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Some Critical Properties of Ornstein-Zernike Systems and Spherical Models

W. K. Theumann*†
Institutt for Teoretisk Fysikk, Norges Tekniske Høgskole, Trondheim, Norway
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A recent work on the critical properties of Ornstein-Zernike (OZ) systems in which the direct correlation function $C(\vec{r})$ behaves as $-(kT)^{-1}w(\vec{r})$, for $\vec{r}>0$, where $w(\vec{r})$ is the finite part of the pair potential between particles of a lattice gas with point hard cores, is extended to long-range interactions $w(r)\propto r^{-(d+\sigma)}$, for $\sigma>0$, where $r=|\vec{r}|$ and d is the dimensionality. The relationship between OZ systems, the spherical model, and the mean spherical model is established, noting that the conditions defining an OZ system are precisely those of the mean spherical model. Explicit expressions for the asymptotic correlation functions in the critical region are obtained, and it is shown that, despite the long-range nature of the interaction, the relation between the exponent η and the shape of the critical isotherm coincides with the relation predicted by the scaling theory, within a certain range of σ for fixed d. The equation of state is considered both above and below the critical temperature T_c, and a breakdown of Widom's homogeneity argument is exhibited. The equation of state for $T<T_c$ makes possible the determination of the coexistence curve for all values of d and σ for which the system has a critical point; and it is shown that, when applied to short-range interactions, the difficulties found previously by Stell no longer appear.

I. INTRODUCTION

The use of exactly solvable models which exhibit a phase transition to study the nature of the critical point is commonly recognized. Among these models the ideal Bose gas[1,2] and the spherical model of a lattice gas or ferromagnet[3] have recently been reconsidered and the behavior of the thermodynamic properties and correlation functions in the critical region have been obtained with considerable detail.

A class of exactly solvable systems, which may also be viewed as models, the so-called Ornstein-Zernike (OZ) systems, have recently been considered by Stell.[4] If the pair interaction between particles a distance of $r=|\vec{r}\,|$ apart is given by $w(\vec{r}\,)$ outside a hard-core radius a, these systems are defined by the statement that the direct correlation function $C(\vec{r})=-\beta w(\vec{r})$ for *all* $r>a$, where $\beta=(k_BT)^{-1}$, k_B is Boltzmann's constant, and T is the temperature. For $r<a$, the direct correlation function is determined by the condition that the radial distribution function $g(\vec{r})$ vanishes inside the hard core. The OZ systems thus defined involve a stronger assumption about $C(\vec{r})$ than the usual OZ hypothesis,[5] that $C(\vec{r})$ behaves as $-\beta w(\vec{r})$ only for r such that $\beta w(\vec{r})\ll 1$.

The study of the critical properties of OZ systems with short-range interactions reveals some interesting aspects of the recent theories of the critical point described by Widom's homogeneity arguments[6] and Kadanoff's scaling hypothesis.[7] A breakdown of homogeneity is found for a particular value of d, the dimensionality of the system, and a result which is not in agreement with scaling already appears when $d\geq 4$. These results come from an interplay between correlations at large and small r, also present in the ideal Bose gas and spherical model, but apparently they have not been fully appreciated in the recent works on these models. We believe this is of some significance, since the scaling hypothesis only refers to correlations at large r (large compared to the lattice spacing in the case of the Ising model or lattice gas).

In this paper we consider OZ systems with long-range interactions of the form $r^{-(d+\sigma)}$, for $r>0$, and $\sigma>0$. Our motivations may be summarized by the following remarks. First, we note the role the dimensionality plays in exhibiting the previous features of OZ systems with short-range interactions and ask if there are similar breakdowns for a long-range interaction with varying range, for a fixed d. It should be noted that the scaling hypothesis makes the implicit assumption that the interactions cannot be too long ranged and it would be interesting to find out what this precisely means, at least for OZ systems.

Second, the remark has been made that the spherical model is an OZ system.[4] The work available on OZ systems presents then a difficulty in the subcritical region. For a fixed $T<T_{\rm crit}$ the correlation length remains finite on the coexistence curve for $d>4$, whereas it does not seem possible to locate the coexistence curve for $d=3$. This should be compared with the behavior of the spherical model, which has a well-defined coexistence curve when $d=3$ and for all higher d, as follows from a generalization of the standard calculations for the spherical model.[8,9] In all cases the correlation length is infinite on the coexistence curve. We may therefore ask if the spherical model, and the closely related mean spherical model, are indeed OZ systems as suggested by Stell. A clarification of this point may enable a proper comparison with the recent work on the ideal Bose gas, which has a critical behavior similar to that of the spherical model.

Our main results for a system of particles on a regular lattice are the following. First, we recognize that the conditions which define an OZ system are the same as the conditions on the direct correlation function for the mean spherical model introduced by Lewis and Wannier[10] and extended by Lebowitz and Percus.[11] We introduce a conveniently generalized correlation length familiar for systems with short-range interactions, when $\sigma > 2$, and obtain an explicit expression for the asymptotic correlation function in the critical region, which exists for $m < d$, where $m = \min[2, \sigma]$. The critical exponents of the new correlation length are obtained for $T \geq T_c$, where T_c is the critical temperature. The exponents predicted by mean field theory are obtained when $\sigma > 2$ and $d > 4$. Next, the equation of state is obtained from a modified fluctuation relation and the exponents γ and δ, describing the inverse compressibility on the critical isochore and the shape of the critical isotherm, respectively, are shown to exhibit the classical mean field values for $m < d - m$. Nonclassical exponents are obtained for $m > d - m$ and a relation between d, δ, and η, the exponent describing the decay of the asymptotic correlation function is obtained. This relation coincides with the one derived from scaling theory when $m > d - m$, despite the long-ranged nature of the interaction. We also note that the equation of state is nonhomogeneous when $m = \frac{1}{2}d$.

We use the modified fluctuation relation to show how the coexistence curve can be derived for *all* d such that $m < d$, and remark that in the same way the coexistence curve for $d = 3$, in the case of short-range interactions can be derived. We find that the correlation length is infinite on the coexistence curve for *all* $d > m$, but that the compressibility remains finite, and the exponent γ' has its mean field value, for $m < d - m$.

The critical exponents we obtain are those of the spherical model and the reason why this is so is discussed in some detail and the difficulties previously encountered with OZ systems are, hopefully, somewhat clarified.

II. FORMAL RELATIONS

We consider a simple "cubic" d-dimensional lattice of Ω sites, with unit volume per site. Then $\vec{r}_i$, the position vector of the ith site, will be a vector with integer components and the length of a side of the lattice, $L = \Omega^{1/d}$, will also be an integer which we assume to be even. The lattice is assumed to be wrapped on a torus to ensure periodic boundary conditions. We shall restrict the discussions to a lattice gas of N particles and point out that similar results can be obtained for the corresponding ferromagnet.

The particles are assumed to interact via a pair potential $v(\vec{r})$ with a "point hard-core" part $q(\vec{r})$, which excludes multiple occupancy of a lattice site. It is conventient to break $v(\vec{r})$ into

$$v(\vec{r}) = q(\vec{r}) + w(\vec{r}) , \tag{2.1a}$$

where

$$q(\vec{r}) = \infty , \quad \vec{r} = 0$$

$$= 0, \quad \vec{r} \neq 0 \tag{2.1b}$$

$$w(\vec{r}) = 0 \ \text{ for } \vec{r} = 0 . \tag{2.1c}$$

A convenient occupation-number description of the lattice gas, consistent with (2.1b), is then provided by the occupation variable $\tau_i \equiv \tau(\vec{r}_i)$ taking the values 0 or 1.

In the spherical model,[8] τ_i can take any real value subject to the spherical constraint

$$\sum_{i=1}^{\Omega} [2(\tau_i - \tfrac{1}{2})]^2 = \Omega , \tag{2.2}$$

while in the mean spherical[10,11] model the condition

$$\sum_{i=1}^{\Omega} \langle [2(\tau_i - \tfrac{1}{2})]^2 \rangle = \Omega \tag{2.3}$$

must be satisfied. The average is over the particle distribution and, for a uniform system, $\langle [2(\tau_i - \frac{1}{2})]^2 \rangle$ equals unity.

The lattice-gas analog of the radial distribution function $g(\vec{r})$ and the pair correlation function $h(\vec{r})$, or the related function $\chi(\vec{r})$, are defined by

$$g(\vec{r}_{ij}) = [\langle \tau_i \tau_j \rangle - \langle \tau_i \rangle \delta_{i,j}] / \langle \tau_i \rangle^2$$

$$= h(\vec{r}_{ij}) + 1, \tag{2.4a}$$

$$\chi(\vec{r}_{ij}) = [\langle \tau_i \tau_j \rangle - \langle \tau_i \rangle^2] / \langle \tau_i \rangle$$

$$= \langle \tau_i \rangle \, h(\vec{r}_{ij}) + \delta_{i,j} , \tag{2.4b}$$

where $\delta_{i,j}$ is the Kronecker δ and the system is assumed to be uniform; τ_i being a typical occupation number. Equations (2.4) can be expressed in terms of $\langle \tau_i \rangle = \rho$, the number density of the system. The constraint of the mean spherical model states then that

$$g(r_{ij}) = 0 \ \text{ when } r_{ij} = 0 , \tag{2.5}$$

where $r_{ij} = |\vec{r}_{ij}| = |\vec{r}_i - \vec{r}_j|$. In the spherical model, Eq. (2.5) only holds on the average.

The correlation function $\chi(\vec{r})$ and the lattice-gas analog of the direct correlation function $C(\vec{r})$ are related to one another – via Eq. (2.4b) – by an equation which takes its simplest form in terms of Fourier lattice sums,

$$\tilde{\chi}(\vec{k}) = 1 + \rho\tilde{h}(\vec{k}) = [1 - \rho\tilde{C}(\vec{k})]^{-1} , \qquad (2.6)$$

where

$$\tilde{f}(\vec{k}) = \sum_{\vec{r}} f(\vec{r}) e^{-i\vec{k}\cdot\vec{r}} , \qquad (2.7)$$

the summation being over all lattice vectors and

$$f(\vec{r}) = \Omega^{-1} \sum_{\vec{k}} \tilde{f}(\vec{k}) e^{i\vec{k}\cdot\vec{r}} \to (2\pi)^{-d} \int \tilde{f}(\vec{k}) e^{i\vec{k}\cdot\vec{r}} d\vec{k} \quad \text{as } \Omega \to \infty , \qquad (2.8)$$

where in the summation $\vec{k}$ is confined to the first Brillouin zone, $\vec{k} = (2\pi/L)\vec{n}$, $\vec{n}$ having integer components with values between $-\frac{1}{2}L$ and $\frac{1}{2}L$. The integral goes for $\vec{k}$ from $\vec{0}$ to 2π.[12]

The correlations are normally assumed to be related to thermodynamic properties by means of the fluctuation relation

$$\beta \frac{\partial p}{\partial \rho} = \beta\rho \frac{\partial \mu}{\partial \rho} = [\tilde{\chi}(\vec{k})]^{-1}_{\vec{k}=0} , \qquad (2.9)$$

where p is the pressure and μ is the chemical potential. At the critical point, where $(\partial p/\partial \rho) = (\partial \mu/\partial \rho) = 0$, one has with (2.6), $[\tilde{\chi}(0)]^{-1} = 1 - \rho\tilde{C}(0) = 0$. In the neighborhood of the critical point one expects the behavior of $\tilde{\chi}(\vec{k})$ and $\tilde{C}(\vec{k})$, for small $\vec{k}$, to be relevant.

The critical behavior of the thermodynamic properties will be assumed to be expressed in terms of critical exponents defined as follows[13]:

$$\frac{\partial p}{\partial \rho} = \rho \frac{\partial \mu}{\partial \rho} \sim (T - T_c)\gamma \quad \text{as } T \to T_c^+ \text{ for } \rho = \rho_c , \qquad (2.10a)$$

$$\sim (T_c - T)^{\gamma'} \quad \text{as } T \to T_c^- \qquad (2.10b)$$

on the coexistence curve.

$$p - p_c \sim \mu - \mu_c \sim |\rho - \rho_c|^{\delta} \operatorname{sgn}(\rho - \rho_c) \quad \text{as } \rho \to \rho_c \text{ for } T = T_c , \qquad (2.11)$$

where the subscript c stands for the critical point. The specific heat C_v can be described either by

$$C_v \sim (T - T_c)^{-\alpha} \quad \text{as } T \to T_c^+ \text{ for } \rho = \rho_c , \qquad (2.12)$$

or, more conveniently, in terms of the singular part of C_v,

$$C_v \sim A(T - T_c)^{-\alpha_s} + B \quad \text{as } T \to T_c^+ \text{ for } \rho = \rho_c , \qquad (2.13)$$

where A is not necessarily a constant but proportional to $\ln(T - T_c)$ if α_s is an integer. The shape of the coexistence curve is given by

$$|\rho - \rho_c| \sim (T_c - T)^{\beta} \quad \text{as } (T, \rho) \to (T_c, \rho_c) , \qquad (2.14)$$

where the exponent β is not to be confused with $\beta = (k_B T)^{-1}$ used as a coefficient throughout this work.

III. PAIR CORRELATION FUNCTION FOR OZ SYSTEMS

For a lattice gas with point hard cores it is convenient to separate the direct correlation function $C(\vec{r})$ into

$$C(\vec{r}) = C_0 \delta_{r,0} + C_1(\vec{r}) \qquad (3.1a)$$

such that

$$C_1(\vec{r}) = 0 \quad \text{for } \vec{r} = 0 . \qquad (3.1b)$$

The OZ systems we shall consider in this paper are then defined by[14]

$$C_1(\vec{r}) = -\beta w(\vec{r}) \quad \text{for } all\ \vec{r} > 0 , \qquad (3.2)$$

and C_0 is determined by the condition that

$$g(\vec{r}) = 0 \quad \text{for } \vec{r} = 0 . \qquad (3.3)$$

Equation (3.2) also defines $C_1(\vec{r})$ in the spherical[3,8] and mean spherical model,[11] while Eq. (3.3) coincides with the mean spherical constraint (2.5). Therefore, the direct correlation function $C(\vec{r})$ and the thermodynamic limit of the pair correlation function $\chi(\vec{r})$, for OZ systems, are identical to those of the mean spherical model. Then it follows that the Helmholtz free energy obtained by the integration of the configurational internal energy

$$U_{\text{conf}} = \tfrac{1}{2}\rho[\tilde{w}(0) + \textstyle\sum_{\vec{r}} w(\vec{r})\, h(\vec{r})] \qquad (3.4)$$

over β – the β dependence of $h(\vec{r})$ is not displayed in Eq. (3.4) – is also the same for OZ systems and the mean spherical model. The work of Lebowitz and Percus[11] can then be used to obtain some of the thermodynamic properties of OZ systems, which we consider later in this paper.

We extend here the work of Stell on OZ systems to long-range interactions of the form $r_{ij}^{-(d+\sigma)}$ between particles at the ith and jth sites of the lattice. We take $\sigma > 0$ and normalize the interaction to yield a finite energy per particle,

$$w(\vec{r}_{ij}) = w_0 r_{ij}^{-(d+\sigma)} \Big/ \sum_{i,j}{}' r_{ij}^{-(d+\sigma)} , \qquad (3.5)$$

where $w_0 < 0$ and finite, and the prime denotes summation over $i \neq j$.

The Fourier lattice sum of $C(\vec{r})$ is obtained from Eqs. (3.1), (3.2), and (3.5). In the critical region, where one expects the small-k behavior of $\tilde{C}(\vec{k})$ to be relevant, one obtains

$$\tilde{C}(\vec{k}) = \tilde{C}(0) - A_2 k^2 - A_\sigma k^\sigma + \cdots , \qquad (3.6)$$

where $k = |\vec{k}|$, A_2 and A_σ are non-negative finite constants, and $C(0)$ is finite and positive. The leading power is k^2 when the second moment of $w(\vec{r})$ exists, i.e., when $\sigma > 2$, and it becomes k^σ when $\sigma < 2$. Furthermore, the leading power in k is the same for *all* states of the system. This is no longer the case for the lattice gas and the Ising model where $C(\vec{r})$ is much more complicated. Nevertheless, for a $w(\vec{r})$ of the form here considered one still expects to find a $\tilde{C}(\vec{k})$ like Eq. (3.6) with an additional term that *at* the critical point appears to be of the form $A_p k^p$. For the nearest-neighbor case the k^σ term is absent but one still has a competition between the k^p and k^2 terms at the critical point. In the two-dimensional Ising model with nearest-neighbor interactions $p = \frac{7}{4}$, and the k^p term dominates.

Introducing (3.6) in Eq. (2.6) one finds that

$$[\tilde{\chi}(\vec{k})]^{-1} \simeq \rho A_m \kappa^m [1 + (k/\kappa)^m] , \qquad (3.7)$$

where

$$\kappa = [\rho A_m \tilde{\chi}(0)]^{-1/m} \qquad (3.8)$$

and

$$m = \min[2, \sigma] . \qquad (3.9)$$

It should be noted that Eq. (3.7) is an asymptotically exact expression for OZ systems in the critical region. When $m = 2$, following the argument of Fisher and Burford,[15] κ^{-1} may be taken as an effective correlation length. Upon Fourier inversion of Eq. (3.7) one expects that, regardless of m, $\chi(\vec{r})$ for large r will be a function of κr with two different asymptotic forms, one for $\kappa r \ll 1$ and the other for $\kappa r \gg 1$; both for small κ. It is in this sense that we will refer to κ^{-1} as a correlation length whenever $\sigma < 2$ in the course of this paper.

The explicit asymptotic forms of $\chi(\vec{r})$ follow from Eqs. (3.7) and (2.8). Transforming to polar coordinates in the latter, one has, in the critical region,

$$\beta\rho |w_0| \chi(r, \kappa) \simeq D r^{1-d/2} \int_0^\pi \frac{k^{d/2} J_{d/2-1}(kr)}{\kappa^m + k^m} dk , \qquad (3.10)$$

where $r = |\vec{r}|$, D is a constant, and $J_s(x)$ is the Bessel function of first kind. The integral can be evaluated, for small κ, by a procedure outlined in the Appendix and we find, for any fixed r,

$$[\beta\rho |w_0| \chi(r, \kappa)]_{\kappa r \ll 1} \simeq f_0(r) + f_1(r)\kappa^m + f_2(r)\kappa^{d-m} + f_3(r)\kappa^{d-m} \ln\kappa + \cdots , \qquad (3.11)$$

where $f_0(r)$, $f_1(r)$, $f_2(r)$ are finite nonzero functions at $r = 0$, $f_3(r) = 0$ for all r, unless $d = nm$, where n is an integer equal or greater than 2. Equation (3.11) is, of course, meaningful for a finite β at the critical point only when $m < d$. Using the asymptotic forms of $f_i(r)$, for large and fixed r, one also finds that

$$[\beta\rho |w_0| \chi(r, \kappa)]_{\kappa r \ll 1} = [\beta\rho |w_0| \chi(r, \kappa r)]_{\kappa r \ll 1} \simeq [c_0 + c_1(\kappa r)^m + c_2(\kappa r)^{d-m} + c_3(\kappa r)^{d-m} \ln(\kappa r) + \cdots]/r^{d-m} , \qquad (3.12)$$

where c_0, c_1, c_2 are finite constants and $c_3 = 0$ unless $d = nm$.

We also find, in the limit of very large r,

$$[\beta\rho |w_0| \chi(r, \kappa r)]_{\kappa r \gg 1} \sim d_0(\kappa r)^{-2\sigma}/r^{d-\sigma} + \cdots , \qquad (3.13)$$

where d_0 is a finite constant. Equations (3.12) and (3.13) hold in the critical region, where $\kappa \sim 0$. The former is for large and fixed r, while the latter for $r \to \infty$. It can also be seen that $\chi(r, \kappa r)$ is a homogeneous function of r and κ^{-1}, for large r and small κ.

Comparing $\chi(r, \kappa r)$ with the usual asymptotic form of the correlation function in the critical region, it follows that the exponent η is given by

$$\eta = 2 - m. \qquad (3.14)$$

When $m = 2$ one recovers the expression for η and $\chi(r, \kappa r)$, if $\kappa r \ll 1$, already found by Stell for nearest-neighbor interactions. On the other hand, when $m = \sigma$ our results generalize those obtained by Joyce for the spherical model.

We describe the critical behavior of κ in terms of exponents as follows:

$$\kappa \sim (T - T_c)^{\nu(m)} \text{ as } T \to T_c^+ \text{ for } \rho = \rho_c \qquad (3.15a)$$

$$\sim |\rho - \rho_c|^{\epsilon(m)} \text{ as } \rho \to \rho_c \text{ for } T = T_c \qquad (3.15b)$$

$$\sim (T_c - T)^{\nu'(m)} \text{ as } T \to T_c^- \text{ on the coexistence curve.} \qquad (3.15c)$$

The explicit critical behavior of the asymptotic correlation function in terms of $|T - T_c|$ and $|\rho - \rho_c|$ – via κ – follows by taking into account condition (3.3). This states that $\chi(r)|_{r=0} = 1 - \rho$. Together with Eq. (3.11) we then obtain

$$\beta\rho(1-\rho) \simeq [\beta\rho(1-\rho)]_c + \mathcal{O}(\kappa^m) + \mathcal{O}(\kappa^{d-m}) + \mathcal{O}(\kappa^{d-m}\ln\kappa) , \qquad (3.16)$$

where the subscript c denotes the value at the critical point. Depending on which of the terms in the right-hand side dominates near the critical point, one obtains the following set of equations:

$$-\rho_c^2 \,\Delta\tilde{\beta} + \tilde{\beta}_c M^2 \simeq \mathcal{O}(\kappa^m) \text{ for } m < d - m$$

$$\simeq \mathcal{O}(\kappa^{d-m}) \text{ for } m > d - m$$

$$\simeq \mathcal{O}(\kappa^{d-m}\ln\kappa) \text{ for } m = \tfrac{1}{2}d , \qquad (3.17)$$

where $\tilde{\beta} = (k_B T)^{-1}$ to distinguish from the exponent β of the coexistence curve; $\Delta\tilde{\beta} = \tilde{\beta} - \tilde{\beta}_c$ and $M = |\rho - \rho_c|$ are small quantities and terms of the order $M^2 \Delta\tilde{\beta}$ have been neglected.

Several points should be noted. Equations (3.17) determine completely the critical behavior of κ, for $T \geq T_c$, in terms of exponents. In fact, with the definitions (3.15) we obtain

$$\nu(m) = 1/m \quad \text{for } m < d - m, \qquad \epsilon(m) = 2/m \quad \text{for } m < d - m, \tag{3.18a}$$

$$\nu(m) = 1/(d - m) \quad \text{for } m > d - m, \qquad \epsilon(m) = 2/(d - m) \quad \text{for } m > d - m, \tag{3.18b}$$

where, for simplicity, we restrict ourselves to $m \neq \frac{1}{2}d$. When $m = \frac{1}{2}d$, it is clear from Eq. (3.17) that κ is *not* a homogeneous function of $\Delta\tilde{\beta}$ and M^2. What this implies about the equation of state will be made clear in Sec. IV. It can also be seen from these results that the classical exponents are recovered when $m = 2$ and $d > 4$.

It should be noted that while the exponent η is determined by the behavior of $\chi(r, \kappa r)$ for large r, the temperature and density dependence of the correlation function for *any* r is determined by the small-r behavior of $\chi(r, \kappa r)$.

Equation (3.17) is valid in the one-phase region around the critical point, both for $T > T_c$ and $T < T_c$. The computation of $\nu'(m)$ requires, however, the form of the coexistence curve and will therefore be considered in Sec. IV.

Finally, we note that despite of the fact that $\chi(r, \kappa r)$ is a homogeneous function in r and κ^{-1}, it is not a homogeneous function in $\Delta\tilde{\beta}$ and M^2 when $m = \frac{1}{2}d$.

IV. EQUATION OF STATE AND THERMODYNAMIC RESULTS FOR OZ SYSTEMS

For systems for which the fluctuation relation holds the equation of state may be obtained, up to a function of T, by the integration of Eq. (2.9). As shown by Lebowitz and Percus, however, the mean spherical model – and according to our previous discussion, OZ systems in general – does not satisfy the usual fluctuation relation. One obtains instead[11]

$$\beta \frac{\partial p}{\partial \rho} = \beta\rho \frac{\partial \mu}{\partial \rho} = \rho A_m \kappa^m + \rho(\rho - \rho_c) A_m \frac{\partial \kappa^m}{\partial \rho} . \tag{4.1}$$

This should be compared with Eq. (2.9) expressed in terms of κ with the aid of Eq. (3.8),

$$\beta \frac{\partial p}{\partial \rho} = \beta\rho \frac{\partial \mu}{\partial \rho} = \rho A_m \kappa^m . \tag{4.2}$$

The source of the difference between the normal fluctuation relation and the one satisfied by the mean spherical model has been discussed elsewhere and we shall not go into it. We simply discuss the implications of Eq. (4.1).

The nonhomogeneity of κ as a function of $\Delta\tilde{\beta}$ and M^2, referred to in Sec. III, implies that for $m = \frac{1}{2}d$ the equation of state will not be homogeneous in these two variables. This contradicts Widom's homogeneity hypothesis and the point to be made here is that, for OZ systems, this is due to the interplay between the correlations for small and large r.

The derivative of the equation of state given by Eq. (4.1) yields further relations for critical exponents. Thus, on the critical isochore the usual relation

$$\gamma = (2 - \eta)\,\nu(m) \tag{4.3}$$

is obtained. On the critical isotherm one finds that

$$(\delta - 1) = (2 - \eta)\,\epsilon(m) , \tag{4.4}$$

both for $m \neq \frac{1}{2}d$. It should be noted that Eq. (4.4) is the same as the relation that follows from the usual fluctuation relation, Eq. (4.2).

Using Eqs. (3.18) we then obtain

$$\gamma = 1 \quad \text{for } m < d - m, \qquad \delta = 3 \quad \text{for } m < d - m, \tag{4.5a}$$

$$\gamma = m/(d - m) \quad \text{for } m > d - m, \qquad \delta = (d + m)/(d - m) \quad \text{for } m > d - m . \tag{4.5b}$$

The mean field results are obtained when $m < d - m$. This is the case when $d > 4$ for a long-range interaction [Eq. (3.5)] with finite second moment, and when $d > 2\sigma$ if $\sigma < 2$. One also notes that when use is made of Eq. (3.14) one finds

$$\eta = 2 - d(\delta - 1)/(\delta + 1) \quad \text{for } m > d - m , \tag{4.6a}$$

$$\eta > 2 - d(\delta - 1)/(\delta + 1) \quad \text{for } m < d - m . \tag{4.6b}$$

The first is the relation predicted by the scaling laws but the second is not. The scaling-law theory of the critical point is somehow based on the assumption that the interaction should not be too long ranged. What this precisely means does not seem to be known and Eq. (4.6a) illustrates, at least as far as OZ systems are concerned, that the interaction may be as long ranged as Eq. (3.5), provided $d < 2m$, where m is given by Eq. (3.9).

The conjecture has been made[7] that for any fixed d, no matter how large, a region around the critical point should exist where the predictions of the scaling-law theory should hold. The interaction (3.5), when $\sigma > 2$, leads to a critical behavior for OZ systems which in many aspects is that of a system with a short-range interaction, and Eq. (4.6b) illustrates that the dimensionality conjecture breaks down already for $d = 4$ when $m = 2$.

The behavior of η exhibited by Eq. (4.6) is a consequence of having imposed condition (3.3) on $\chi(\vec{r})$. In the scaling-law theory the fluctuations scale on a distance r which is large compared to the lattice spacing. For our particular choice of a lattice made in Sec. II this means $r \gg 1$. Therefore, correlations for small r, either $r=0$ or $r\approx 1$, are already outside the frame of the scaling laws and one should not be too surprised, perhaps, that (4.6b) does not support the dimensionality conjecture.

We wish to emphasize that our results for OZ systems, based on the exact asymptotic expressions for the correlation function in the critical region, are exact. Equation (4.6) should be compared with the inequality for quite general systems obtained through a plausible argument by Gunton and Buckingham.[16] The same inequality seems to hold also for non-OZ systems.[17]

We turn now to the equation of state in the subcritical region, with special interest in the coexistence curve. First, we note that Eq. (4.1) is not restricted to the one-phase region but it also holds inside the transition region of the mean spherical.[11] For any fixed $T<T_c$ ($\tilde{\beta}>\tilde{\beta}_c$) we may therefore write

$$\frac{\mu(\rho,\tilde{\beta})-\mu(\rho_c,\tilde{\beta})}{\rho-\rho_c}=\frac{1}{\rho-\rho_c}\int_{\rho_c}^{\rho}\frac{\partial\mu(n,\tilde{\beta})}{\partial n}\,dn$$

$$=\frac{A_m}{\tilde{\beta}(\rho-\rho_c)}\int_{\rho_c}^{\rho}\left(\kappa^m(n,\tilde{\beta})+(n-\rho_c)\frac{\partial\kappa^m(n,\tilde{\beta})}{\partial n}\right)dn\ . \tag{4.7}$$

As noted before, the correlation functions and, hence, the solutions of Eq. (3.17) are only definitely valid in the one-phase region, and they may not hold in states of the two-phase region.[12] To determine the coexistence curve, however, all we need is the analytic continuation of the one-phase κ in Eq. (4.7) combined with the condition

$$\mu(\rho_c+M,\tilde{\beta})=\mu(\rho_c-M,\tilde{\beta})\ , \tag{4.8}$$

the transition taking place at $\rho=\rho_c\pm M$.

Integration by parts converts Eq. (4.7) into

$$\frac{\mu(\rho,\tilde{\beta})-\mu(\rho_c,\tilde{\beta})}{\rho-\rho_c}=A_m\tilde{\beta}^{-1}[\kappa(\rho,\tilde{\beta})]^m\ , \tag{4.9}$$

and condition (4.8) yields

$$\kappa(\rho,\tilde{\beta})=0,\quad \text{coexistence curve} \tag{4.10}$$

or, in terms of Eq. (3.17),

$$-\rho_c^2\Delta\tilde{\beta}+\tilde{\beta}_c(\rho-\rho_c)^2=0\quad \textit{all } m<d\ . \tag{4.11}$$

Several points should be noted here. First, Eq. (4.9) combined with Eq. (3.17) becomes

$$\tilde{\beta}\,\frac{\mu(\rho,\tilde{\beta})-\mu(\rho_c,\tilde{\beta})}{\rho-\rho_c}=\text{const}\times[-\rho_c^2\Delta\tilde{\beta}+\tilde{\beta}_c(\rho-\rho_c)^2]\qquad \text{for } m<d-m$$

$$=\text{const}'\times[-\rho_c^2\Delta\tilde{\beta}+\tilde{\beta}_c(\rho-\rho_c)^2]^{m/(d-m)}\quad \text{for } m>d-m\ . \tag{4.12}$$

When $m=2$ and $d=3$, the second has precisely the same form as the equation of state of the three-dimensional spherical model with short-range interactions, derived by Langer.[9] The first equation has the form one finds for the d-dimensional spherical model, odd $d\geq 5$, by a straightforward generalization of the work of Langer.

Equation (4.10) identifies the coexistence curve with the locus of $\kappa=0$, for *all* $m<d$. When $m=2$, the analog of short-range interactions, this is the case for *all* $d\geq 3$, in contrast to the result of Stell, who found that the coexistence curve does not coincide with the locus of $\kappa=0$ for $d\geq 4$ and that there is no coexistence curve for $d=3$, if the usual fluctuation relation, Eq. (4.2), is assumed to hold. Equation (4.10) also says that the correlation length κ^{-1} is infinite on the coexistence curve for *all* $m<d$. This implies that $\nu'(m)$, the exponent in (3.15c), is undefined. It should be noted that the same occurs in the spherical, which is briefly considered in Sec. V. We note also that the exponent β of Eq. (2.14) is, according to (4.11),

$$\beta=\tfrac{1}{2}\ . \tag{4.13}$$

The inverse compressibility on the coexistence curve (denoted by the subscripts c.c.) obtained from Eq. (4.1) and (4.11) is given by

$$\left.\frac{\partial p}{\partial\rho}\right|_{\text{c.c.}}=\rho\left.\frac{\partial\mu}{\partial\rho}\right|_{\text{c.c.}}\sim(T_c-T)\quad \text{for } m<d-m, \tag{4.14a}$$

$$\left.\frac{\partial p}{\partial\rho}\right|_{\text{c.c.}}=\rho\left.\frac{\partial\mu}{\partial\rho}\right|_{\text{c.c.}}=0\quad \text{for } m>d-m\ , \tag{4.14b}$$

and in terms of the exponent γ' this means

$$\gamma'=1\quad \text{for } m<d-m, \tag{4.15a}$$

$$\gamma',\ \text{undefined}\quad \text{for } m>d-m\ . \tag{4.15b}$$

Again, these results are the same as those for the spherical model with long-range interactions (3.5)[3] when $m=\sigma<2$, and those for short-range interactions when $d\geq 3$.[18]

We consider now the critical behavior of the specific heat C_V. This requires a term-by-term differentiation in Eq. (3.4), justified by the finite specific heat which is thus obtained. Making use of (3.11) and (3.15a) we find, for

$\rho=\rho_c$ and $T>T_c$,

$$C_V\sim\mathcal{O}[(\Delta T)^{m\nu-1}]+\mathcal{O}[(\Delta T)^{(d-m)\nu-1}]$$

$$+\theta_m \mathcal{O}\left[(\Delta T)^{(d-m)\nu-1}\ln(\Delta T)\right], \quad (4.16)$$

where $\Delta T = T - T_c$ and

$$\theta_m = 1 \text{ for } d = nm,\ n\text{: integer} \geq 2$$
$$= 0 \text{ otherwise.} \quad (4.17)$$

The case where $m = 2$ leads to the same results as those already obtained by Stell and we shall, therefore, restrict ourselves to $m = \sigma$. We are interested in C_V for $\Delta T \to 0$, and the leading term in Eq. (4.16) will thus be the one with the smallest positive power or largest negative power. Comparison with Eq. (2.12) then yields

$$\nu = (1-\alpha)/\sigma \quad \text{for } \sigma < d - \sigma, \quad (4.18a)$$

$$\nu = (1-\alpha)/(d-\sigma), \quad \text{for } \sigma > d - \sigma. \quad (4.18b)$$

From this and Eqs. (3.18) it follows that $\alpha = 0$ for all $d > \sigma$, and the specific heat remains finite. One is interested then in the "singular part" of C_V and in the exponent α_s. This is determined as follows. Let

$$l = \min[\sigma,\ d-\sigma]. \quad (4.19)$$

When $l = \sigma$ the dominant part of C_V is given by the first term in Eq. (4.16) and the next to dominant term has an exponent

$$-\alpha^* = (d - 2\sigma)/\sigma > 0, \quad d \neq n\sigma, \quad (4.20)$$

where use has been made of Eqs. (3.18). Moreover, since $d \neq n\sigma$, $-\alpha^*$ is not an integer and C_V has a singular part, with

$$\alpha_s = \alpha^*. \quad (4.21)$$

When $d = n\sigma$ the $\ln(\Delta T)$ term is the next to dominant one in Eq. (4.16) and there is again a singular part of C_V.

On the other hand, when $l = d - \sigma$, the dominant part of C_V is given by the second term in Eq. (4.16) and the next to dominant one has an exponent

$$-\alpha^* = (2\sigma - d)/(d-\sigma) > 0. \quad (4.22)$$

In this case, C_V has a singular part and we have $\alpha_s = \alpha^*$ only for $d/\sigma \neq (n_0+1)/n_0$, where n_0 is an integer equal or greater than 2. This behavior is similar but somewhat more involved than in the case of short-range interactions, where there is only one d, namely, $d = 3$, for which no singularity in C_V appears.

The above results can be summarized, for $d \neq n\sigma$, in the form

$$\alpha_s = (2\sigma - d)/\sigma \quad \text{for } \sigma < d - \sigma \quad (4.23a)$$

$$= (d - 2\sigma)/(d-\sigma) \quad \text{for } \sigma > d - \sigma, \quad (4.23b)$$

or, with Eq. (3.18),

$$\alpha_s = 2 - d\nu. \quad (4.24)$$

This relation is consistent with the result obtained from scaling theory. When $\alpha_s < 0$ we have thus a way of deciding between $\alpha = 0$ and $\alpha = 2 - d\nu$, whereas scaling theory does not. This result is the same as for short-range interactions.

The simple considerations made up to here cannot be used to determine C_V for $T < T_c$ due to the fact that ν' is undetermined. One would expect, however, that if the specific heat is determined from a full knowledge of the configurational internal energy, the exponent α' on the coexistence curve would satisfy the symmetry $\alpha' = \alpha = 0$.

V. COMPARISON WITH SPHERICAL MODEL

Our previous results indicate a clear resemblance with the results for the spherical model. This is perhaps not surprising after our identification of OZ systems with the mean spherical model. Despite the fact that the constraints of the spherical and mean spherical model are not precisely the same, the two models are expected to have the same thermodynamic properties, as argued explicitly by Yan and Wannier[19] for the case of short-range interactions. A straightforward extension of their work to allow for long-range interactions of the form (3.5) shows that the distribution of the variable $\omega_i \equiv 2(\tau_i - \frac{1}{2})$ is a Gaussian with average $\langle \omega_i \rangle = 1 - \rho/\rho_c$ and $\langle \omega_i^2 \rangle = 1$, for $T > T_c$, and a superposition of two displaced Gaussians with $\langle \omega_i \rangle = \pm(1 - \rho/\rho_c)$ and $\langle \omega_i^2 \rangle = 1$, on the coexistence curve, for $T < T_c$. One also expects the correlation functions in the thermodynamic limit to be the same for the spherical and mean spherical model but some differences may occur in the explicit form of the fluctuation relation, as is apparent from the work of Lebowitz and Percus.[11]

In addition to these remarks it is interesting to note the following. The correlation function $\chi(\vec{r})$, for $\vec{r} = 0$, can be expressed for OZ systems in the form

$$\beta\rho(1-\rho)\,|w_0| = (2\pi)^{-d}\int\left[\xi - \frac{\tilde{w}(\vec{k}) - \tilde{w}(0)}{\tilde{w}(0)}\right]^{-1} d\vec{k}, \quad (5.1)$$

where $\tilde{w}(\vec{k})$ is the Fourier lattice sum of $w(\vec{r})$ and

$$\xi = \kappa^m, \quad (5.2)$$

for the specific long-range interaction we consider. Equation (5.1) is then formally the same as the saddle-point equation for the spherical model in which ξ is the saddle-point parameter.[20] Similarly, $\chi(\vec{r})$ for $r \neq 0$ is also the correlation function for the spherical model, and Eq. (5.2) then associates the inverse correlation length κ with $\xi^{1/m}$, a power of the saddle-point parameter. The critical point and the phase transition of the spherical model are characterized by $\xi = 0$, which means then, an infinite correlation length. This is a result for the spherical model which does not depend on dimensionality provided the system has a transition, of course, and it illustrates the fact that also in this model the coexistence curve coincides with the locus of $\kappa = 0$, as we found to be the case for OZ systems, for *all* $d > m$.

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APPENDIX

We consider the integral

$$I(r, \kappa) = r^{-\rho} \int_0^{\pi} \frac{k^{\rho+1} J_\rho(kr)}{\kappa^m + k^m}\, dk \;, \qquad \text{(A1)}$$

where $\rho = \frac{1}{2}d - 1$, m is given by Eq. (3.9), and we first let $0 < \sigma < 2$. The extension to $\sigma > 2$ will be commented later on. For $r \neq 0$ it is convenient to rewrite (A1) as

$$I(r, \kappa) = F_\kappa(\kappa r)/r^{2(\rho+1)-\sigma} \;, \qquad \text{(A2)}$$

where

$$F_\kappa(\kappa r) \equiv (\kappa r)^{\rho+2-\sigma} \int_0^{\pi/\kappa} \frac{\xi^{\rho+1} J_\rho(\xi\kappa r)}{1+\xi^\sigma}\, d\xi, \qquad \text{(A3)}$$

the dependence on κ alone coming from the upper limit of integration. We approximate $F_\kappa(\kappa r)$ by $F_0(\kappa r)$, noting that this should yield the correct asymptotic dependence on κr, for large r and small κ, and the task is then to compute the resulting integral in (A3). We do not know of a simple evaluation of such an integral and are forced to use the following somewhat lengthy procedure. First, we compute the integral for $d < \sigma$, the range of convergence, and then we give the extension to $d > \sigma$, the physically interesting case in this paper.

Take the integral representation of the Bessel function[21]

$$J_\rho(x) = \frac{1}{2\pi i} \int_{-i\infty}^{i\infty} \frac{\Gamma(-t)\,(x/2)^{\rho+2t}}{\Gamma(\rho+t+1)}\, dt$$

and insert it in $F_0(\kappa r)$. After interchange of the order of integration, use of the integral

$$\int_0^\infty \frac{\xi^{u-1}}{1+\xi^v}\, d\xi = \frac{1}{v}\, \Gamma\!\left(\frac{u}{v}\right) \Gamma\!\left(1-\frac{u}{v}\right) ,$$

and making the substitution

$$2t + d - \sigma = 2\tau \;,$$

we obtain

$$F_0(z) = \left(\frac{1}{\sigma 2^{\sigma-(d+1)/2}}\right) \frac{1}{2\pi i} \int_{(d-\sigma)/2-i\infty}^{(d-\sigma)/2+i\infty} \frac{\Gamma(d/2-\sigma/2-\tau)\Gamma[-(2/\sigma)\tau]\,\Gamma[1+(2/\sigma)\tau]}{\Gamma(\sigma/2+\tau)}\, z^{2\tau} d\tau \;, \qquad \text{(A4)}$$

where $z = \frac{1}{2}\kappa r$. The integral is to be computed closing the contour of integration in the complex τ plane. For $z \ll 1$, this is achieved by a semicircle to the right of the line $R_e\,\tau = \frac{1}{2}(d-\sigma)$ and a deformation of the contour to include only the poles of the integrand with $R_e\,\tau \geq 0$. For $z \gg 1$, the contour is closed by a semicircle to the left of that line. The poles of the integrand may be simple or double, as emerges from Table I. Since $d > 0$, double poles may occur only among those of types 1 and 2, and this is the case when

$$\tau = p + \tfrac{1}{2}(d-\sigma) = \tfrac{1}{2}\sigma l \qquad \text{(A5)}$$

is satisfied. Thus, if $d < \sigma$, the pole with $p = 0$ is a simple pole. Figure 1 enables to visualize when double poles do occur. The residues of these poles are given by

$$[a_0(\tau) + a_1(\tau)\ln z]\, z^{2\tau} \;,$$

evaluated at τ satisfying (A5), where $a_0(\tau)$ and $a_1(\tau)$ are regular, nonzero functions of τ, d, and σ.

The extension to $d > \sigma$ is obtained noting that the poles of type 2 move to the right together with the contour, whereas the poles of types 1 and 3 stay where they are. To obtain $F_0(z)$, for $z \ll 1$, the contour of integration must be deformed to include the poles of type 1 which remain outside the old contour when shifted to the right. The new contours, for $z \ll 1$ and $z \gg 1$, in the case where $d < 2\sigma$, are shown in Fig. 2. When $d > 2\sigma$, the pole of type 2 with largest residue lies to the right of $\tau = \frac{1}{2}\sigma$, whereas the double pole with largest residue occurs when $p = 0$ in (A5), i.e., at $\tau = \frac{1}{2}\sigma$ if $d = 2\sigma$. It is also clear that further double poles occur for integers n such that $d = n\sigma$, $n \geq 3$, but their contributions

TABLE I. Poles of the integrand in Eq. (A4). Only the simple poles are listed explicitly for $d<\sigma$. l and p are positive integers or zero, q is a positive integer.

Function	Poles	Residues
$\Gamma[-(2/\sigma)\tau]$	(1) $\tau=\frac{1}{2}\sigma l$	$\frac{(-1)^1}{1!}\frac{\Gamma(\frac{1}{2}d-\frac{1}{2}\sigma-\frac{1}{2}\sigma l)\Gamma(1+l)}{\Gamma[\frac{1}{2}\sigma(1+l)]}z^{\sigma l}$
$\Gamma[\frac{1}{2}d-\frac{1}{2}\sigma-\tau]$	(2) $\tau=p+\frac{1}{2}(d-\sigma)$	$\frac{(-1)^p}{p!}\frac{\Gamma[1-d/\sigma-(2/\sigma)p]\Gamma[d/\sigma+(2/\sigma)p]}{\Gamma(p+\frac{1}{2}d)}z^{2p+d-\sigma}$
$\frac{\Gamma[1+(2/\sigma)\tau]}{\Gamma[\sigma/2+\tau]}$	(3) $\tau=-\frac{1}{2}\sigma(q+1)$	$\frac{(-1)^q}{q!}\frac{\Gamma(\frac{1}{2}d+\frac{1}{2}\sigma q)\Gamma(1+q)}{\Gamma(-\frac{1}{2}\sigma q)}z^{-\sigma(q+1)}$

to $F_0(z)$, for $z \ll 1$, are dominated by poles of type 1 with $l<2$. Also, the larger d/σ becomes, the more poles that have to be included by deforming the contour in the way of Fig. 2.

The residues of the simple poles for $d>\sigma$ may be obtained from Table I by analytic continuation. For this purpose, we assume that in the first part d and σ were such that $(\sigma-d)<2$ in the integral (A4), *before* the extension to $d>\sigma$. Then one obtains, for small κ and large r, the results for (A1) in the form

$$I(r;\ \kappa r \ll 1)=[c_0+c_1(\kappa r)^\sigma+c_2(\kappa r)^{d-\sigma}+c_3(\kappa r)^{d-\sigma}\ln(\kappa r)+\cdots]/r^{d-\sigma}, \quad (\text{A6})$$

$$I(r;\ \kappa r \gg 1)=d_0(\kappa r)^{-2\sigma}/r^{d-\sigma}+\cdots, \quad (\text{A7})$$

where c_0 and d_0 are positive constants, as they should be, since the results are proportional to the correlation function. Also, from our discussion it follows that $c_3=0$ unless $d=n\sigma$, where $n\geq 2$.

A simple test of Eq. (A6) may be provided computing explicitly the ratio c_1/c_0 for $d=3$ and $\sigma=1$. The result is $-\pi/2$, and coincides with the one obtained by Joyce[3] who studied $I(r,\kappa)$ only for $\sigma=1$ and $d=2$ and $d=3$. One can also see that the κr and r dependence of Eqs. (A6) and (A7) are those obtained by Joyce in the particular cases he considered.

The procedure outlined for $\sigma<2$ can be extended to $\sigma>2$, i.e., $m=2$ only for $\kappa r \ll 1$. This is due to the fact that a gamma function in the numerator of (A4) cancels with the one in the denominator, for all τ, and consequently, all the poles to the left of the contour are removed and the integral for $\kappa r \gg 1$ would be zero, which we know cannot be right from the standard expression for $I(r, \kappa r \gg 1)$ when $m=2$. However, for $\kappa r \ll 1$, one obtains Eq. (A6) with σ replaced by 2, which has the known form of $I(r, \kappa r \ll 1)$ for this case.

We look now at $I(r,\kappa)$ for small κ and $r\to 0$ and note that the integral has been obtained by Joyce in the analysis of the saddle-point equation of the spherical model. His results may be summarized in the form

$$[I(r,\kappa)]_{r\to 0}=b_0+b_1\kappa^\sigma+b_2\kappa^{d-\sigma}+b_3\kappa^{d-\sigma}\ln\kappa+\cdots, \quad (\text{A8})$$

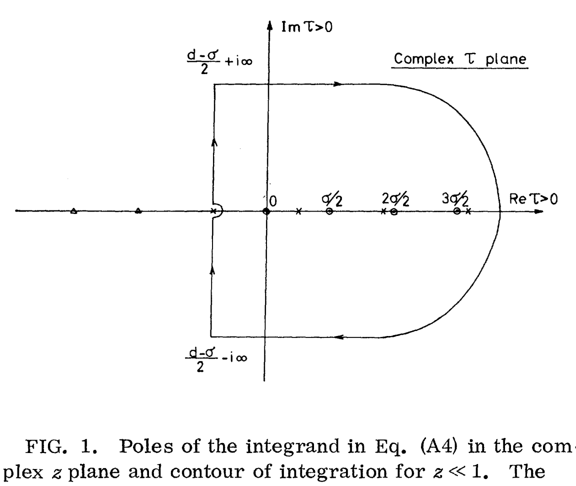

FIG. 1. Poles of the integrand in Eq. (A4) in the complex z plane and contour of integration for $z \ll 1$. The poles of type 1 are indicated by ⊙, those of type 2 by ×, and of type 3 by △. The case $d<\sigma$ is illustrated.

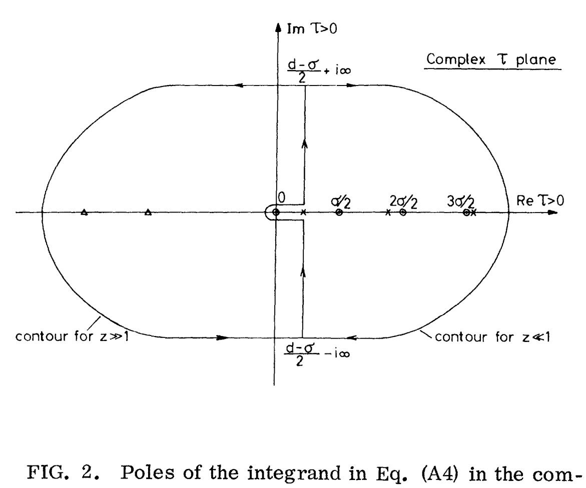

FIG. 2. Poles of the integrand in Eq. (A4) in the complex z plane and contours of integration for $z \ll 1$ and $z \gg 1$ in the case where $\sigma<d<2\sigma$.

where b_0, $b_1, \ldots$ are constants and $b_3 = 0$ unless $d = 2\sigma$. It is possible to see from Joyce's work that additional logarithmic terms do appear for $d = n\sigma$, with n an integer larger than 2. These terms are, however, of higher order and they can be included formally in Eq. (A8) extending b_3 to be zero unless $d = m\sigma$, where $m = 2, 3, \ldots$

Equations (A6) and (A7) are valid in the limit of very large r. For large but finite r, the constants in these equations become functions of r and in the limit of $r \to 0$ one should expect them to go over into the constants in Eq. (A8), if $I(r, \kappa)$ has the correct dependence on κr, for small κ and any fixed r. In other words, for any fixed r, we have

$$I(r;\ \kappa r \ll 1) = f_0(r) + f_1(r)\kappa^\sigma + f_2(r)\kappa^{d-\sigma} + f_3(r)\kappa^{d-\sigma}\ln\kappa + \cdots , \qquad \text{(A9)}$$

where $f_0(r)$, $f_1(r)$, and $f_2(r)$ are finite and nonzero for $r = 0$ and $f_3(r) = 0$ unless $d = m\sigma$, where $m = 2, 3, \ldots$

*Norges Teknisk-Naturvitenskapelige Forskningsråd, Postdoctoral Fellow.

†Address after October 1, 1970: Physique Théorique et Hautes Energies Bâtiment 211. Faculté des Sciences, 91-Orsay, France.

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Energy Eigenvalues, Eigenfunctions, and Transition Probabilities for a Paramagnetic Ion

S. K. Gupta and M. L. Narchal

Physics Department, Punjabi University, Patiala, India

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The energy eigenvalues, eigenfunctions, and radiatively induced transition probabilities are computed perturbatively for an axially symmetric paramagnetic ion for arbitrary relative orientations of the crystal symmetry axis, static magnetic field, and time-varying magnetic field. Exact calculations are also reported for a system in which $S=\frac{1}{2}$, $I=\frac{1}{2}$. The bearing of these results on dynamic-nuclear-orientation experiments in paramagnetic samples is also discussed.

I. INTRODUCTION

The EPR spectra of many paramagnetic ions that have been successfully studied experimentally[1-8] can be understood in terms of the spin Hamiltonian

$$\mathcal{H} = \beta \sum_{kl} H_k g_{kl} S_l + \sum_{kl} I_k A_{kl} S_l + g_n \beta \vec{H} \cdot \vec{I} , \qquad (1.1)$$

where the symbols have their usual significance. The energy eigenvalues, eigenfunctions, and radiatively induced transition probabilities for such a system have been calculated perturbatively for