}\tilde{\beta}_c w_1 M^2 \simeq \rho_c^{\,2} w_1 \Delta\tilde{\beta} \tag{5.23}$$

in the critical region. The critical exponent β is given by

$$\beta = \tfrac{1}{2}, \tag{5.24}$$

and the dome of metastability in the $(\rho, \tilde{\beta})$ plane can be reasonably identified with the locus of points at which $\kappa = 0$.

For $d = 3$, all of this is changed. When we use Eqs. (5.12) and (5.21) we find instead

$$\frac{\mu(\rho, T) - \mu(\rho_c, T)}{\Delta\rho} \sim w_1^{\,2}\rho_c^{\,4}\Delta\tilde{\beta}^2 + \tfrac{2}{3}\tilde{\beta}_c w_1^{\,2}\rho_c^{\,2}\Delta\tilde{\beta}M^2 + \tfrac{1}{5}\tilde{\beta}_c^{\,2} w_1^{\,2} M^4, \sim w_1^{\,2}[\rho_c^{\,4}\Delta\tilde{\beta}^2 + \tfrac{2}{3}\tilde{\beta}_c\rho_c^{\,2}\Delta\tilde{\beta}M^2 + \tfrac{1}{5}\tilde{\beta}_c^{\,2}M^4]. \tag{5.25}$$

There is no real value of $\Delta\tilde{\beta}$ for which $\mu(\rho_c + M, T) = \mu(\rho_c - M, T)$ according to (5.25). Thus we can-

not find a coexistence curve by means of the analytic continuation of our expression for κ or μ into the subcritical region, and there appears to be no natural alternative to such continuation that suggests itself as a means of locating the coexistence curve.

This is somewhat surprising because the spherical model, which is an OZ system, has a coexistence curve such that $\beta = \frac{1}{2}$ when $d = 3$ (as well as when $d \geq 4$). However, as indicated in footnote 13, Eq. (2.7) does not have its normal status in the case of this model. Our computation suggests that OZ systems in which Eq. (2.7) does have its usual status may not exist for $d = 3$ when the potential is of short range. It further suggests that for $d = 3$ and short range $V(\vec{r})$, approximations that satisfy the OZ condition, such as the PY approximation, may be associated with pathological subcritical behavior of the compressibility when that quantity is obtained from $h(\vec{r})$ thru Eqs. (2.7) and (2.10).

The borderline case of $d = 4$ is complicated by the appearance of the $\kappa^2 \ln\kappa$ in (5.4) and we forego its analysis here.

6. GENERALIZATIONS OF THE PRECEDING RESULTS

The preceding analysis was centered on the lattice-gas case in which (4.8) and (4.9b) were assumed to hold. These equations involve a stronger assumption than (3.1), however, which implies in the nearest-neighbor case only that

$$\begin{aligned} &c_0 \text{ is such that } h(0) = -1, \\ &c_1 \text{ is undetermined,} \\ &c(\vec{r}) = 0, \quad \text{for } r > 1. \end{aligned} \tag{6.1}$$

On the basis of (6.1), our previous analysis is unchanged through Eq. (5.3) but to go further we must examine what can be said about the temperature and density dependence of c_1. Here the invariance of c_1 under the interchange of ρ and $2\rho_c - \rho$ which follows directly from the hole-particle symmetry of a lattice gas enters strongly It implies that c_1 is an even function of $\Delta\rho$.

If we further assume that c_1 must be analytic in $\tilde{\beta}$ and ρ about $(\tilde{\beta}_c, \rho_c)$, then c_1 must be of the form

$$c_1 = c_{1c} + aM^2 + b(\Delta\tilde{\beta}) + \cdots . \tag{6.2}$$

Assuming $b > 0$, which is reasonable, then there are three distinct possibilities, depending upon the relative values of $\rho_c{}^2 a$ and c_{1c}. If $\rho_c{}^2 a < c_{1c}$, as would be the case of c_1 were essentially independent of ρ, all the critical exponents found in Sec. 5 would remain unchanged. In contrast, the very special ρ dependence of c_1 represented by $\rho_c{}^2 a = c_{1c}$ would result in some exponents that are different (for example, when $d = 3$, then $\epsilon = 4$) while $\rho_c{}^2 a > c_{1c}$ would lead to unacceptable negative or imaginary values of κ when $\Delta\tilde{\beta} = 0$.

Another departure from (4.8) can be attained by relaxing the requirements of analyticity at $(\tilde{\beta}_c, \rho_c)$. For example, if Δc_1 were a homogeneous function of M and $(\Delta T)^{\nu/\epsilon}$ of degree p, then when $M = 0$, (5.11) would yield $p = \epsilon$ for $d = 3$ and $p = 2\epsilon$ for $d \geq 4$. When $\Delta T = 0$, (5.11) would yield $\epsilon \leq 2$ for $d = 3$ and $\epsilon \leq 1$ for $d \geq 4$, which would imply $\delta \leq 5$ for $d = 3$ and $\delta \leq 3$ for $d \geq 4$, with ν not subject to any obvious constraints. Thus it appears that for $d = 3$ an approximation could be constructed that has values of ν, ϵ, γ, and δ that are very close to those actually observed in the Ising model. For example, by setting Δc_1 to a function that becomes, for small M and ΔT,

$$\Delta c_1 \simeq [\text{const}\, M^{16} + \text{const}\, (\Delta T)^5]^{1/8}, \tag{6.3}$$

we would have $\nu = \frac{5}{8}$, $\epsilon = 2$, $\gamma = \frac{5}{4}$, $\delta = 5$. However, there appears to be no way of changing $\alpha = 0$ and certainly no way of changing the $\eta = 0$ by means of a judicious choice of c_1. Moreover, a more thorough investigation of the approximation that such a choice of Δc_1 defines would have to be made before it is clear that it is free of serious inconsistencies and that it can be associated with a reasonable coexistence curve by means of the condition $\mu(\rho_c + M, T) = \mu(\rho_c - M, T)$.

If we do not restrict our attention to the nearest-neighbor case we would still expect to find the same kinds of results as long as we continue to look at short-range potentials all of whose moments exist. Equation (4.8) can be used as it stands and Eqs. (6.2) and (6.3) can also be used if they are taken to hold for any $\vec{r} \neq 0$. When (4.8) is used, computations can still be done explicitly in the case of certain potentials (such as the Green's function[17] for the lattice analog of the Helmholtz equation) that lend themselves to the necessary manipulations.

If we consider potentials that are of the form $-1/r^{d+\sigma}$ for large r, the results are quite different. Joyce[5] has treated the case of such potentials in great detail for the spherical model, and we show in a separate article that most of his results are valid for any OZ system. For example, it can be shown that assuming (4.9),

$$h(\vec{r}) \sim \text{const}/r^{d-s}, \quad \text{as } r \to \infty, \tag{6.4}$$

at the critical point, where s = minimum of 2 and σ, while off the critical point,

$$h(\vec{r}) \sim -\tilde{\beta} w(\vec{r}) [\hat{\chi}(0)]^2, \quad \text{as } r \to \infty, \tag{6.5}$$

rather than (5.2).

This brings up a point concerning terminology that is a source of ambiguity in the literature. The result (5.2) is often referred to as *the* OZ

result irrespective of the potential whereas the results consistent with (2.1) and (4.9) are very much dependent upon the form of $V(\vec{r})$, as (6.4) and (6.5) indicate. Moreover, in a quantum system it is an effective potential – the actual pair potential modified by quantum effects – that must be considered rather than the potential itself if one wishes to apply the reasoning of Ornstein and Zernike; for example, for a Bose gas in its ground state one expects[23] $V_{\text{eff}}(\vec{r}) \sim 1/r^2$ and hence, according to (3.1) one must expect $c(\vec{r}) \sim 1/r^2$ rather than $c(\vec{r}) \sim 0$ for large r.

The full generalization of the results of Sec. 5 to a fluid presents technical difficulties associated with the extended repulsive core characteristic of any reasonable intermolecular potential, but certain of the preceding results appear to generalize without difficulty. In particular, assuming (3.1), we expect to again find (5.2) for all κ, $r \to \infty$, and (5.4) for a fixed $\vec{r}$ as $\kappa \to 0$. This is consistent with the general observation based on (2.9) that when (4.8) is used the case of a $w(\vec{r})$ extending over arbitrarily many lattice sites cannot be essentially different from the nearest-neighbor case as long as all the moments of $w(\vec{r})$ exist. If is also supported by the following more specific argument. Except for small r, we expect $h(\vec{r})$ to behave like the solution

$$(\kappa r)^{(d-2)/2} K_{(d-2)/2}(\kappa r)/2\pi^{d/2} r^{d-2} \qquad (6.6)$$

of the Helmholtz equation

$$\nabla^2 h(\vec{r}) - \kappa^2 h(\vec{r}) = 0,$$

but for fixed $\vec{r}$ and $\kappa \to 0$, (6.6) behaves precisely like the right-hand side of (5.4),

$$O(1) + O(\kappa^2) + O(\kappa^{d-2}) + \theta O(\kappa^{d-2} \ln \kappa),$$

just as the transform of (3.4) does.

ACKNOWLEDGMENTS

The author gratefully acknowledges numerous discussions with Dr. W. K. Theumann concerning the contents of this article, as well as the support of the National Science Foundation through the Science Development Program at the Polytechnic Institute of Brooklyn, where much of the work in this article was done.

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*This work was supported in part by the Science Development Program of the National Science Foundation while the author was at the Polytechnic Institute of Brooklyn, Brooklyn, New York.

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PHYSICAL REVIEW VOLUME 184, NUMBER 1 5 AUGUST 1969

Positronium Formation in Hydrogen

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(Received 23 December 1968)

The cross section for positronium formation by positron collisions in hydrogen is calculated from equations of three-particle scattering. We find $\sigma = 1.45\ \pi a_0^2$ at the peak, about 25% higher than the Born approximation value, but at high energies our value is lower. Comparison with other calculations is also reported.

The problem of positronium formation by scattering positrons in atomic hydrogen is often considered theoretically. The process may have some astrophysical significance. Experiments have not yet been attempted in atomic hydrogen. The reported theoretical calculations, however, do not agree very well among themselves, emphasizing the difficulty of making reliable approximations in rearrangement collisions.

The first cross-section calculation performed by Massey and Mohr[1] used the Born approximation. Both the incoming positron and the outgoing positronium were represented by plane waves. The cross section of positronium (both ortho and para types) formation rises rapidly from the threshold 6.8 eV of the positron energy to a maximum $\sigma \sim 4.5\ \pi a_0^2$ at about 14 eV and then falls away. Above 10.2 eV there are other inelastic processes, which we shall not consider, and which will compete with positronium formation in any experiment. Hence the most important point in the cross section is the position and value of the maximum quite close to the threshold. As an improvement of the incoming positron wave function, Massey and Mohr computed the s-wave phase shift approximately, and thereby obtained total production cross section lower by a factor of 2. Cheshire[2] has employed the impulse approximation and obtained the peak value of the cross section to be ten times higher than the Born value. Bransden and Jundi[3] investigated the first two partial waves. They found that without polarization the p wave cross section was much larger than the s wave, but with polarization correction the situation reversed. In absolute magnitude the cross section was not very different from the Born term. They did not find out how many partial waves were contributing appreciably at any energy. Recently Fels and Mittleman[4] considered the problem. They took account of the polarization of hydrogen and positronium through phenomenological potentials. Retaining only four partial waves, of which $l = 1$ was dominant, they obtained a cross section 40 times below the value of Massey and Mohr. The precise form of the polarization potentials near the origin did not affect the result. However, there are several points unclear in the calculation. The cross section at the peak is $0.06\ \pi a_0^2$, while out of the four partial waves the supposedly dominant $l = 1$ partial wave gives a contribution $0.02\ \pi a_0^2$, the $l = 0$ partial wave being extremely small. More recently, T. Roy and J. Das[5] calculated the positronium formation cross section in positron-hydrogen collisions in the lowest-order approximation from a field theory point of view for bound states in quantum electrodynamics. It turns out that their final result is completely equivalent to a straightforward stripping calculation given in Appendix I. However, this stripping calculation is open to criticism, and the calculations of Roy and Das are also subject to the same.

Positron scattering from hydrogen is a three-body problem and should be handled, in principle, by the rigorous three-body equations of Faddeev.[6] We hope to report on a calculation along this line later. Here we present a calculation based on standard equations of the scattering theory developed in Newton's book.[7] These equations can of