we have

$$\eta^{-2}\exp[-Xt+\tau Ye^{-t/\tau}]-\bar{\eta}^{-2}e^{\tau Y}$$
$$=8b\gamma\int_0^t \exp[-Xt'+\tau Ye^{-t'/\tau}]dt'. \quad (A11)$$

For the quenching case, $\tau\to 0$, and we get

$$\eta^{-2}e^{-Xt}-\bar{\eta}^{-2}=8b\gamma\int_0^t e^{-Xt'}dt'=8b\gamma\frac{1-e^{-Xt}}{X},$$

so that

$$\eta^2=e^{-Xt}/[(8b\gamma/X)(1-e^{-Xt})+\bar{\eta}^{-2}]$$
$$=\frac{\eta_0^2\exp[-4a_0\gamma(T_f-T_c)t]}{\exp[-4a_0\gamma(T_f-T_c)t]-1+(\eta_0/\bar{\eta})^2}. \quad (A12)$$

For the annealing case, $\tau\to\infty$, and

$$\tau Ye^{-t/\tau}\simeq\tau Y(1-t/\tau)=\tau Y-Yt.$$

Thus

$$\eta^{-2}\exp[-(X+Y)t+\tau Y]-\bar{\eta}^{-2}e^{\tau Y}$$
$$=8b\gamma e^{\tau Y}\int_0^t e^{-(X+Y)t'}dt'.$$

Hence

$$\eta^2=\frac{\eta_0^2\exp[-4a_0(T_i-T_c)\gamma t]}{\exp[-4a_0\gamma(T_i-T_c)t]-1+(\eta_0/\bar{\eta})^2}. \quad (A13)$$

These are the two special cases of Eq. (16) that are of interest in isothermal relaxation.

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Critical Correlations in the Ising Model

EUGENE HELFAND
Bell Telephone Laboratories, Murray Hill, New Jersey
AND
J. S. LANGER
Carnegie Institute of Technology, Pittsburgh, Pennsylvania

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The Ising-model correlation function $C(R_{12})=\langle\mu_1\mu_2\rangle$ is studied in terms of a novel N-fold integral representation. This formula stems from a procedure proposed by Montroll and Berlin. The integral is estimated by maximizing the integrand, an approximation related to the spherical-model assumptions. The correlation function is not of the Ornstein-Zernike type, just above the critical point, but rather $C(R)\propto R^{-1-\eta}$ for $R\ll 1/\kappa$, and $C(R)\propto\kappa^\eta R^{-1}\exp(-\kappa R)$ for $R\gg 1/\kappa$. The correlation length $1/\kappa$ becomes infinite at the critical point. The calculated value $\eta=0.646$ is too large, reflecting the omission of important terms in the evaluation of the integral. The unusual mechanism inducing the nonclassical behavior is carefully examined.

I. INTRODUCTION

THERE now exists a large body of evidence concerning anomalous behavior of correlation functions near critical points. For the nearest-neighbor Ising model, in particular, information has been obtained analytically in two dimensions, and numerically in three dimensions. There occur marked qualitative deviations from the correlations predicted by the classical theory of Ornstein and Zernike. In spite of this wealth of data, however, there has been very little progress toward a general analytic theory of the critical point. In fact, it has so far turned out to be remarkably difficult to recover anything but the Ornstein–Zernike correlation function from either soluble models or systematic approximations. In response to this difficulty, we have attempted to find a new formulation of the theory of critical correlations which might provide a means for calculating the known nonclassical behavior. Our attempt has not been completely successful, but we hope that several of our results may provide useful clues in the search for a correct theory.

We consider an Ising model consisting of N spins with values $\mu_i=\pm 1$, $i=1,\cdots,N$, located at sites $\mathbf{r}_i$ on an s-dimensional cubic lattice. The energy E is a simple ferromagnetic coupling of the form

$$E=-\tfrac{1}{2}J\sum_{i,j=1}^{N}v_{ij}\mu_i\mu_j. \quad (1.1)$$

Here the dimensionless v_{ij} is a function only of the distance between the lattice points $|\mathbf{r}_i-\mathbf{r}_j|$, and is of strictly finite range. The partition function is

$$Z=\sum_{\{\mu_i=\pm 1\}}\exp\{K\sum_{ij}v_{ij}\mu_i\mu_j\}, \quad (1.2)$$

$$K=J/2k_BT, \quad (1.3)$$

and the pair-correlation function may be written

$$C_{mn}=Z^{-1}\sum_{\{\mu_i=\pm 1\}}\mu_m\mu_n\exp\{K\sum_{ij}v_{ij}\mu_i\mu_j\}. \quad (1.4)$$

We shall consider only zero external magnetic field, and shall concentrate on temperatures at or just above the critical temperature, so that there is no long-range order.

Emphasis in the subsequent development will be placed largely on the evaluation of C_{mn} for large separations of the lattice points m and n. A class of approximations very closely related to the spherical model of Berlin and Kac[1] will be employed. In Eqs. (1.3) and (1.4), the sum over the configurations $\{\mu_i=\pm1\}$ is performed over a hypercube in the N-dimensional μ space. In the pure spherical model, this sum is replaced by an integration over the hypersphere specified by

$$\sum_{i=1} \mu_i^2=N, \tag{1.5}$$

which passes through the points $\{\mu_i=\pm1\}$. The partition function then becomes

$$Z_{\mathrm{SM}}=\mathfrak{N}_N\int_{-\infty}^{\infty}\cdots\int d\mu_1\cdots d\mu_N\delta\Big(\sum_{i=1}^{N}\mu_i^2-N\Big)\times\exp\{K\sum_{ij}v_{ij}\mu_i\mu_j\}, \tag{1.6}$$

with normalization $\mathfrak{N}_N$ chosen to give the correct result for a noninteracting system. This quantity Z_{SM} is best thought of as the exact partition function for a well-defined but nonphysical "spherical" model of a ferromagnet; but also may be interpreted as a crude approximation to the partition sum for the Ising model. In fact, a variety of approximate solutions to the Ising problem turn out to be essentially identical to the spherical model.[2]

Note that the sphere defined by Eq. (1.5) is just one of a large class of quadratic surfaces of the form

$$\sum_{i=1}^{N}\phi_i\mu_i^2=\sum_{i=1}^{N}\phi_i, \tag{1.7}$$

each of which contains every point for which all the μ_i are ±1; that is, each surface contains all of the points in μ space that describe the allowed configurations of the true Ising model. The intersection of all possible surfaces of the form (1.7) must reduce to just these configuration points. This observation is a geometric interpretation of an analytic formulation of the Ising problem proposed originally by Montroll and Berlin,[3] and is central to the present work. One interpretation of the present work is that it attempts to improve upon the spherical approximation to the correlation function by including in the integrand a few constraints of the form (1.7), in which ϕ_i is not just a constant as in Eq. (1.5). It turns out that a very natural choice of ϕ_i may be obtained from a study of the Montroll–Berlin formalism. The result is a novel form of the correlation function with qualitatively satisfactory deviations from the Ornstein-Zernike theory.

In Sec. II of this paper we shall review the Montroll–Berlin formalism and emphasize its relation to the spherical model. Then, in Sec. III, we shall apply this technique to the calculation of the correlation function. Throughout these sections we shall pay attention to the dependence of our results on the dimensionality of the system in accord with the apparent fact that critical phenomena are much more sensitive to dimensionality than they are to, say, lattice structure or the details of the spin–spin interaction. Because our mathematics will remain similar to that of the spherical model, we shall not be able to consider two-dimensional systems, for which the spherical model predicts no phase transition. Three dimensions turn out to be the most interesting, with the most significant deviations from the Ornstein-Zernike behavior. There occurs a weak anomaly in four dimensions, and for five or more dimensions, we recover the Ornstein–Zernike theory.

In Sec. III a number of crude mathematical approximations will be made so as not to obscure the essential features of this theory. In Sec. IV we shall describe our best attempt to date at making a quantitative calculation of the three-dimensional correlation function. The critical correlation function calculated in this fashion decays like $R^{-1-\eta}$; but our best estimate of η turns out to be much too large to agree with the numerical calculations of Fisher and Burford.[4]

The specific heat in the neighborhood of the critical point is related to a four-spin correlation function.[5] A calculation of this four-spin average within the context of the present theory is presented in Sec. V.

In an Appendix, we present a discussion of an alternative formulation of the Ising model which is structurally similar to that employed in the body of the paper.

II. FORMULATION OF MONTROLL AND BERLIN

Montroll and Berlin[3] have cast the Ising partition function, Eq. (1.2), into an alternative analytic form by inserting Dirac delta functions to convert the summation to an integration

$$Z=\int_{-\infty}^{\infty}\cdots\int d\mu_1\cdots d\mu_N\Big[\prod_{j=1}^{N}2\delta(1-\mu_j^2)\Big]\times\exp\{K\sum_{ij}v_{ij}\mu_i\mu_j\}. \tag{2.1}$$

[Note that Eq. (2.1) may be said to be derived by choosing a special set of functions ϕ_i in Eq. (1.7) such that the jth function is $\phi_i^{(j)}=\delta_{ij}$. Clearly any function defined over the lattice sites may be expressed as a linear combination of these ϕ's.] With the integral

[1] T. H. Berlin and M. Kac, Phys. Rev. **86**, 821 (1952).
[2] R. Brout, *Phase Transitions* (W. A. Benjamin Inc., New York, 1965).
[3] E. W. Montroll and T. H. Berlin, Commun. Pure Appl. Math. **4**, 23 (1951).
[4] M. E. Fisher and R. J. Burford, Phys. Rev. **155**, 583 (1967).
[5] F. H. Stillinger, Phys. Rev. **146**, 209 (1966).

representation of the delta function,

$$\delta(1-\mu^2)=\frac{K}{2\pi i}\int_{-i\infty}^{i\infty}\exp\{Kt(1-\mu^2)\}dt, \qquad (2.2)$$

the partition function becomes

$$Z=\left(\frac{K}{\pi i}\right)^N\int_{-\infty}^{\infty}\cdots\int d\mu_1\cdots d\mu_N\int_{-i\infty}^{i\infty}\cdots\int dt_1\cdots dt_N$$
$$\times\exp\{K\sum_j t_j\}\exp\{-K\sum_{ij}(\mathsf{T}-\mathsf{V})_{ij}\mu_i\mu_j\}. \qquad (2.3)$$

The matrix T is diagonal, with t_i in the ii position; while V is the cyclic matrix with v_{ij} as elements.

If the t contours are deformed sufficiently far to the right such that the real part of $\mathsf{T}-\mathsf{V}$ is positive definite, then the order of μ and t integrations may be interchanged. A possible choice of t contours $\mathcal{C}$ is $-i\infty+\gamma$ to $i\infty+\gamma$ with

$$\gamma>\sum_j v_{ij}. \qquad (2.4)$$

The integrand for the μ integrations is an N-dimensional Gaussian, and the integral may be evaluated by diagonalizing the quadratic form. With complex elements along the diagonal the existence of an orthogonal transformation for this purpose is not guaranteed.[6] Thus, in Appendix B we proceed via a congruent transformation which simultaneously diagonalizes the real and imaginary parts of $\mathsf{T}-\mathsf{V}$. We then obtain the formula

$$Z=i^{-N}\left(\frac{K}{\pi}\right)^{N/2}\int_{\mathcal{C}} d\{t\}\exp\{K\sum_j t_j\}\,|\,\mathsf{T}-\mathsf{V}\,|^{-1/2}, \qquad (2.5)$$

where $\{t\}\equiv t_1\cdots t_N$.

A similar procedure may be employed for evaluation of the pair-correlation function (cf. Appendix B):

$$C_{mn}\equiv\langle\mu_m\mu_n\rangle$$
$$=(1/2KZ)\,i^{-N}\left(\frac{K}{\pi}\right)^{N/2}\int_{\mathcal{C}} d\{t\}$$
$$\times\exp\{K\sum_j t_j\}\,|\,\mathsf{T}-\mathsf{V}\,|^{-1/2}G_{mn}. \qquad (2.6)$$

The matrix G, the inverse (Green's function) of the matrix $\mathsf{T}-\mathsf{V}$, satisfies

$$\sum_l (t_m\delta_{ml}-v_{ml})G_{ln}=\delta_{mn}. \qquad (2.7)$$

It should be noted that although Eq. (2.5) is an exact analytical representation of the partition function for the Ising model, it bears a very close relationship to the spherical model. For K less than a critical value the integrand in Eq. (2.7) has a stationary point $\{\bar{t}\}$ in the allowed part of the N-dimensional t space; and the value of the integrand at this point turns out to be proportional to the partition function for the spherical model. To see this consider the stationary condition

$$0=\partial/\partial t_j[K\sum_i t_i-\tfrac{1}{2}\ln|\,\mathsf{T}-\mathsf{V}\,|]_{\{t\}=\{\bar{t}\}} \qquad (2.8)$$
$$=K-\tfrac{1}{2}G_{jj}\{\bar{t}\}, \qquad j=1\cdots N, \qquad (2.9)$$

where the last equality is derived in Appendix B. In order for G_{jj} to be independent of j, we must have $\bar{t}_j$ independent of j; say, $\bar{t}_j=t_s$. With periodic boundary conditions and a spatially uniform t_j, a spectral representation of the matrix $\mathsf{T}-\mathsf{V}$ becomes appropriate.[7] The eigenvectors $\mu_j^{(p)}$ are simply plane waves, and the eigenvalues are

$$\lambda^{(p)}=t_s-\tilde{v}(p), \qquad (2.10)$$

where

$$\tilde{v}(\mathbf{p})=\sum_{j=1}^{N}v_{ij}\exp[i(\mathbf{r}_i-\mathbf{r}_j)\cdot\mathbf{p}]. \qquad (2.11)$$

The allowed $\mathbf{p}$'s are s-dimensional vectors in a Brillouin zone

$$p=\left(\frac{2\pi n_1}{L_1},\frac{2\pi n_2}{L_2},\cdots,\frac{2\pi n_s}{L_s}\right),$$

where the n's are integers and the L's are the lengths of sides of the lattice in units of the lattice spacing. Equation (2.9) becomes

$$K=(1/2N)\sum_{\mathbf{p}}\{1/[t_s-\tilde{v}(p)]\}, \qquad (2.12)$$

which is equivalent to Eq. (C.15) in Berlin and Kac. This equation may be solved to determine t_s as a function of temperature K as long as K is small enough that $t_s>\tilde{v}(0)$. The critical point for the spherical model (SM) occurs when $t_s=\tilde{v}(0)$, i.e.,

$$K_c=(1/2N)\sum_{\mathbf{p}}\{1/[\tilde{v}(0)-\tilde{v}(p)]\} \qquad \text{(spherical model)}. \qquad (2.13)$$

Finally, we may insert $t_s(K)$ into the integrand in Eq. (2.7) to obtain

$$\ln Z_{\mathrm{SM}}=-\tfrac{1}{2}N\ln K+NKt_s-\tfrac{1}{2}\sum_{\mathbf{p}}\ln[t_s-\tilde{v}(p)], \qquad (2.14)$$

which also agrees with Berlin and Kac, Eq. (C.11), except for some simple normalization terms.

The next logical step in a straightforward analysis of the Ising model via Eq. (2.5) would be an expansion of the argument of the exponential out to terms quadratic in, say, t_j-t_s, and then evaluation of the resulting Gaussian integrals. It turns out that all of these integrals converge; but the result does not make sense near the critical point. This, and difficulties in passing into the low-temperature region, indicate that all higher-order terms must be considered. This interesting line of attack is being pursued, but we shall not follow

[6] C. L. Dolph, J. E. McLaughlin, and I. Marx, Commun. Pure Appl. Math. 7, 621 (1954).

[7] **$\mathsf{T}-\mathsf{V}$ is a normal matrix (its real and complex parts commute) even if t_s is complex.**

it here. Rather, taking the point of view that the above zeroth-order spherical approximation makes some sense by itself, we shall attempt a similar zeroth-order calculation for the correlation function as given by Eq. (2.6). The result is a correlation function quite different from that predicted by the pure spherical model.

III. PRELIMINARY CALCULATION OF THE CORRELATION FUNCTION

We now wish to apply the methods of the last section to a direct calculation of the correlation function as expressed in Eq. (2.6). Specifically, let us seek a point $\{\bar{t}\}$ in the N-dimensional t space at which the integrand in (2.6) is stationary. Because of the factor $G_{mn}\{t\}$ in this integrand, $\{\bar{t}\}$ may be expected to differ from that found previously. In particular, $\bar{t}_j$ will be a nontrivial function of the position $\mathbf{r}_j$.

The criterion for stationarity may be written in the form [cf. Eq. (2.9)]

$$K=\tfrac{1}{2}G_{jj}\{\bar{t}\}-\partial/\partial t_j \ln G_{mn}\{t\}|_{\{\bar{t}\}}. \tag{3.1}$$

For spatially nonuniform $\{\bar{t}\}$, however, the evaluation of the right-hand side presents difficulties not encountered previously.

We may simplify the following mathematics somewhat by going to a continuum approximation for functions defined over the lattice sites. This should be particularly appropriate near the critical point where it is expected that the essential contributions to the singular behavior come from regions where functions like G and t vary very slowly over distances of the order of the lattice spacing. Measuring $\mathbf{r}$ in units of the lattice spacing, we write Eq. (2.7) in the form

$$t(\mathbf{r})G(\mathbf{r},\mathbf{r}_0)-\int d^s r' v(\mathbf{r}-\mathbf{r}')G(\mathbf{r}',\mathbf{r}_0)=\delta(\mathbf{r}-\mathbf{r}_0), \tag{3.2a}$$

which may be formally expressed as

$$[t(\mathbf{r})-\tilde{v}(-i\nabla_r)]G(\mathbf{r},\mathbf{r}_0)=\delta(\mathbf{r}-\mathbf{r}_0). \tag{3.2b}$$

If the interaction $v(\mathbf{r}-\mathbf{r}')$ has a short range, Eq. (3.2) may be further simplified by approximating the integral operator by a differential operator, i.e., expand $\tilde{v}$ to second order in powers of $-i\nabla$. One finds

$$[t(r)-\tilde{v}(0)-\sigma^2\nabla^2]G(\mathbf{r},\mathbf{r}_0)=\delta(\mathbf{r}-\mathbf{r}_0), \tag{3.3}$$

where

$$\tilde{v}(0)=\int d^s r\, v(r), \tag{3.4}$$

and

$$\sigma^2=(1/2s)\int d^s r\, r^2 v(r) \tag{3.5}$$

is a measure of the range of the interaction. Truncation of the power series in $-i\nabla$ at gradient terms is again appropriate for slowly varying G. It should be noted that this differential approximation leads to short-wavelength divergences similar to those which occur in field theory. Occasionally we shall have to return to the exact equation, or invoke an appropriate cutoff.

The term involving G_{mn} in Eq. (3.1) should affect the function $\bar{t}(\mathbf{r})$ only for values of $\mathbf{r}$ near $\mathbf{r}_m$ and $\mathbf{r}_n$. Elsewhere in the system, $\bar{t}$ should be very near the constant value t_s computed previously. It is therefore convenient to adopt the notation

$$t(\mathbf{r})=t_s+\phi(\mathbf{r}), \tag{3.6a}$$

$$t_s-\tilde{v}(0)=\epsilon, \tag{3.6b}$$

and sometimes, for compactness,

$$\epsilon=\kappa^2\sigma^2. \tag{3.6c}$$

It is understood that $\phi(\mathbf{r})$ goes to zero as $\mathbf{r}$ moves away from the positions of the two correlated spins. As in the spherical model, ϵ vanishes at the critical point. Equation (3.3) now becomes

$$[-\sigma^2\nabla^2+\epsilon+\phi(\mathbf{r})]G(\mathbf{r},\mathbf{r}_0)=\delta(\mathbf{r}-\mathbf{r}_0). \tag{3.7}$$

Finally, we shall rewrite Eq. (3.1) in the form

$$K=\tfrac{1}{2}G(\mathbf{r},\mathbf{r}\,|\,\bar{\phi})-\delta[\ln G(\mathbf{R},0\,|\,\phi)]/\delta\phi(\mathbf{r})|_{\phi=\bar{\phi}}. \tag{3.8}$$

[The derivative with respect to t_j has become a functional derivative with respect to $\phi(\mathbf{r})$.] The lattice points $\mathbf{r}_n$ and $\mathbf{r}_m$ are now called $\mathbf{R}$ and 0; and the functional dependence of G upon ϕ is indicated in an obvious notation.

For present purposes, it will be sufficient to consider certain semiclassical approximations for the Green's functions which appear in the two terms on the right-hand side of Eq. (3.8). One fairly crude approximation, valid only in the limit of extremely slowly varying $\phi(\mathbf{r})$, may be obtained as follows[8]. Assume that, for purposes of calculating $G(\mathbf{r},\mathbf{r}')$,

$$\phi\cong\phi[\tfrac{1}{2}(\mathbf{r}+\mathbf{r}')]=\text{const}$$

throughout a large region surrounding $\mathbf{r}$ and $\mathbf{r}'$. Then the eigenstates, appropriate for calculating G from a spectral representation, are simply plane waves; and the eigenvalues of $\mathsf{T}-\mathsf{V}$ are

$$\begin{aligned}\lambda^{(p)}&\approx\tilde{v}(0)-\tilde{v}(p)+\{\epsilon+\phi[\tfrac{1}{2}(\mathbf{r}+\mathbf{r}')]\}\\&\approx\sigma^2p^2+(\epsilon+\phi).\end{aligned} \tag{3.9}$$

Thus

$$G(\mathbf{r},\mathbf{r}'\,|\,\phi)\approx N^{-1}\sum_p\frac{\exp[i\mathbf{p}\cdot(\mathbf{r}-\mathbf{r}')]}{[\tilde{v}(0)-\tilde{v}(p)]+\epsilon+\phi[\frac{1}{2}(r+r')]}. \tag{3.10}$$

Clearly (3.10) cannot be used for large separation, $\mathbf{r}-\mathbf{r}'$, but it turns out to possess apparently correct

[8] M. Kac, W. L. Murdock, and G. Szego, J. Rat. Mech. Anal. **2**, 767 (1953); this is related to the treatment of inhomogeneity in the development of the Thomas-Fermi approximation as presented by G. A. Baraff and S. Borowitz, Phys. Rev. **121**, 1704 (1961).

qualitative features for $\mathbf{r}=\mathbf{r}'$ and for the kind of functions ϕ which we shall be led to consider. A more systematic calculation of $G(\mathbf{r}, \mathbf{r})$, leading to a result similar to (3.10), will be presented in Sec. IV, but to present the full treatment here might obscure the essential features of the theory.

Let us now use Eq. (3.10) to evaluate the first term on the right-hand side of Eq. (3.8):

$$\tfrac{1}{2}G(\mathbf{r}, \mathbf{r} \mid \bar{\phi}) = (2N)^{-1} \sum_{\mathbf{p}} \{[\tilde{v}(0) - \tilde{v}(p)] + \epsilon + \phi(\mathbf{r})\}^{-1}. \tag{3.11}$$

This expression should be examined for various dimensionalities, s, and for small values of ϵ and ϕ. For $s>2$, (3.11) remains finite when ϵ and ϕ are zero. According to Eq. (2.13), its value is K_c, the spherical-model critical temperature. The first corrections in $\epsilon+\phi$ are listed below.

$$s=3:\quad \tfrac{1}{2}G = K_c^{(3)} - (1/8\pi\sigma^3)(\epsilon+\phi)^{1/2} + \cdots, \tag{3.12}$$

$$s=4:\quad \tfrac{1}{2}G = K_c^{(4)} + (1/32\pi^2\sigma^4)(\epsilon+\phi)\ln(\epsilon+\phi) + \cdots, \tag{3.13}$$

$$s\geq 5:\quad \tfrac{1}{2}G = K_c^{(s)} - A^{(s)}(\epsilon+\phi) + \cdots, \tag{3.14}$$

where

$$A^{(s)} = (1/2N) \sum_{\mathbf{p}} [\tilde{v}(0) - \tilde{v}(p)]^{-2}, \tag{3.15}$$

and $A^{(s)}$ is finite for $s>4$.

Let us turn next to a calculation of the second term on the right-hand side of Eq. (3.8). This term will be quite sensitive to the manner in which G falls to zero for large distances R between the two spin sites. In this case, it is appropriate to use the semiclassical WKB approximation [Eq. (3.10) is insufficient]. To do so, however, we must make some simplifying assumptions about the stationary potential $\bar{\phi}(\mathbf{r})$. It is almost certain that the exact $\bar{\phi}$ will be symmetric under interchange of the two spin sites, and will have cylindrical symmetry about the line joining these sites. Perhaps the simplest such function is the sum of identical, spherically symmetric functions centered about each site; and it is just such a function which we shall examine in Sec. IV. Although this kind of function is already oversimplified, we shall see that it requires rather complicated analysis. It turns out, however, that the qualitative aspects of the theory may be obtained by assuming that $\bar{\phi}(\mathbf{r})$ has spherical symmetry about only one of the two sites, say the one chosen to be at the origin. We shall consider only such ϕ's for the remainder of this section.

With the assumption of spherical symmetry about the origin, Eq. (3.7) becomes

$$\left\{-\sigma^2\left(\frac{d^2}{dr^2} + \frac{s-1}{r}\frac{d}{dr}\right) + [\epsilon+\phi(r)]\right\} G(r) = \frac{\delta(r)}{4\pi r^2}. \tag{3.16}$$

In this case to use the WKB method, one must make the transformation

$$r = e^x, \tag{3.17}$$

so that (3.16) becomes

$$-(d^2G/dx^2) - (s-2)(dG/dx) + w(x)G = 0, \qquad x \neq -\infty, \tag{3.18}$$

where

$$w(x) = \sigma^{-2} e^{2x} [\epsilon+\phi]. \tag{3.19}$$

Now we may write

$$G = \exp Q(x), \tag{3.20}$$

where Q satisfies

$$-Q'' - Q'^2 - (s-2)Q' + w(x) = 0. \tag{3.21}$$

(Primes denote differentiation with respect to x.)

In terms of the quantities appearing in Eq. (3.21), the criterion for validity of the WKB method is that $w(x)$ varies slowly enough, so that the second derivative Q'' is small compared to Q' or Q'^2. We now can see that this will be true for all cases of interest to us. Consider, first, situations in which ϕ is negligible compared to ϵ; that is, let R become large with ϵ fixed. Then $w(x) \propto e^{2x}$; $Q' \propto e^x$; and $Q'' \propto e^x \ll Q'^2$. Next, consider holding R fixed and approaching the critical point by letting ϵ vanish. We shall be interested in ϕ's which behave like inverse powers of $r=e^x$. As long as ϕ decreases no more rapidly than r^{-2}, the above argument holds, because w still increases exponentially with x. If $\phi \propto r^{-2}$, then w is independent of x, and (3.21) is solved exactly with $Q''=0$. Finally, if ϕ decreases more rapidly than r^{-2}, w vanishes for large x, and the appropriate solution of (3.21) is $Q' \approx 2-s$, $Q'' \approx 0$ again.

The WKB solution now may be constructed in the standard fashion. As usual, it is necessary to include the first correction, of order Q''. The result is

$$Q(x) \approx -\int^x \{\tfrac{1}{2}(s-2) + [\tfrac{1}{4}(s-2)^2 + w(x')]^{1/2}\} dx' - \tfrac{1}{4}\ln[\tfrac{1}{4}(s-2)^2 + w(x)] + \cdots. \tag{3.22}$$

This implies that $G(R \mid \phi)$ has the form

$$G(R \mid \phi) \approx \frac{\text{const}}{R^{\frac{1}{2}s-1}\{\tfrac{1}{4}(s-2)^2 + (R/\sigma)^2[\epsilon+\phi(R)]\}^{1/4}} \times \exp\left[-\int_\sigma^R dr \left\{\frac{(s-2)^2}{4r^2} + \frac{1}{\sigma^2}[\epsilon+\phi(r)]\right\}^{1/2}\right]. \tag{3.23}$$

As a lower limit on the integral σ is used, and all effects from 0 to σ are contained in the constant. Note that if we set $\phi=0$, G behaves exactly like the Ornstein–Zernike correlation function: If R becomes large while ϵ remains finite,

$$G \underset{R\to\infty}{\approx} (A/R)^{\frac{1}{2}(s-1)} e^{-\kappa R} \tag{3.24}$$

($\kappa=\epsilon^{1/2}/\sigma$); if ϵ vanishes with R held fixed,

$$G \underset{\epsilon\to 0}{\approx} A'/R^{s-2}. \tag{3.25}$$

It remains to employ the Green's function of Eq. (3.23), along with Eqs. (3.12) through (3.14), in the saddle point Eq. (3.8) to compute $\bar{\phi}(r)$. For purposes of taking the functional derivative indicated in (3.8), we should neglect the prefactor in (3.23), because it depends upon ϕ evaluated only at the single point $r=R$. Furthermore, we must turn the radial integral into a volume integral by writing

$$\int_\sigma^R dr\cdots=\int_{\sigma<|\mathbf{r}|<R} d^s r/A_s(r)\cdots, \tag{3.26}$$

where

$$A_s(r)=2\pi^{s/2}r^{s-1}/\Gamma(\tfrac{1}{2}s) \tag{3.27}$$

is the area of an s-dimensional hypersphere of radius r. Then

$$\frac{\delta}{\delta\phi(\mathbf{r})}\ln G(R\,|\,\phi)|_{\bar{\phi}}\cong-\frac{\theta(R-r)}{2\sigma^2 A_s(r)}\left[\frac{(s-2)^2}{4r^2}+\frac{1}{\sigma^2}(\epsilon+\bar{\phi})\right]^{-1/2},\quad r>\sigma. \tag{3.28}$$

For $r>R$, the right-hand side of (3.28) vanishes in this approximation, as is indicated by the step function $\theta(R-r)$. The equation is inappropriate for the short-range effects, $r\lesssim\sigma$.

Consider, first, the case $s=3$. Equation (3.8) is

$$K-K_c^{(3)}\cong(8\pi\sigma^3)^{-1}(\epsilon+\bar{\phi})^{1/2}+\frac{\theta(R-r)}{8\pi r^2\sigma^2}\left[(4r^2)^{-1}+(\sigma^2)^{-1}(\epsilon+\bar{\phi})\right]^{-1/2}. \tag{3.29}$$

The limit obtained by letting r and R go to infinity before going to the critical point simply tells us again that $\epsilon=0$ at $K=K_c^{(3)}$, because $\bar{\phi}$ is supposed to vanish for large values of its argument. The most interesting situation occurs when r is held fixed while $\epsilon\to 0$, so that $\bar{\phi}$ becomes much larger than ϵ. Setting $\epsilon=0$ and $K=K_c^{(3)}$ in Eq. (3.29), and solving for $\bar{\phi}$ we obtain

$$\bar{\phi}\cong(\omega\sigma^2/r^2)\theta(R-r),$$
$$\omega=[(65)^{1/2}-1]/8. \tag{3.30}$$

The fact that $\bar{\phi}$ turns out to vary as r^{-2} for $s=3$ is the most important result of this paper. Only this particular r dependence of ϕ, when inserted into the exponent of Eq. (3.23), can modify G so that it exhibits something other than the Ornstein–Zernike power law at the critical point. Specifically, if $\phi=\omega\sigma^2/r^2$, then, for $s=3$,

$$G(R)\propto R^{-1/2-(1/4+\omega)^{1/2}}, \tag{3.31}$$

according to Eq. (3.23). Clearly the purely numerical factor ω is a measure of the deviation from the classical behavior. Note that this factor turns out to be independent of any of the parameters in the problem, e.g., the range of interaction, σ, or the value of the critical temperature.

Equation (3.31), however, should not be interpreted as the actual critical correlation function $C(R)$. The modification of the determinant in Eq. (2.6) by the inclusion of $\bar{\phi}=\omega\sigma^2/r^2$ leads to a further power of R factor in the correlation function. This is clearly illustrated within the context of the present approximations. Recall that $G(\mathbf{r},\ \mathbf{r}\,|\,\phi)$ is the partial derivative $\partial\ln|\mathsf{T}-\mathsf{V}|/\partial\phi(\mathbf{r})$. Hence, reintegrating the Green's function in the form of Eq. (3.12) yields (cf. Appendix B)

$$-\tfrac{1}{2}\ln|\mathsf{T}-\mathsf{V}|=-\tfrac{1}{2}\ln|t_s\mathbf{1}-\mathsf{V}|+K_c^{(3)}\int d^3r\bar{\phi}(r)-(12\pi\sigma^3)^{-1}\int d^3r[\epsilon+\bar{\phi}(r)]^{3/2} \tag{3.32}$$

$$=-\tfrac{1}{2}\ln|t_s\mathbf{1}-\mathsf{V}|+K_c^{(3)}\int d^3r\bar{\phi}(r)-\tfrac{1}{3}\omega^{3/2}\ln R+C, \tag{3.33}$$

where C is a constant which accounts for the $r\lesssim\sigma$ effects. The $\ln R$ appearing in the exponent yields a power of R in the correlation function. This source of R dependence will be more fully examined in the context of the improved formulas of Sec. IV.

Before leaving the three-dimensional case, we should consider the behavior of the correlation function for ϵ small but finite; i.e., the temperature is slightly above T_c. The previous solution (3.30) of Eq. (3.29) for $\bar{\phi}$ is still appropriate when $\bar{\phi}(r)\gg\epsilon$, which implies

$$r\ll 1/\kappa.$$

(The critical correlation length for this solution is $1/\kappa$.) Thus for R in the range $\sigma\ll R\ll 1/\kappa$ the previous treatment of the correlation function is correct. For $R\gg 1/\kappa$, however, the correlation function reverts to an Ornstein–Zernike form, but with an important nonclassical modification of the prefactor. Consider again the integrals which appear in the exponent, for instance in Eq. (3.23) for $G(R)$. To estimate the integral divide it into two ranges: from σ to $1/\kappa$, and $1/\kappa$ to R. Then, to leading order, one finds

$$\int_\sigma^R dr\{\tfrac{1}{4}r^{-2}+\sigma^{-2}[\epsilon+\phi(r)]\}^{1/2}\approx\int_\sigma^{1/\kappa}\frac{dr(\frac{1}{4}+\omega)^{1/2}}{r}+\int_{1/\kappa}^R\kappa\,dr\approx(\tfrac{1}{4}+\omega)^{1/2}\ln(\kappa\sigma)^{-1}+\kappa R. \tag{3.34}$$

The $\ln\kappa^{-1}$ will bring down the same power of $1/\kappa$ as the power of R previously brought down. A similar situation arises in the evaluation of the determinant.

The net result[9] is that if

$$C(R) \approx B/R^{1+\eta}, \qquad R \ll 1/\kappa, \tag{3.35}$$

(B is such that as $R \to \sigma$, C is of order unity) then

$$C(R) \approx \kappa^{\eta}(B'/R)e^{-\kappa R}, \qquad R \gg 1/\kappa. \tag{3.36}$$

This dependence of the prefactor on κ (or the inverse correlation length), which persists for the more precise treatment of the next section, is completely in accord with the scaling laws in the critical region.[4]

We complete this section of the paper by outlining the results for higher dimensionalities. In the following, we shall set $\epsilon = 0$ immediately and solve only for the Green's function $G(R)$ right at the critical point. For $s=4$, Eq. (3.8) becomes, after rearrangement,

$$\bar{\phi} \ln \bar{\phi} \cong 8(\sigma/r)^2 \theta(R-r)[1+r/\sigma^2]^{-1/2}. \tag{3.37}$$

The leading term in $\bar{\phi}$ is thus

$$[4\sigma^2/(r^2 \ln r)]\theta(R-r); \tag{3.38}$$

and then a short calculation using Eq. (3.23) yields

$$G(R) \propto 1/(R \ln R)^2. \tag{3.39}$$

This is a very weak deviation from Ornstein–Zernike.

Finally, for $s>4$, the analog of Eq. (3.35) is

$$\bar{\phi} \cong \frac{\Gamma(\frac{1}{2}s)\theta(R-r)}{2\pi^{\frac{1}{2}s}\sigma^2 A^{(s)}} \frac{1}{r^{s-2}} \left[\frac{(s-2)^2}{4} + \frac{2r^2}{\sigma^2}\bar{\phi}\right]^{-1/2}, \tag{3.40}$$

where the constant $A^{(s)}$ was defined in Eq. (3.15). The leading term in $\bar{\phi}$ now becomes

$$\bar{\phi} \cong \frac{\Gamma(\frac{1}{2}s)}{\pi^{\frac{1}{2}s}(s-2)\sigma^2 A^{(s)}} \frac{\theta(R-r)}{r^{s-2}}, \qquad s \geq 5. \tag{3.41}$$

Returning to Eq. (3.23) for $G(R)$, we see that $\bar{\phi}$ vanishes too rapidly to make any long-range contribution in either the exponent or the prefactor; and $G(R)$ returns to the Ornstein–Zernike behavior given by Eq. (3.25).

IV. IMPROVED CALCULATION OF THE CORRELATION FUNCTION

In establishing the $1/r^2$ nature of the $\bar{\phi}$ function we have introduced a variety of approximations. Some were employed only because they simplified demonstration of the nature of the results to be expected. These include:

(i) Only functions spherically symmetric about *one* of the centers $\mathbf{r}_m$ or $\mathbf{r}_n$ were considered. In this section a functional form more in conformity with the symmetry of the problem will be used.

(ii) The Kac–Murdock–Szego estimate was adopted for the Green's function $G(\mathbf{r}, \mathbf{r} \mid \phi)$. A $1/r^2$ variation of $\bar{\phi}$ is the borderline of applicability of this approximation; the predictions are qualitatively, but not quantitatively correct. Hence we will subsequently calculate this Green's function using the same level of WKB approximation as was previously demonstrated to be applicable for $1/r^2$.

On the other hand, the retention of only the leading term in the saddle-point approximation is a more difficult matter with which to deal. Hence, this level of approximation will be essentially retained. We have, however, demonstrated the relation of this estimate to the spherical model, at least in the case of the partition function. Similarly, we shall now place our development for the correlation function in the context of a spherical-model type of assumption, so that the mathematical steps may be justified.

The pure spherical model assumes that the spins may vary continuously between $-N^{1/2}$ and $N^{1/2}$ as long as the entire array of spins satisfies

$$\sum_i \mu_i^2 = N. \tag{1.5}$$

In the calculation of $C_{mn} \equiv \langle \mu_m \mu_n \rangle$ it may be desirable to inhibit large local fluctuations of the spins in the neighborhood of $\mathbf{r}_m$ and $\mathbf{r}_n$. For this purpose let us introduce two further constraints. These are quadratic conditions of the form (1.7); in particular,

$$\sum_i \phi_{ik} \mu_i^2 = \sum_i \phi_{ik}, \qquad k = n, m, \tag{4.1}$$

where

$$\phi_{ik} = \phi(|\mathbf{r}_i - \mathbf{r}_k|).$$

Based on the considerations of the previous section we shall select for the function ϕ

$$\begin{aligned} \phi(r) &= (\sigma^2/r^2) q(r/R), \qquad & r > \sigma; \\ &= 0(1), & r \lesssim \sigma. \end{aligned} \tag{4.2}$$

The function q provides a cutoff to ϕ at some distance $r/R = 0(1)$. The detailed nature of the q function is unimportant for leading-order behavior, as long as

$$\begin{aligned} q(x) &\to 1, \qquad & x \ll 1, \\ &\to 0, & x \gg 1. \end{aligned}$$

The cutoff of ϕ may be effected within a shell several σ's in thickness at some radius of the order of R, let us say bR [i.e., $q(x) \approx \theta(b-x)$]. On the other hand, a function like $q(x) = [1+(x/b)]^{-1}$ would do as well.

The three constrains of Eqs. (1.5) and (4.1) may be introduced into the μ integral for the correlation function by means of δ functions, in the integral representation (2.2). The μ integrations may again be performed first. The resulting equation, intermediate in character between the pure-spherical model and the

[9] The same result can be obtained by noting the relation of Eq. (3.16) for $G(R)$ to the Bessel equation when $\phi = \omega\sigma^2/r^2$ (cf. Appendices C and D).

Ising-model formula (2.6), is

$$C_{mn}=\left(\frac{1}{2KZ}\right)\mathfrak{M}_N\iiint_{\mathfrak{C}} dz\,d\omega\,d\omega'$$
$$\times\exp[K\sum_j(z+\omega\phi_{jm}+\omega'\phi_{jn})]|\mathbf{T}-\mathbf{V}|^{-1/2}G_{mn}. \quad (4.3)$$

The matrix $\mathbf{T}$ is diagonal, with jjth element

$$t_j=z+\omega\phi_{jm}+\omega'\phi_{jn}. \quad (4.4)$$

(The reuse of t_j suggests the relation to the previous development.) $\mathfrak{M}_N$ is made up of a normalization factor and a factor which arises from the μ integrals. It also appears in the partition function, which is

$$Z=\mathfrak{M}_N\iiint_{\mathfrak{C}} dz\,d\omega\,d\omega'\exp[K\sum_j t_j]|\mathbf{T}-\mathbf{V}|^{-1/2}. \quad (4.5)$$

The contours $\mathfrak{C}$ run from $-i\infty+\gamma$ to $i\infty+\gamma$ in such a manner as to keep $\mathrm{Re}(\mathbf{T}-\mathbf{V})$ positive-definite.

The z, ω, and ω' integrals may now be performed by the saddle-point method, and as we shall see this is a mathematically legitimate procedure. Operationally, the intermediate calculations are identical with those called for by the technique of the previous section. Now that we have an appreciation of the type of results to be expected, let us carry out these steps to the best of our ability. We will work exclusively in three dimensions.

The z integral may be performed immediately. Since the new constraints are only effective in the neighborhood of $\mathbf{r}_m$ and $\mathbf{r}_n$, z is determined by the remainder of the volume and has as a saddle value that of the spherical model [cf. Eq. (2.12)],

$$z_s=t_s. \quad (4.6)$$

We define the constants ϵ and κ again by

$$\epsilon=t_s-\tilde{v}(0)=\kappa^2\sigma^2. \quad (3.6)$$

From the spherical-model calculations[1] one finds [cf. Eq. (3.29) with $r\rightarrow\infty$]

$$\kappa=8\pi\sigma^2[K-K_c^{(3)}]. \quad (4.7)$$

Consider next the equation for the Green's function. In continuum language, and with the gradient expansion of the integral operator, this is

$$[-\sigma^2\nabla^2+\epsilon+\omega\phi(|\mathbf{r}-\mathbf{r}_m|)+\omega'\phi(|\mathbf{r}-\mathbf{r}_n|)]$$
$$\times G(\mathbf{r},\mathbf{r}_0;\epsilon)=\delta(\mathbf{r}-\mathbf{r}_0). \quad (4.8)$$

It will be conceptually valuable to discuss the solution of this equation in terms of an inverse Laplace transform on ϵ. Thus consider the Green's function $\hat{G}$

$$\hat{G}(\mathbf{r},\mathbf{r}_0;t)=(2\pi i)^{-1}\int_{-i\infty+\theta}^{+i\infty+\theta}e^{\epsilon t}G(\mathbf{r},\mathbf{r}_0;\epsilon)\,d\epsilon, \quad (4.9)$$

$$G(\mathbf{r},\mathbf{r}_0;\epsilon)=\int_0^\infty e^{-\epsilon t}\hat{G}(\mathbf{r},\mathbf{r}_0;t)\,dt. \quad (4.10)$$

The transform equation for $\hat{G}$ is

$$[d/dt-\sigma^2\nabla^2+\omega\phi(|\mathbf{r}-\mathbf{r}_m|)$$
$$+\omega'\phi(|\mathbf{r}-\mathbf{r}_n|)]\hat{G}(\mathbf{r},\mathbf{r}_0;t)=0, \quad (4.11)$$

with "initial" condition

$$\hat{G}(\mathbf{r},\mathbf{r}_0;0)=\delta(\mathbf{r}-\mathbf{r}_0). \quad (4.12)$$

$\hat{G}$ is the solution of a diffusion problem, i.e., $\hat{G}(\mathbf{r},\mathbf{r}_0;t)$ is the density at point $\mathbf{r}$ at a time t under the following circumstances. A δ-function distribution of material is placed at $\mathbf{r}_0$ at time zero and diffuses with diffusion constant σ^2. In addition, for ω and ω' real there is a distributed sink with intensity at each point equal to $[\omega\phi(|\mathbf{r}-\mathbf{r}_m|)+\omega'\phi(|\mathbf{r}-\mathbf{r}_n|)]$, times the density at that point (as in a first-order decomposition reaction with position-dependent rate constant). If ω and ω' are complex, the real and imaginary parts of $\hat{G}$ may be regarded as the densities of two materials which can diffuse, decompose, and interconvert. Another expression for the Green's function, which brings out the relation to a diffusional process, is the path-integral formula[10]

$$\hat{G}(\mathbf{r},\mathbf{r}_0;t)\propto\int_{\text{paths}}\delta_p\mathbf{r}(t')\exp\left\{-\int_0^t dt'\left[\sigma^2\left|\frac{d\mathbf{r}(t')}{dt'}\right|^2\right.\right.$$
$$\left.\left.+\omega\phi(|\mathbf{r}(t')-\mathbf{r}_m|)+\omega'\phi(|\mathbf{r}(t')-\mathbf{r}_n|)\right]\right\}, \quad (4.13)$$

where the paths of integration go from $\mathbf{r}_0$ to $\mathbf{r}$ in time t.

The function $\hat{G}$ satisfies a Smoluchowski equation

$$\hat{G}(\mathbf{r}_n,\mathbf{r}_m;t)=\int d^3r\,\hat{G}(\mathbf{r}_n,\mathbf{r};t-\bar{t})\hat{G}(\mathbf{r},\mathbf{r}_m;\bar{t}) \quad (4.14)$$

for any $\bar{t}$ between 0 and t. We will approximate $\hat{G}(\mathbf{r},\mathbf{r}_m;\bar{t})$ by the value it would have if there were no "sink" term centered about $\mathbf{r}_n$, and likewise for $\hat{G}(\mathbf{r}_n,\mathbf{r};t-\bar{t})$ we assume no sink centered about $\mathbf{r}_m$.

In terms of the path integral (4.13) the approximation would be valid if the paths which determine the dominant R dependence pass out of the region surrounding $\mathbf{r}_m$ and go to $\mathbf{r}$ in $\bar{t}$ without lingering near a region about $\mathbf{r}_n$, and in $t-\bar{t}$ to t go to $\mathbf{r}_n$ without lingering near $\mathbf{r}_m$. The results seem to imply that "lingering near" means entering within a distance of order less than R and staying for a "time" of order $\epsilon R^2/\sigma^2$.

In the context of the approximation just described the two-center solution may be determined from the one-center solutions previously calculated, with only minor modifications arising from the cutoff function $q(r/R)$. The one-center Green's functions are (cf. Appendix C): for $\kappa R\gg1$,

$$G_1(r,\epsilon)\propto\kappa^\nu r^{-1/2}K_\nu(\kappa r), \quad (4.15)$$

[10] M. Kac, *Probability and Related Topics in Physical Sciences* (American Mathematical Society, Providence, Rhode Island, 1957), Chap. IV.

where $\nu=(\omega+\frac{1}{4})^{1/2}$, and K_ν is a modified Bessel function; and for $\kappa R\ll 1$,

$$G_1(r,\kappa)\propto R^{-\nu-1/2}f(r/R),\qquad \kappa r\ll 1,$$
$$\propto R^{-\nu+1/2}r^{-1}e^{-\kappa r},\qquad \kappa r\gg 1,\qquad (4.16)$$

where

$$f(x)\propto x^{-\nu-1/2},\qquad x\ll 1,$$
$$\propto x^{-1},\qquad x\gg 1.\qquad (4.17)$$

Primes on ν or f will indicate ω' replaces ω.

In Appendix C this result is used to derive $G(R)$ from the Smoluchowski equation, which may be written in the alternative form

$$G(R)=2\sigma^2\int_\kappa^\infty \kappa'\,d\kappa'\int d^3r\,G(\mathbf{r}_n,\mathbf{r};\kappa')G(\mathbf{r},\mathbf{r}_m;\kappa').\qquad (4.18)$$

Heuristically the result for $G(R)$ follows from dimensional analysis. We introduce the symbol $\Leftrightarrow$ for "dimensionally equal to," and l for length in units of the lattice spacing; then

$$\kappa \Leftrightarrow l^{-1},$$
$$G_1(r,\kappa)\Leftrightarrow \sigma^{-2}l^{-\nu-1/2}.$$

(It is clear from Eq. (C1) that G is proportional to σ^{-2}.) Inserting these into the Smoluchowski equation (4.18) reveals that

$$G(R,\kappa)\Leftrightarrow \sigma^{-2}l^{-\nu-\nu'}.\qquad (4.19)$$

In the region $\kappa R\ll 1$, where $G(R,\kappa)$ is, to leading order, independent of κ, Eq. (4.20) implies

$$G(R;\kappa)=B/R^{\nu+\nu'};\qquad \sigma\ll R\ll 1/\kappa.\qquad (4.20)$$

On the other hand, in the Ornstein–Zernike region the R dependence must be $e^{-\kappa R}/R$, so

$$G(R;\kappa)=B'\kappa^{\nu+\nu'-1}e^{-\kappa R}/R,\qquad \kappa R\gg 1.\qquad (4.21)$$

The arguments of Appendix C are essentially the same, except imbedded in the context of definite equations. The result is independent of $q(x)$, because the cutoff condition was such as to allow the entire functional dependence on $q(x)$ to be put into $f(x)$ and other dimensionless parts of the problem.

Attention shall now be directed to the determinant term, which we write in the form suggested in Appendix B, Eq. (B18):

$$|\mathsf{T}-\mathsf{V}|^{-1/2}=\exp\{-\tfrac{1}{2}\sum_{\mathbf{p}}\ln[t_s-\tilde{v}(p)]-\tfrac{1}{2}L\},\qquad (4.22)$$

$$L=\int_0^1 d\tau\int d^3r[\omega\phi(|\mathbf{r}-\mathbf{r}_m|)$$
$$+\omega'\phi(|\mathbf{r}-\mathbf{r}_n|)]G(\mathbf{r},\mathbf{r}\,|\,\tau\omega\phi_m+\tau\omega'\phi_n).\qquad (4.23)$$

It can be demonstrated that the important regions of r in this integral are $|\mathbf{r}-\mathbf{r}_m|/R$ or $|\mathbf{r}-\mathbf{r}_n|/R\ll 1$. In each of these regions we can approximate the Green's function by its value neglecting the other center, so

$$L\approx L(\omega)+L(\omega'),\qquad (4.24)$$

$$L(\omega)=\omega\int_0^1 d\tau\int_{r>\sigma} d^3r\left(\frac{\sigma}{r}\right)^2 q\left(\frac{r}{R}\right)G(\mathbf{r},\mathbf{r}\,|\,\tau\omega\phi)+L_0,\qquad (4.25)$$

where L_0 represents the contribution from $r\lesssim\sigma$. G may be expanded in spherical harmonics as

$$G(\mathbf{r},\mathbf{r}_0\,|\,\tau\phi)=\sum_{l=0}^{\infty}\sum_{m=-l}^{l}G_l(r,r_0)Y_{lm}(\Omega)Y_{lm}^*(\Omega_0),\qquad (4.26)$$

$$\left[\kappa^2-\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr}+\frac{l(l+1)}{r^2}+\frac{\tau\omega q(r/R)}{r^2}\right]G_l(r,r_0)$$
$$=(\sigma^2r_0^2)^{-1}\delta(r-r_0),\qquad (4.27)$$

where simplifications arising from the spherical symmetry of ϕ have been incorporated. A complication, arising from the use of the differential operator as $\mathbf{r}_0\to\mathbf{r}$, will be treated presently. The angular integration in (4.24) is easily performed, resulting in

$$L(\omega)=\omega\int_0^1 d\tau\int_\sigma^\infty r^2dr\left(\frac{\sigma}{r}\right)^2 q\left(\frac{r}{R}\right)$$
$$\times\sum_l(2l+1)G_l(r,r)+L_0.\qquad (4.28)$$

In Appendix D it is shown that for $\kappa R\ll 1$ the leading order of G_l is

$$G_l(r,r)=(1/2\sigma^2r)[(l+\tfrac{1}{2})^2+\tau\omega]^{1/2},\qquad r\ll R\ll 1/\kappa.\qquad (4.29)$$

Note that because of the q cutoff at $r=0(R)$, the r integration yields $\log R$, just as in the previous section (cf. Appendix D).

However, a difficulty is immediately apparent in that the l summation appears to diverge. For angular index l and radius r the gradient expansion breaks down for "wavelengths" $r/l\lesssim\sigma$, so that the l summation should be cut off at $l_u\approx r/\sigma$. We shall handle this upper cutoff in an implicit manner. The term $\omega K\sum_j\phi_{jm}$ also occurs in the exponent of the integral for C_{mn}, Eq. (4.3). A relation between K and a Green's function is, as in the spherical model Eq. (2.9),

$$K=\tfrac{1}{2}G_{jj}\{t_j=t_s\}.$$

This expression may be evaluated, as in Eq. (2.12), without resorting to the gradient expansion. Rather, let us write

$$\omega K\sum_j\phi_{jm}\approx\tfrac{1}{2}\omega\int_\sigma d^3r\,\phi(r)G(\mathbf{r},\mathbf{r}\,|\,\phi=0),\qquad (4.30)$$

and evaluate this by the differential-equation approximations embodied in Eqs. (4.26)–(4.29). Combining the two terms in which we have made compensating high l errors yields a convergent result,

$$\omega K \sum_j \phi_{jm} - \tfrac{1}{2}L(\omega) = [-\ln R \sum_{l=0}^{\infty}(l+\tfrac{1}{2}) \times \{[(l+\tfrac{1}{2})^2+\omega]^{1/2} - (l+\tfrac{1}{2}) - \tfrac{1}{2}\omega/(l+\tfrac{1}{2})\}] + C(\omega), \quad (4.31)$$

where $C(\omega)$, which is of $0(1)$ in R, contains contributions from the $r \lesssim \sigma$ region, and also depends on the specific form of the q cutoff.

We may now put together the various terms [Eqs. (4.31), (4.24), (4.22), (4.20), and (4.3)] for the case of $\kappa R \ll 1$

$$C(R) = \left(\frac{Z_{\mathrm{SM}}}{Z}\right)\left[\int_{\mathfrak{C}} d\omega\, D(\omega)\, \exp[-M(\omega)\,\ln R]\right]^2. \quad (4.32)$$

The identity and independence of the ω and ω' integrations has led to the integral squared; $D(\omega)$ is a collection of $0(1)$ terms; and

$$M(\omega) = (\omega+\tfrac{1}{4})^{1/2} + \sum_{l=0}^{\infty}(l+\tfrac{1}{2})\{[(l+\tfrac{1}{2})^2+\omega]^{1/2} - (l+\tfrac{1}{2}) - \tfrac{1}{2}\omega/(l+\tfrac{1}{2})\}. \quad (4.33)$$

The first term on the right is from G_{mn}, the second from the determinant. In Appendix E it is argued that any spurious dependence of Z_{SM}/Z upon R, arising from the R-dependent constraints, results, at worst, in a $(\ln R)^{-2}$ factor.

The saddle-point technique is appropriate for the ω integration, $\ln R$ being the large parameter. The saddle value of ω is determined by

$$0 = (\omega_s+\tfrac{1}{4})^{-1/2} + \sum_{l=0}^{\infty}(l+\tfrac{1}{2})\{[(l+\tfrac{1}{2})^2+\omega_s]^{-1/2} - (l+\tfrac{1}{2})^{-1}\} \quad (4.34)$$

with solution

$$\omega_s = 0.935, \quad (4.35)$$

$$M(\omega_s) = 0.823. \quad (4.36)$$

We thus find for the correlation function

$$C(R) \propto R^{-1.646}, \qquad \kappa R \ll 1. \quad (4.37)$$

There are again logarithmic factors arising from the integration away from the saddle point, but these, together with the logarithmic factors from the partition function, will be disregarded as higher-order corrections.

A calculation in the case of $\kappa R \gg 1$ would be quite repetitious. Essentially, $1/\kappa$ replaces $0(R)$ as an effective cutoff distance of the $1/r^2$ terms of the differential equations. Hence, many R's are replaced by $1/\kappa$. Also, terms of the type $e^{-\kappa R}$ must be carefully regarded. The result is

$$\kappa^{0.646} R^{-1} e^{-\kappa R}, \qquad \kappa R \gg 1. \quad (4.38)$$

The susceptibility is proportional, by a fluctuation theorem, to the integral over $\mathbf{R}$ of the correlation function. According to Eq. (4.7), κ vanishes as $T-T_c$ so that Eqs. (4.37) and (4.38) imply a susceptibility which diverges as $(T-T_c)^{-1.354}$.

These results fail to agree with the calculation of Fisher and Burford[4] which predicts that the power of R in Eq. (4.37) should be -1.056 ± 0.008. Furthermore the temperature dependence of the correlation length $1/\kappa$ should be $(T-T_C)^{-0.64}$, rather than the $(T-T_C)^{-1}$ which follows from the spherical model. Finally, the susceptibility is incorrect. Comments on the significance of these errors are reserved for the discussion.

V. FOUR-SPIN CORRELATIONS AND THE SPECIFIC HEAT

In continuation of our probing of this alternative approach to the Ising model we shall also examine the specific heat as determined via long-ranged correlation functions. These will be calculated by the method of Sec. IV, although results based on the leading saddle point in the t_j variables are identical.

Stillinger[5] has used the relation between specific heat and energy fluctuations to write

$$c_H = (2K^2/N) \sum_{\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{r}_4} v(r_{13})v(r_{24})\Gamma(13\,|\,24), \quad (5.1)$$

$$\Gamma(13\,|\,24) = \langle\mu_1\mu_2\mu_3\mu_4\rangle - \langle\mu_1\mu_3\rangle\langle\mu_2\mu_4\rangle. \quad (5.2)$$

The factors $v(r_{13})$ and $v(r_{24})$ keep $\mathbf{r}_1$ near $\mathbf{r}_3$ and $\mathbf{r}_2$ near $\mathbf{r}_4$. A divergence of the specific heat implies long-range correlations when four spins are divided into two groups, (13) and (24). If

$$\Gamma(13\,|\,24) \sim 1/R^\theta, \qquad \text{for } \kappa R \ll 1, \quad (5.3)$$

$$\kappa \sim (T-T_C)^\nu, \quad (5.4)$$

where

$$R = r_{12} \approx r_{34},$$

then the specific heat will diverge in s dimensions as

$$c_H \sim (T-T_C)^{-\alpha}, \quad (5.5)$$

$$\alpha = \nu(s-\theta). \quad (5.6)$$

The calculation of $\Gamma(13\,|\,24)$ is easily executed by the foregoing techniques. The spherical constraint (1.5) and the further ones

$$\sum_i \phi_{in}\mu_i^2 = \sum_i \phi_{in}, \qquad n = 1, 2, 3, 4, \quad (5.7)$$

may be introduced by means of δ functions into the expression for $\langle\mu_1\mu_2\mu_3\mu_4\rangle$:

$$\langle\mu_1\mu_2\mu_3\mu_4\rangle \propto (1/Z)\int_{-\infty}^{\infty}\cdots\int d\mu_1\cdots d\mu_N \iiiint\!\!\int_{\mathfrak{C}} dz\, d\omega_1\, d\omega_2\, d\omega_3\, d\omega_4 \times \mu_1\mu_2\mu_3\mu_4 \exp[K\sum_j t_j - K\sum_{jk}(\mathsf{T}-\mathsf{V})_{jk}\mu_j\mu_k], \quad (5.8)$$

$$t_j = z + \sum_{n=1}^{4} \omega_n \phi_{jn}. \quad (5.9)$$

Performing the μ integrations first, we obtain

$$\langle\mu_1\mu_2\mu_3\mu_4\rangle \propto \left(\frac{1}{Z}\right) \int\!\!\int\!\!\int\!\!\int_{\mathfrak{C}}\!\!\int dz\, d\omega_1\cdots d\omega_4$$

$$\times\exp(K\sum_j t_j)\,|\,\mathsf{T}-\mathsf{V}\,|^{-1/2}[G_{12}G_{34}+G_{14}G_{32}+G_{13}G_{24}]. \tag{5.10}$$

If the pairs (13) and (24) are widely separated then the term with $G_{13}G_{24}$ reduces to $\langle\mu_1\mu_3\rangle\langle\mu_2\mu_4\rangle$.[11] To leading order, therefore, we may write

$$\Gamma(13\,|\,24) \propto \left(\frac{1}{Z}\right)\int dz\, d\omega\, d\omega'$$

$$\times\exp(K\sum_j t_j)\,|\,\mathsf{T}-\mathsf{V}\,|^{-1/2}[G(R)]^2. \tag{5.11}$$

Here the variables $\omega=\omega_1+\omega_3$ and $\omega'=\omega_2+\omega_4$ have been introduced; variables $\omega_1-\omega_3$ and $\omega_2-\omega_4$ have been integrated out and contribute only a $0(1)$ factor which has been suppressed; also, for leading order we set $\phi_{j3}=\phi_{j1}$ and $\phi_{j4}=\phi_{j2}$.

Except for the square on the Green's function the equations are as in Sec. IV. In particular, we obtain formulas like (4.32)–(4.34), but with a 2 multiplying the first term on the right-hand side of Eqs. (4.33) and (4.34). The result is $\omega_s=1.923$ and

$$\Gamma(12\,|\,34) \propto R^{-4.233}, \qquad \sigma\ll R\ll 1/\kappa. \tag{5.12}$$

Unfortunately, the approximations of this theory produce a large R behavior too weak to yield a divergence of the specific heat.

VI. DISCUSSION

The quantitative errors which emerge in our detailed application of this theory make it clear that terms arising from fluctuations from the saddle condition of the t_j's must be treated. Series developments diverge at the critical point, but we hope that we can use the mechanisms outlined in this paper to handle contributions from all higher-order terms. We view the calculations presented here as important guidelines for the future development.

One may be tempted to believe that the calculation of the correlation function has a validity beyond that of the partition function, which cancels out from numerator and denominator. We believe, rather, that the calculation of further terms of both the partition function and correlation function are linked, in the same sense that higher-order corrections in diagram theories frequently proceed via the correlation or Green's functions.

It should be mentioned that a number of other theoretical problems can be cast into a form quite similar to that of the present paper. We refer to the grand partition function[12] and Green's function of many-body systems, and to the S matrix and Green's functions of certain field theories.[13] We suspect that just as similarities are reflected in the diagram theories for a variety of problems, there will be a variety of analogs to this Ising formulation (cf. Appendix A).

There is also a resemblence to the formulation employed by Edwards[14] in solution of aspects of the excluded-volume problem. In fact the present project was largely motivated by Edwards' papers.

[11] Possible residual R dependence will be assumed to be negligible, or of the same order as the terms retained.

APPENDIX A: ALTERNATIVE ISING-MODEL FORMULATION

We outline in this Appendix an alternative formulation of the Ising model which is structurally related to the Montroll–Berlin partition function Eq. (2.5) and the correlation functions Eq. (2.6).

Let us proceed via an intermediate formula due to Siegert.[15] Consider first the partition function

$$Z=\exp(-NKv_0)\sum_{\{\mu\}}\exp[K\sum_{ij}v_{ij}\mu_i\mu_j]. \tag{A1}$$

A self-interaction $v_0\equiv v_{ii}$ has been added and subtracted. The strength of v_0 is sufficient to make V positive definite. Siegert employs the identity

$$\exp[K\sum_{ij}v_{ij}\mu_i\mu_j]=\pi^{-N/2}\,|\,\mathsf{V}\,|^{-1/2}\int_{-\infty}^{\infty}\cdots\int dx_1\cdots dx_N$$

$$\times\exp[-\sum_{ij}B_{ij}x_ix_j+2K^{1/2}\sum_i x_i\mu_i] \tag{A2}$$

(where $\mathsf{B}=\mathsf{V}^{-1}$), to produce a form in which the μ summations may be performed. The result is

$$Z=\exp(-NKv_0)\,(4/\pi)^{N/2}\,|\,\mathsf{V}\,|^{-1/2}\int_{-\infty}^{\infty}\cdots\int dx_1\cdots dx_N$$

$$\times\exp[-\sum_{ij}B_{ij}x_ix_j]\prod_i\cosh(2K^{1/2}x_i). \tag{A3}$$

In order to manipulate Siegert's partition function into one like that of Montroll and Berlin, we introduce a function $Q(y)$ by

$$\cosh x=\left(\frac{1}{2\pi i}\right)\int_{-i\infty+\gamma}^{i\infty+\gamma}e^{yx^2}e^{Q(y)}dy, \tag{A4}$$

$$Q(y)=\ln\left\{\int_0^{\infty}e^{-yz}\cosh z^{1/2}dz\right\}, \qquad \mathrm{Re}\,y>0. \tag{A5}$$

The similarity of Eq. (A4) to the integral representation of the δ function [Eq. (2.2)] allows us to perform

[12] R. L. Stratonovich, Dokl. Akad. Nauk SSSR **115,** 1097 (1957) [English transl.: Soviet Phys. Doklady **2,** 416 (1958)]; J. Hubbard, Phys. Rev. Letters **3,** 77 (1959); S. F. Edwards, Phil. Mag. **4,** 1171 (1959); A. J. F. Siegert, Physica Suppl. **26,** S30 (1960).

[13] N. N. Bogoliubov and D. V. Shirkov, *Introduction to the Theory of Quantized Fields* (Interscience Publishers, Inc., New York, 1959), Chap. 7.

[14] S. F. Edwards, Proc. Phys. Soc. (London) **85,** 613 (1965).

[15] A. J. F. Siegert, *Statistical Physics 3, Brandeis Summer Institute 1962* (W. A. Benjamin, Inc., New York, 1963).

the x integrals in (A3) just as the μ integrals in Eq. (2.3) were performed. The result is

$$Z=\exp(-NKv_0)(4\pi Ki)^{-N}|\mathsf{V}|^{-1/2}\int_{\mathfrak{C}}\cdots\int ds_1\cdots ds_N \times\exp[\sum_1 Q(s_i/4K)]|\mathsf{B}-\mathsf{S}|^{-1/2}, \quad \text{(A6)}$$

where S is a diagonal matrix with ii element s_i. The contours of the s_i integrals run from $-i\infty+\gamma_i$ to $i\infty+\gamma_i$ in such a manner as to keep $\mathrm{Re}(\mathsf{B}-\mathsf{S})$ positive definite. Since B is positive definite, this can be achieved with all $\gamma_i<0$.

In like manner it may be demonstrated that

$$C_{mn}=\exp(-NKv_0)(4\pi Ki)^{-N}|\mathsf{V}|^{-1/2} \times(1/2KZ)\int_{\mathfrak{C}}\cdots\int ds_1\cdots ds_N s_m s_n \times\exp[\sum_i Q(s_i/4K)]|\mathsf{B}-\mathsf{S}|^{-1/2}G_{mn}\{s\}, \quad \text{(A7)}$$

where

$$\mathsf{G}=(\mathsf{B}-\mathsf{S})^{-1}.$$

If we employ the approximation of assigning to C_{mn} the value of the integrand at the saddle point in s space, we obtain the same critical correlation function as that determined in Sec. IV.

It might be noted, also, that one of the authors (J.S.L.)[16] has attempted to restore the correct analytic structure to the phase transition of the spherical model by supplementing the spherical condition [Eq. (1.5)] with the further constraint

$$\sum_i \mu_i^4=N, \quad \text{(A8)}$$

introduced in a canonical fashion with conjugate variable α. The resulting partition function is

$$Z\propto\int_{\mathfrak{C}} dz\exp(NKz)\int d\mu_1\cdots d\mu_N \times\exp[-K\sum_{ij}(z\mathbf{1}-\mathsf{V})_{ij}\mu_i\mu_j-\alpha\beta\sum_i\mu_i^4], \quad \text{(A9)}$$

with $\beta=1/k_BT$. After employing the integral

$$\exp(-\alpha\beta\mu_i^4)=i^{-1}(KJ/8\pi\alpha)^{1/2}\int_{-i\infty}^{i\infty}dt_i \times\exp[(J/8\alpha)Kt_i^2]\exp[Kt_i\mu_i^2], \quad \text{(A10)}$$

we obtain a partition function quite similar to Eqs. (2.5) and (A6). Thus, this model probably does capture the essential analytic features of the Ising-model transition. The correlation functions, likewise, are similar structurally to those employed in the body of the text.

[16] J. S. Langer, Phys. Rev. **137**, A1531 (1965).

APPENDIX B: SEVERAL GAUSSIAN INTEGRALS

In this Appendix we concern ourselves with the evaluation of the integral

$$I=\int_{-\infty}^{\infty}\cdots\int dx_1\cdots dx_N\exp[-\sum_{jk}(\mathsf{R}+i\mathsf{M})_{jk}x_jx_k], \quad \text{(B1)}$$

and related integrals. R and M are real symmetric matrices but they do not in general commute; R is positive definite. For application to Sec. II,

$$\mathsf{R}=K(\gamma\mathbf{1}-\mathsf{V}), \quad \text{(B2)}$$

$$\mathsf{M}=K(\mathsf{T}-\gamma\mathbf{1}). \quad \text{(B3)}$$

A nonsingular matrix H exists such that[17]

$$\mathsf{H}^T\mathsf{R}\mathsf{H}=\mathbf{1}, \quad \text{(B4)}$$

$$\mathsf{H}^T\mathsf{M}\mathsf{H}=\mathbf{\Omega}, \quad \text{(B5)}$$

$$\mathsf{H}^T(\mathsf{R}+i\mathsf{M})\mathsf{H}=\mathbf{1}+i\mathbf{\Omega}. \quad \text{(B6)}$$

where $\mathbf{\Omega}$ is a diagonal matrix with jj element ω_j. Consider the change of variables

$$\mathbf{x}=\mathsf{H}\mathbf{y}, \quad \text{(B7)}$$

where $\mathbf{x}$ is a column matrix with elements x_i. Under this transformation Eq. (B1) becomes

$$I=|\mathsf{H}|\int_{-\infty}^{\infty}\cdots\int dy_1\cdots dy_N\exp[-\sum_j(1+i\omega_j)y_j^2]$$

$$=\pi^{N/2}|\mathsf{H}||\mathbf{1}+i\mathbf{\Omega}|^{-1/2} \quad \text{(B8)}$$

$$=\pi^{N/2}|\mathsf{R}+i\mathsf{M}|^{-1/2}, \quad \text{(B9)}$$

where for the final result the determinant of Eq. (B6) has been used.

The moments matrix

$$\mathbf{\Gamma}=I^{-1}\int\cdots\int dx_1\cdots dx_N\mathbf{x}\mathbf{x}^T\exp[-\mathbf{x}^T(\mathsf{R}+i\mathsf{M})x], \quad \text{(B10)}$$

required in Eq. (2.6), may be evaluated by the same transformation. It is easy to see that

$$\mathbf{\Gamma}=\tfrac{1}{2}\mathsf{H}(\mathbf{1}+i\mathbf{\Omega})^{-1}\mathsf{H}^T \quad \text{(B11)}$$

$$=\tfrac{1}{2}(\mathsf{R}+i\mathsf{M})^{-1}, \quad \text{(B12)}$$

where for the final result the inverse of Eq. (B6) has been used.

The formula

$$\partial\ln|T-V|/\partial t_j=G_{jj}, \quad \text{(B13)}$$

[17] R. Bellman, *Introduction to Matrix Analysis* (McGraw-Hill Book Company, Inc., New York, 1960), p. 58. This is the fact employed in small-vibration theory to simultaneously diagonalize the potential and kinetic energy.

used in Eq. (2.9), follows as a special case from the obvious relation between (B1) and (B10),

$$i^{-1}(\partial/\partial M_{jk})I=-I\Gamma_{jk}. \qquad \text{(B14)}$$

Equation (B13) suggests the interesting method of writing $\ln|\mathbf{T}-\mathbf{V}|$ employed in Eq. (4.23). Equation (B13) may be reintegrated as a line integral from the point $\{t_s\}$ to $\{t\}$ in the N-dimensional t space:

$$\ln|\mathbf{T}-\mathbf{V}|\equiv\ln|t_s\mathbf{1}-V|+L, \qquad \text{(B15)}$$

$$L\equiv\int_{\{t_s\}}^{\{t\}} d\mathbf{l}\{t'\}\cdot\nabla_t\ln|\mathbf{T}'-\mathbf{V}|. \qquad \text{(B16)}$$

One possible "path" is the straight line parameterized by τ,

$$(\mathbf{l})_j=\tau(t_j'-t_s)\equiv\tau\phi_j, \qquad \text{(B17)}$$

so that

$$L=\sum_j\int_0^1 d\tau\phi_jG_{jj}\{\tau\phi\}. \qquad \text{(B18)}$$

(τ acts like a charging parameter.)

APPENDIX C: TWO-CENTER GREEN'S FUNCTION

In this Appendix we shall examine solutions of the two-center Green's function equation (4.8), constructing these solutions by means of the approximate Smoluchowski equation from the one-center Green's function, given by

$$[-\sigma^2\nabla^2+\kappa^2\sigma^2+\omega(\sigma^2/r^2)q(r/R)]G_1(r)=\delta(\mathbf{r}). \qquad \text{(C1)}$$

Consider first the simpler case of $\kappa R\gg1$. The term κ^2 in Eq. (C1) dominates the $1/r^2$ term before the effects of the q cutoff are important. With q neglected the solution of Eq. (1) can be written in terms of a modified Bessel function[18]

$$G_1(r)=A\kappa^{\nu+1/2}x^{-1/2}K_\nu(x), \qquad \text{(C2)}$$

where

$$x=\kappa r, \qquad \nu=(\omega+\tfrac{1}{4})^{1/2}. \qquad \text{(C3)}$$

The Smoluchowski equation (4.18) can be written in the form

$$G(R)=A'R^{-\nu-\nu'}\int_{\kappa R}^\infty dXX^{\nu+\nu'-1}W(X), \qquad \text{(C4)}$$

$$W(X)=\int d^3x\,x^{-1/2}K_\nu(x)|\mathbf{X}-\mathbf{x}|^{-1/2}K_{\nu'}(|\mathbf{X}-\mathbf{x}|). \qquad \text{(C5)}$$

[18] *Handbook of Mathematical Functions*, edited by A. Abramowitz and I. A. Stegun (U. S. Department of Commerce, National Bureau of Standards, Washington, D. C., 1964), Appl. Math. Ser. 55, p. 355.

The required convolution is best performed if we convert to a Gaussian x dependence by the integral representation

$$x^{-1/2}K_\nu(x)$$
$$=2^{\nu-1}\Gamma(\tfrac{1}{2}\nu+\tfrac{3}{4})\left(\frac{i}{2\pi}\right)\int_0^\infty dt\int_{\mathcal{H}} ds(-s)^{-1/2\nu-3/4}t^{-\nu-1}$$
$$\times\exp[-\tfrac{1}{4}t-x^2(t^{-1}+s)]. \qquad \text{(C6)}$$

The Hankel contour $\mathcal{H}$ for the s integral starts from infinity, encircles the origin counterclockwise, and returns to infinity. The x integration may be performed yielding

$$W(X)=\pi^{3/2}2^{\nu+\nu'-2}\Gamma(\tfrac{1}{2}\nu+\tfrac{3}{4})\Gamma(\tfrac{1}{2}\nu'+\tfrac{3}{4})$$
$$\times\left(\frac{i}{2\pi}\right)^2\int_0^\infty\int_0^\infty dt_1dt_2\int_{\mathcal{H}}\int_{\mathcal{H}} ds_1ds_2(-s_1)^{-1/2\nu-3/4}$$
$$\times(-s_2)^{-1/2\nu'-3/4}t_1^{-\nu-1}t_2^{-\nu'-1}(s_1+s_2+t_1^{-1}+t_2^{-1})^{3/2}$$
$$\times\exp[-\tfrac{1}{4}(t_1+t_2)-X^2(t_1^{-1}+s_1)$$
$$\times(t_2^{-1}+s_2)(t_1^{-1}+t_2^{-1}+s_1+s_2)^{-1}], \qquad \text{(C7)}$$

To handle the case of $X\gg1$, one extracts, in the exponent, terms of zeroth order and first order in s. The exponential of the remaining expression is then set to unity, which can be shown to be correct to lowest order in X^{-1}. The resulting integrals can all be performed exactly, yielding

$$W(X)\propto X^{1/2}K_{|\nu+\nu'-3/2|}(X)[1+O(X^{-1})], \qquad \text{(C8)}$$

$$G(R)\propto\kappa^{\nu+\nu'-1/2}R^{-1/2}K_{\nu+\nu'-1/2}(\kappa R), \qquad \kappa R\gg1. \qquad \text{(C9)}$$

It is interesting to study the case $\kappa R\ll1$ even though this neglects the cutoff functions q. The substitution $s_i=\sigma_i/X^2$ and $t_i=\tau_iX^2$ reveals that $W(X)$ goes like $X^{2-\nu-\nu'}$ for small X. Thus the integral in Eq. (C5) is $0(1)$ and $G(R)\propto R^{-\nu-\nu'}$. This result agrees, of course, with the conclusion of the dimensional arguments in the body of the paper.

To correctly examine the case $R\ll1/\kappa$, where the q function may be important, employ the WKB solution (3.23) of Eq. (C1) for G_1, with $\phi(r)=\omega(\sigma^2/r^2)q(r/R)$, with $s=3$, and with r replacing R. The essential behavior of G_1 is summarized in Eqs. (4.16) and (4.17).

In order to obtain the leading order of the two-center Green's function we will divide the integrals in the Smoluchowski equation (4.18) into intervals, and use the small and large κr expressions for G_1 right up to the limits of the integrals; thus,

$$G(R,\kappa)\approx I_1+I_2+I_3, \tag{C10}$$

$$I_1\propto\int_\kappa^{1/R}\kappa'\,d\kappa'\left(\frac{2\pi}{R}\right)\int_0^{1/\kappa'}dr\,r\left[R^{-\nu+1/2}r^{-1}f\left(\frac{r}{R}\right)\right]$$

$$\times\int_{|R-r|}^{R+r}ds\,s\left[R^{-\nu'+1/2}s^{-1}f'\left(\frac{r}{R}\right)\right], \tag{C11}$$

$$I_2\propto\int_\kappa^{1/R}\kappa'\,d\kappa'\left(\frac{2\pi}{R}\right)\int_{1/\kappa'}^{\infty}dr\,r[R^{-\nu+1/2}r^{-1}e^{-\kappa' r}]$$

$$\times\int_{r-R}^{r+R}ds\,s[R^{-\nu'+1/2}s^{-1}e^{-\kappa' s}], \tag{C12}$$

$$I_3\propto\int_{1/R}^{\infty}\kappa'\,d\kappa'\int d^3r\,G_1(r,\kappa')G_1(|\mathbf{R}-\mathbf{r}|,\kappa'). \tag{C13}$$

The convolution is performed with coordinates $r=|\mathbf{r}-\mathbf{r}_m|$, $s=|\mathbf{r}-\mathbf{r}_n|$. After the change of variables $r=yR$, $s=zR$, and $X=\kappa' R$, the behavior of I_1 and I_2 is easily determined.

I_1 becomes

$$I_1\propto R^{-\nu-\nu'}\int_{\kappa R}^1 X\,dX\int_0^{1/X}dy\,f(y)\int_{|1-y|}^{1+y}dz\,f'(z). \tag{C14}$$

For small κR the integral goes to a constant. I_2 can be explicitly evaluated and shown to be

$$I_2\propto R^{-\nu-\nu'}. \tag{C15}$$

Finally I_3 involves mainly the large $\kappa' R$ region, so that our earlier considerations neglecting q apply:

$$I_3=G(R;\kappa=1/R)\propto R^{-\nu-\nu'}. \tag{C16}$$

All these integrals are positive, so that

$$G(R)\propto R^{-\nu-\nu'},\qquad \kappa R\ll 1. \tag{C17}$$

APPENDIX D: THE DETERMINANT TERM

In this Appendix we consider the Green's function necessary to evaluate the determinant according to Eqs. (4.22)–(4.27). As we shall see, interest centers on the Green's function for $r\ll R$. Thus the q in Eq. (4.27) is effectively unity and the solution in terms of Bessel functions[18] is

$$G_l(r,r\,|\,\tau\phi)=(1/\sigma^2 r)K_\mu(\kappa r)I_\mu(\kappa r), \tag{D1}$$

$$\mu^2=(l+\tfrac{1}{2})^2+\tau\omega. \tag{D2}$$

This reduces in limiting cases to

$$G_l(r,r\,|\,\tau\phi)\sim 1/2\sigma^2\mu r,\qquad \kappa r\ll 1, \tag{D3}$$

$$\sim 1/2\sigma^2\kappa r^2,\qquad \kappa r\gg 1. \tag{D4}$$

In evaluating the integral

$$J=\int_\sigma^\infty dr\,q\left(\frac{r}{R}\right)G_l(r,r\,|\,\tau\phi), \tag{D5}$$

we again distinguish between $\kappa R\ll 1$ and $\kappa R\gg 1$. In the former case make the change of variables $r/R=y$. The integral

$$J=R\int_{\sigma/R}^\infty dy\,q(y)G_l(yR,yR\,|\,\tau\phi), \tag{D6}$$

may be performed by parts, integrating y^{-1} and differentiating $Ry\,q(y)G(yR,yR\,|\,\tau\phi)$. This yields from the lower limit

$$J\sim(1/2\sigma^2\mu)\ln R,\qquad \kappa R\ll 1, \tag{D7}$$

as the dominant term if $Ry\,q(y)G_l(yR,yR\,|\,\tau\phi)$ goes from $0(1)$ to a small value on a scale $y=0(1)$.

On the other hand, for $\kappa R\gg 1$ the switchover of G_l from $1/r$ to $1/\kappa r^2$ behavior is more important than the q cutoff. Thus make the change of variables $\kappa r=y$. The integration by parts reveals that the dominant behavior is

$$J\sim-(1/2\sigma^2\mu)\ln\kappa,\qquad \kappa R\gg 1. \tag{D8}$$

APPENDIX E: THE PARTITION FUNCTION

In this Appendix we analyze the ratio Z/Z_{SM} required in Sec. IV. Using the determinant representation of Eqs. (4.22)–(4.25) we find that

$$Z/Z_{\mathrm{SM}}\approx\left[\int_{\mathrm{e}}d\omega\,\exp[-\tfrac{1}{2}L(\omega)]\right]^2. \tag{E1}$$

Since the saddle point of the exponent is $\omega=0$, consider an expansion of $L(\omega)$ in ω. The general term has the structure

$$\sigma^{2n}\frac{\omega^n}{n-1}\int_\sigma^\infty\cdots\int_\sigma^\infty d^3r_1\cdots d^3r_n\frac{q(r_1/R)}{r_1^2}G(r_1,r_2\,|\,\tau=0)$$

$$\times\frac{q(r_2/R)}{r_2^2}G(\mathbf{r}_2,\mathbf{r}_3\,|\,\tau=0)\cdots\frac{q(r_n/R)}{r_n^2}G(\mathbf{r}_n,\mathbf{r}_1\,|\,\tau=0). \tag{E2}$$

The zeroth-order Green's functions go like $1/|\mathbf{r}_i-\mathbf{r}_j|$ for $\kappa\,|\mathbf{r}_i-\mathbf{r}_j|\ll 1$. The change of variables $r=Ry$ indicates that the integral is zeroth order in R, although logarithmic divergences at the lower limit probably produce $(\ln R)^n$. Hence the dominant part of $L(\omega)$ is a function of $\omega\ln R$, at worst. If the major part of the integral in Eq. (E1) comes from the ω region where ω expansion is valid then, at worst,

$$Z/Z_{\mathrm{SM}}\propto(\ln R)^{-2},\qquad \kappa R\ll 1. \tag{E3}$$