Decay of Order in Classical Many-Body Systems. I. Introduction and Formal Theory*

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(Received 20 December 1971; revised manuscript received 2 March 1972)

In this work we briefly review the Ornstein-Zernike prediction for the decay of correlation functions, extend it to treat the decay of correlation near surfaces, and then contrast this prediction with the exactly known results for the two-dimensional Ising model. We develop the transfer-matrix approach to classical statistical mechanics in sufficient generality for its use in later papers in this series, where it is employed to derive general forms for the decay of correlation functions in Ising models away from the critical point, which provide a clear explanation of the failure of the Ornstein-Zernike theory for the two-dimensional Ising model. In particular, we show that the thermodynamic behavior of a classical system with short-range interactions reduces, when the system becomes infinite in at least one dimension, to the calculation of the largest eigenvalue of the transfer matrix. Using the Perron-Fröbenius theorem, we show that for a system infinite in *no more than* one dimension, an arbitrary correlation function defined on the system decays at least exponentially fast. One is able to predict whether the decay of correlation is monotone or oscillatory on the basis of the largest few eigenvalues of the transfer matrix.

I. INTRODUCTION

We consider the behavior of classical many-body systems interacting with strictly short-range forces.[1] The system of interest is an N-particle (or N-spin) system, or equivalently, a system with chemical potential μ and average particle number $\bar{N}$, with pairwise short-range interactions. We shall largely restrict our treatment to systems whose particles (or spins) lie upon an underlying lattice, although some of our results are easily extended to continuum systems.

Given such a system, the joint expectation value $G_{AB}(\vec{R})$ of the two locally defined quantities $\underline{A}(\vec{0})$ and $\underline{B}(\vec{R})$ may be defined as

$$G_{AB}(\vec{R}) \equiv \langle \underline{A}(\vec{0})\underline{B}(\vec{R}) \rangle \ , \tag{1.1}$$

where $\langle \cdots \rangle$ denotes a thermal average with respect to the appropriate ensemble. Such a joint expectation is known as a pair-correlation function. In cases in which the product $\langle \underline{A}(\vec{0}) \rangle \langle \underline{B}(\vec{R}) \rangle$ is nonzero, it is useful to use an alternate definition for the pair-correlation function. Let us define the fluctuation $\delta\underline{B}(\vec{R})$ of the quantity $\underline{B}(\vec{R})$ via

$$\delta\underline{B}(\vec{R}) = \underline{B}(\vec{R}) - \langle \underline{B}(\vec{R}) \rangle \ . \tag{1.2}$$

Then we write $G_{AB}(\vec{R})$ as

$$G_{AB}(\vec{R}) \equiv \langle \delta\underline{A}(\vec{0})\delta\underline{B}(\vec{R}) \rangle \ . \tag{1.3}$$

With this definition of the pair-correlation function, it is called variously the net correlation, the excess correlation, or the correlation of fluctuations.

The asymptotic decay of such correlations as $R \to \infty$ was long ago predicted by Ornstein and Zernike[2] to be of the form

$$G_{AB}(\vec{R}) \sim R^{-(d-1)/2} e^{-\kappa R} \ , \tag{1.4}$$

where d is the dimension of the system. This prediction was based on a simple argument which we reproduce and extend somewhat below. The Ornstein-Zernike form (1.4) has since been found to be a consequence of virtually every random-phase-type theory, principal among which are the Curie-Weiss theory and its generalizations,[3] and the Landau-Ginzburg theory.[4]

The form (1.4) loses its validity if the second moment

$$C_2 \equiv \int_\Omega d\vec{R}\, R^2 C_{AB}(\vec{R}) \tag{1.5}$$

of the direct correlation function $C_{AB}(\vec{R})$, defined by

$$G_{AB}(\vec{R}) = C_{AB}(\vec{R}) + \rho \int d\vec{R}'\, C_{AB}(\vec{R} - \vec{R}')G_{AB}(\vec{R}') \ , \tag{1.6}$$

diverges.[5] It is now clear that this generally is the case at the critical point of a second-order phase transition.[5] However, at sufficiently high temperatures and/or low densities there is good reason to believe that C_2 is finite and that (1.4) holds. Additionally, one believes that even at low temperatures and high densities, away from T_c, C_2 will be finite and (1.4) will hold. Thus, for example, neutron scattering cross sections at small angles, away from the critical point of a ferromagnetic

system, yield results consistent with an Ornstein-Zernike form for the decay of correlations.[5] On the other hand, in the exactly soluble case of the two-dimensional zero-field Ising model, exceptions to Ornstein-Zernike theory are found at both high and low temperatures in addition to those expected and found at the critical point. While the spin-correlation function

$$G_s(\vec{R}) \equiv \langle \delta S^{\sigma}(\vec{0}) \delta S^{\sigma}(\vec{R}) \rangle \tag{1.7}$$

is found to decay as

$$G_s(R) \sim R^{-1/2} e^{-\kappa R}, \quad R \to \infty \tag{1.8}$$

for temperatures above the critical temperature,[6] the low-temperature spin-correlation function decays as[7,8]

$$G_s(\vec{R}) \sim R^{-2} e^{-\kappa R}. \tag{1.9}$$

Although one might expect[9] the energy-density correlation functions to decay as (1.4), they are found to exhibit the non-Ornstein-Zernike behavior described by (1.9) at all temperatures in zero field and two dimensions.[10] These violations of the phenomenological predictions and experimental measurements by the two-dimensional Ising model are rather disconcerting in the light of evidence that C_2 should be finite except at a critical point.

One purpose of the work reported here is to understand the underlying cause of this exceptional behavior in the two-dimensional Ising model. (A summary of our approach and conclusions was presented in Ref. 1.) Through an extension of our knowledge of the decay of correlations in the Ising model at both high and low temperatures to higher dimensions and finite magnetic fields which we report in Papers II and III of this series, we are able to systematically catalog exceptions to Ornstein-Zernike behavior and to understand the causes of these exceptions. Invariably it will be found that exceptions are due to some hidden symmetry either of the Hamiltonian or of the lattice involved.[1]

We present the relevant aspects of Ornstein-Zernike theory in Sec. II, including an extension of it to treat the case of a system with free edges. Our calculation, in Paper IV of this series, of the decay of spin-correlation functions in an Ising model with free surfaces confirms that at high temperatures the extended Ornstein-Zernike theory correctly predicts the decay of such correlations near free surfaces.

The transfer-matrix approach employed in this work is a generalization of matrix methods introduced in 1941 by Kramers and Wannier,[11] Montroll,[12] and Lassetre and Howe.[13] In his monumental 1944 work, Lars Onsager[6] used this technique to obtain the partition function of the zero-field two-dimensional Ising model in addition to the spin-correlation function mentioned above. The matrix method has since reappeared in the exact solution of other two-dimensional problems such as the dimer problem[14] and the ice and ferroelectric problems.[15] Ashkin and Lamb[16] discussed the decay of molecular order by means of the matrix method. In this work they demonstrated that the existence of long-range order is implied by a degeneracy of the largest eigenvalue of this matrix. McCoy and Wu[17] have employed the matrix method to study the thermodynamics and correlation functions of a quadratic Ising lattice with each row of vertical bonds varying randomly from row to row. One of the most straightforward matrix treatments of the the Ising problem in two dimensions is that of Schultz, Mattis, and Lieb.[18]

A review of most known results concerning the Ising transfer matrix in two dimensions was presented by Fisher and Burford.[5] They found that for a $N \times N$ lattice, the spectrum of the transfer matrix is broken into $N+1$ bands, the number of states in the nth band being given by the number of ways of putting n Fermi-type particles into the N sites of a lattice row. The largest eigenvalue—corresponding to the zero-Fermion or vacuum state—is nondegenerate for finite N. The size of the largest eigenvalue of the nth band is a decreasing function of Fermion number n. After the vacuum state, the N single-particle states and $\frac{1}{2}N(N-1)$ two-particle states are of greatest importance. Away from the critical point, the form of these states and their eigenvalues determine not only the bulk thermodynamics, but also the asymptotic decay of virtually any pair-correlation function.

Following the lines indicated by Fisher,[4,19] we show in Papers II and III that although the d-dimensional finite-field problem cannot be exactly solved, many qualitative aspects of the two-dimensional case are found to carry over to the more general cases. In particular, the bands remain labeled by a "particle number," with, however, the particles being "hard-core bosons" rather than fermions. By the use of simple perturbation theories appropriate to high and low temperatures, we are able to make quite general statements about the decay of various correlation functions.

The outline of our work is as follows. In Sec. II of this paper, we derive the Ornstein-Zernike prediction for the decay of pair correlations, both within a bulk system and near free surfaces.[1] The remainder of this paper is devoted to an exposition of the theory of the transfer-matrix approach from a general viewpoint[19] which brings out features not, apparently, previously recognized in the literature. General formulas for the thermodynamic functions, and for the decay of pair correlations are derived. We consider the eigenvalue spec-

trum and its consequences for the decay of correlations functions, and we include a short discussion of the asymptotic degeneracy of the largest eigenvalue and its implications about the existence of long-range molecular order.[6,13,19] In Papers II and III we derive, using perturbation theory, the eigenvalue spectrum of the transfer matrix for the Ising model in d dimensions and arbitrary magnetic field, for very high and very low temperatures, respectively, and we use these results to calculate the asymptotic decay of pair correlations—noting exceptions to Ornstein-Zernike behavior. In Paper IV we treat the decay of correlations near free surfaces at both high and low temperatures,[1] and critically compare our results with the predictions of the extended Ornstein-Zernike theory.

II. ORNSTEIN-ZERNIKE THEORY

Given a many-particle (or spin) system with short-range interparticle forces, and a net pair correlation function $G(\vec{R})$ of interest, we introduce the (shorter-ranged) direct correlation function $C(\vec{R})$ via

$$G(\vec{R}) = C(\vec{R}) + \int_\Omega d\vec{R}'\, C(\vec{R}')\, G(\vec{R} - \vec{R}') , \tag{2.1}$$

where we have employed a dimensionless volume in anticipation of specialization to lattice systems. It is easily shown that in the low-density limit $C(\vec{R})$ has essentially the same range as the interparticle potential $V(\vec{R})$ of the system. By the convolution theorem we may write the Fourier transform of (2.1) as

$$\hat{G}(\vec{q}) = \hat{C}(\vec{q}) + \hat{C}(\vec{q})\hat{G}(\vec{q}) \tag{2.2}$$

or as

$$\hat{G}(\vec{q}) = [1 - \hat{C}(\vec{q})]^{-1}\, \hat{C}(\vec{q}) . \tag{2.3}$$

We ordinarily expect $C(\vec{R})$ to be short ranged in the sense that the series

$$\hat{C}(\vec{q}) = \sum_{n=0}^{\infty} \frac{(-q^2)^n}{(2n)!} \int_\Omega d\vec{R} (\hat{\vec{q}} \cdot \vec{R})^{2n}\, C(\vec{R}) \tag{2.4}$$

converges rapidly. This being the case, as $q \to 0$, we may write $\hat{C}(\vec{q})$ as

$$\hat{C}(q) \approx C_0 - q^2 C_2 + \cdots , \tag{2.5}$$

where the integral moments of $C(\vec{R})$ are given by

$$C_{2n} = [(2n)!]^{-1} \int_\Omega d\vec{R} (\hat{\vec{q}} \cdot \vec{R})^{2n} C(\vec{R}) . \tag{2.6}$$

In terms of the moments of $C(\vec{R})$, $\hat{G}(\vec{q})$ becomes

$$\hat{G}(\vec{q}) \approx [q^2 + \kappa^2 + O(q^4)]^{-1} G_0 \quad \text{as } q \to 0, \tag{2.7}$$

where

$$\kappa^2 = (1 - C_0) C_0 / C_2, \quad G_0 = C_0^2 / C_2 . \tag{2.8}$$

We may obtain the asymptotic decay of $G(\vec{R})$ for large R by Fourier-inverting (2.7), as is well known from the Abelian and Tauberian theorems of Fourier analysis. Letting d be the dimension of the system, we obtain

$$G(\vec{R}) \approx G_0 \frac{e^{-\kappa R}}{R^{(d-1)/2}} \quad \text{as } R \to \infty . \tag{2.9}$$

Formula (2.9) is the Ornstein-Zernike prediction for the asymptotic decay of pair-correlation functions within the bulk of a many-body system with short-range interactions.

Our calculation is bound to break down if $C_2 \to \infty$, as is now expected at a critical point,[3,5] for then (2.5) and (2.7) become invalid. However, we shall not here be treating systems at their critical points. Away from $T = T_c$, we ordinarily expect that C_2 will be finite and that ultimately $G(\vec{R})$ decays as (2.9) for $R \to \infty$, at *fixed* T not equal to T_c.

In order to extend the Ornstein-Zernike theory to obtain the decay of pair correlation functions near free surfaces, we notice that (2.7) has the same form as the Fourier transform of the following equation:

$$(\nabla^2 - \kappa^2) G(\vec{R}) = - G_0 \delta(\vec{R}) . \tag{2.10}$$

This is eminently sensible, as $G(\vec{R})$ defined by (2.9) is seen to be the Green's function for $\nabla^2 - \kappa^2$ with homogeneous boundary conditions. In fact, the Landau-Ginsberg theory[4] commences from (2.10) directly rather than from the Ornstein-Zernike relation (2.1). Thus, in order to obtain the decay of correlations near a surface, we are led to solve (2.10) in the presence of a boundary surface.

There are two kinds of boundary conditions of particular interest. In the first kind of boundary condition, $G(\vec{R})$ is taken to go to zero at a small distance beyond the surface. In the other type of boundary condition, the gradient $\nabla G(\vec{R})$ of $G(\vec{R})$ is taken to go to zero at a small distance beyond the boundary surface.

In the theory of electrostatics, the effect of rectangular boundaries is accounted for by a set of image charges arranged so that the boundary surface has the required potential distribution. The image method may also be applied to the scalar Helmholtz equation [our differential equation (2.10)], for which a boundary may either be absorbing or reflecting. For absorbing boundaries, the effect of the boundary is duplicated by an image source (or sources) arranged so that its wave fronts exactly cancel those of a wave impinging upon the barrier; and for reflecting boundaries, the image sources have the same arrangement as that of the image sources for absorbing boundaries, but are opposite in sign. Thus they exactly reinforce a wave front impinging upon the boundary. The case of absorbing boundaries corresponds to

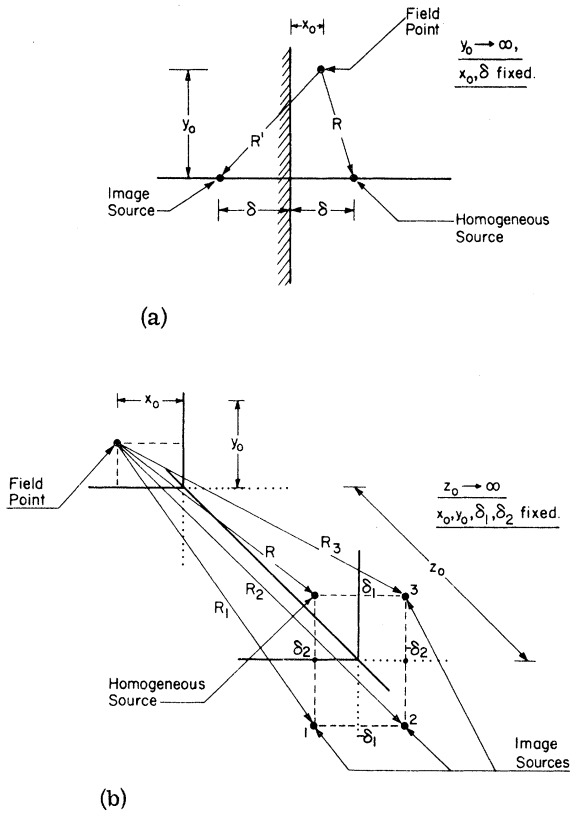

FIG. 1. Correlations near free surfaces: (a) image source for a single surface, (b) image sources for two intersecting surfaces.

the boundary condition that $G(\vec{R})$ be zero at the boundary. Similarly, reflecting boundaries correspond to a zero gradient at the boundary. (Of course, since κ is real, we have diffusion rather than wave propagation. However, the image method is still applicable.) The source terms in (2.10) are composed of the δ function for the homogeneous source together with the δ functions for the various image charges.

In Fig. 1 we demonstrate the array of image sources necessary to duplicate a single surface and that needed to duplicate the intersection of two such surfaces. Of course, the technique may be generalized to d dimensions and up to $d-1$ intersecting surfaces. For simplicity we present the calculation only for the case of a single surface, and then simply state our result for intersecting interfaces for $n = 1, 2, \ldots, d-1$.

We first consider absorbing boundaries. Then in Fig. 1(a) the image source is opposite in sign to that of the homogeneous source, and symmetrically placed across the boundary (so as to exactly cancel the effect of the homogeneous source on the boundary surface). Using the notation of this figure, and employing the superposition principal, we can write the correlation function $G_1(\vec{R})$, between sites $\vec{R}_0$ and $\vec{R}_0+\vec{R}$ near an edge, as

$$G_1(\vec{R}) = G(\vec{R}) - G(\vec{R}') , \tag{2.11}$$

where $G(\vec{R})$ is the correlation function given in (2.9), i.e., that due to a single source. Referring to Fig. 1(a), we write $G_1(\vec{R})$ as

$$G_1(\vec{R}) \approx G_0 \left(\frac{\exp\{-\kappa[y_0^2+(\delta-x_0)^2]^{1/2}\}}{[y_0^2+(\delta-x_0)^2]^{(d-1)/4}} - \frac{\exp\{-\kappa[y_0^2+(x_0+\delta)^2]^{1/2}\}}{[y_0^2+(\delta+x_0)^2]^{(d-1)/4}} \right) , \tag{2.12}$$

where $y_0 \to \infty$ and x_0 and δ are fixed. Expanding the radicals to low order in (δ/y_0) and (x_0/y_0), we can write (2.12) as[1]

$$G_0^{-1} G_1(\vec{R}) \approx A_1(x_0, \delta) \frac{e^{-\kappa R}}{R^{(d-1)/2+1}} , \quad y_0 \to \infty \tag{2.13}$$

where $A_1(x_0, \delta)$ is fixed for fixed finite x_0 and δ, and is zero for x_0 and/or δ zero. Thus with an absorbing boundary, the Ornstein-Zernike prediction for the decay of correlations near a surface differs from that for the decay within the bulk by a factor $[A_1(x_0, \delta)/R]$. In particular, it is predicted that the *same* inverse range of correlation κ applies. The analogous formula for the asymptotic decay of the correlation function $G_n(\vec{R})$ between two points simultaneously near n surfaces (n being 0, 1, 2, ..., $d-1$, where d is the dimensionality) is easily derived, and found to be

$$[G_n(\vec{R})/G_0] \approx A_n \frac{e^{-\kappa R}}{R^{(d-1)/2+n}} , \quad R \to \infty \tag{2.14}$$

where A_n is fixed for fixed finite distances from the n surfaces and is zero if either $\vec{R}_0$ or $\vec{R}_0+\vec{R}$ actually is on one of the n surfaces.

For reflecting boundaries, Fig. 1 still applies. In fact, changing the sign of the image source from negative to positive, we may simply use Eq. (2.12) to determine the asymptotic decay near a surface. To lowest order in (x_0/y_0) and (δ/y_0), this correlation function decays as twice the bulk decay specified in Eq. (2.9). For correlations between two points *simultaneously* near n surfaces, we easily find the decay to be given by 2^n times the bulk decay specified in (2.9). That is,

$$G_n(\vec{R}) \approx 2^n G_0 \frac{e^{-\kappa R}}{R^{(d-1)/2}} . \tag{2.15}$$

We note, however, that with reflecting boundary conditions the component of the gradient of $G_n(\vec{R})$ normal to a given surface is zero if $\vec{R}_0$ and/or $\vec{R}_0+\vec{R}$ actually lies upon the surface.

At high temperatures in the d-dimensional Ising model with free-edge boundary conditions, the decay of the correlation function for two spins *simul-*

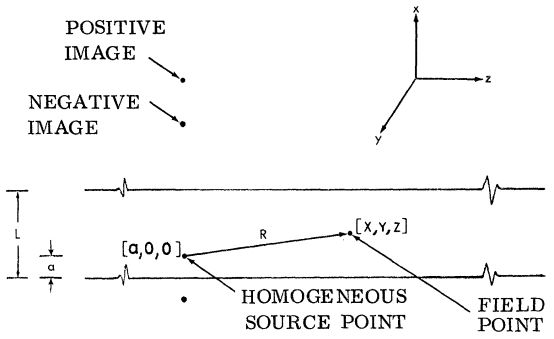

FIG. 2. Correlations in a thin-slab geometry.

taneously near n surfaces is given by (2.14), as we shall show in Paper IV. However, we show therein that the decay at *low* temperatures is too complicated to be correctly given by (2.14).

It is also interesting to consider the decay of correlation in a system which is *finite* in one or more dimensions, e.g., in a thin film. As an example, we consider the slab geometry portrayed in Fig. 2. As shown in the figure, we now need an infinite series of image sources to duplicate the boundary conditions. The image sources are to be located at the positions $(a \pm 2nL, 0, 0)$ and $(-a \pm 2mL, 0, 0)$ for $n = 1, 2, 3, \ldots$ and $m = 0, 1, 2, 3, \ldots$. With $\hat{x} \cdot \nabla G = 0$ on both bounding surfaces, all the image sources are positive; with $G = 0$ on both bounding surfaces, the image sources at $(a \pm 2nL, 0, 0)$ are positive, while those at $(-a \pm 2mL, 0, 0)$ are negative; finally, if $G = 0$ on the lower surface while $\hat{x} \cdot \nabla G = 0$ on the upper surface, the image sources above the slab are all positive, while those below it are negative.

The correlation function $G(\vec{R})$ is written in terms of the correlation function $G_0(\vec{R})$ for homogeneous boundary conditions by again using the superposition principle. For example, with $G = 0$ on both surfaces, we have

$$G(\vec{R}) = G_0(\vec{R}) - G_0(\vec{R} - 2a\hat{x}) + \sum_{n=1}^{\infty} \{[G_0(\vec{R} + 2nL\hat{x}) - G_0(\vec{R} + 2(nL - a)\hat{x})] + [G_0(\vec{R} - 2nL\hat{x}) - G_0(\vec{R} - 2(nL + a)\hat{x})]\} . \tag{2.16}$$

Using (2.16) we can show that if $|\vec{R}| \gg a, L$, then

$$G(\vec{R}) \sim (\kappa/R) G_0(\vec{R}) \quad \text{as } R \to \infty , \tag{2.17}$$

unless $\kappa = 0$ (i.e., $T = T_c$) when we have

$$G(\vec{R}) \sim (1/R^2) G_0(\vec{R}) . \tag{2.18}$$

The above results are in essential agreement with the results for the Ising model, as reported by Camp and Fisher,[1] and as derived in Paper IV of this series.[20]

In this section we have considered the asymptotic decay of pair-correlation functions within the context of the Ornstein-Zernike theory. The principal results are formulas (2.9), (2.14), and (2.15) for the decay of correlations in the bulk, near n absorbing boundaries, and near n reflecting boundaries, respectively. In Papers II, III, and IV we derive essentially exact results for the decay of pair correlations in the Ising model at very high and very low temperatures and compare them critically with these predictions.

III. TRANSFER MATRIX

A. Introduction

In this section we present a rather thorough discussion of the matrix method.[19] Although the transfer-matrix technique is almost always applied to systems with strictly short-range interactions on a regular space lattice, it may be used for any system which has short-range interactions in at least one direction—the layering direction. The layer thickness is chosen to be equal to or greater than this range. Then removing a layer from the system corresponds to breaking it into two noninteracting subsystems. This enables us to think of building up the system one layer at a time. We do so by repeated operation with the so-called layer or transfer matrix which, given an L-layer system, generates an $(L+1)$-layer system. The interactions within a layer and between adjacent layers may vary from layer to layer; but the analytical theory is very much simplified when they do not so vary.

Although the transfer-matrix method can be applied to purely statistical problems for which the physical concept of energy is meaningless, we shall assume that there is always a function analogous to the Hamiltonian and that the desired generating function (partition function) Z is given by

$$Z[\mathcal{H}] = \mathrm{Tr}(e^{-\beta\mathcal{H}}) , \quad \beta = (k_B T)^{-1} . \tag{3.1}$$

We further assume that the Hamiltonian has the form

$$\mathcal{H} \equiv \sum_{n=1}^{L} h_n(n, n+1) . \tag{3.2}$$

[Note that the interlayer Hamiltonian $h_n(n, n+1)$ may generally depend explicitly upon n.] Additionally, we take a purely "classical" point of view. That is, we shall assume that the states of $\mathcal{H}_L$ are specified simply by specifying the configurations of all of the layers of the system, which we shall henceforth assume to be built up in the $\hat{z}$ direction. As an example, consider a simple-cubic lattice of interacting spins. Each layer might then be one or several (0, 0, 1) planes depending upon the range

of interplane forces. Note that we have *not* limited the range of interaction in any direction other than the layering direction $\hat{z}$. Formally we could accommodate long-range intralayer forces in $h_n(n, n+1)$. However, with the inclusion of such forces, the detailed calculational problems soon become prohibitive.

For clarity we present the formalism in a concrete, matrix form and later generalize to more abstract notation. This latter notation makes it clear that systems with a continuity of configurations may be treated, if we replace the transfer matrix by a suitable integral operator.

Assume that our layers are specified by a set of configurations $\{\alpha\}$, and that for the nth layer in configuration α_n, the energy function $h_n(n, n+1)$ is given by $\mathcal{E}(\alpha_n, \alpha_{n+1})$. [We have dropped explicit dependence of $h_n(n, n+1)$ upon the layer index n.] We specify the boundary conditions in the layering direction either by assigning *a priori* weights $\{W_1(\alpha)\}$ and $\{W_{L+1}(\alpha)\}$ to the configurations of the first and last layers, respectively—representing "end walls"—or by taking the first and $(L+1)$th layers to be the same layer—representing cyclic or periodic boundary conditions. The partition function may be written

$$Z_{L,W} = \sum_{\alpha_1} \cdots \sum_{\alpha_{L+1}} W_1(\alpha_1) W_{L+1}(\alpha_{L+1}) \prod_{n=1}^{L} e^{-\beta \mathcal{E}(\alpha_n, \alpha_{n+1})} , \tag{3.3}$$

with end walls, or

$$Z_{L,C} = \sum_{\alpha_1} \cdots \sum_{\alpha_L} \prod_{n=1}^{L} e^{-\beta \mathcal{E}(\alpha_n, \alpha_{n+1})} \quad (1 \equiv L+1) , \tag{3.4}$$

with periodic boundary conditions. These forms for the partition function make clear why the method is essentially restricted to classical systems, since for a quantal system

$$Z_L^Q = \mathrm{Tr}\{\exp[-\beta \sum_{n=1}^{L} h(n, n+1)]\} \neq \mathrm{Tr}\{\prod_{n=1}^{L} \exp[-\beta h(n, n+1)]\} , \tag{3.5}$$

because $e^{\underline{A}+\underline{B}}$ does not equal $e^{\underline{A}} e^{\underline{B}}$ except in the special case that $\underline{A}$ and $\underline{B}$ commute. However, provided that the interlayer and intralayer Hamiltonians commute, we may still have quantum mechanics *within* each layer.

We introduce column vectors $\vec{W}_1$ and $\vec{W}_{L+1}$ whose components are the $\bar{N}$ weights $\{W_1(\alpha)\}$ and $\{W_{L+1}(\alpha)\}$, respectively ($\bar{N}$ being the total number of configurations of a layer). Then the transfer matrix $\underline{K}$ is defined by its (α, α') matrix elements:

$$(\underline{K})_{\alpha,\alpha'} = e^{-\beta \mathcal{E}(\alpha, \alpha')} \quad (\bar{N} \times \bar{N}) . \tag{3.6}$$

Consider the inner product of $\vec{W}_{L+1}$ with $\underline{K}^L \cdot \vec{W}_1$:

$$\vec{W}_{L+1}^{\dagger} \cdot (\underline{K}^L \cdot \vec{W}_1) = \sum_{\alpha_{L+1}} W_{L+1}(\alpha_{L+1}) \sum_{\alpha_L} \cdots \sum_{\alpha_1} W_1(\alpha_1) \prod_{l=1}^{L} e^{-\beta \mathcal{E}(\alpha_l, \alpha_{l+1})} , \tag{3.7}$$

where $\dagger$ indicates the Hermitian conjugate or transpose of a vector or matrix. This inner product is seen to be identical with (3.3) for the partition function in the case of end walls. Hence

$$Z_{L,W} = \vec{W}_{L+1}^{\dagger} \cdot \underline{K}^L \cdot \vec{W}_1 . \tag{3.8}$$

Further, consider the trace of $\underline{K}^L$:

$$\mathrm{Tr}\underline{K}^L = \sum_{\alpha_1 = \alpha_{L+1}} \cdots \sum_{\alpha_L} \prod_{l=1}^{L} e^{-\beta \mathcal{E}(\alpha_l, \alpha_{l+1})} . \tag{3.9}$$

Again, we see that this is the same as (3.4) for the cyclic partition function. Therefore,

$$Z_{L,C} = \mathrm{Tr}\underline{K}^L . \tag{3.10}$$

Since the partition function determines the complete thermodynamic behavior of a system, Eqs. (3.8) and (3.10) are sufficient basis for a thermodynamic study of classical systems with strictly short-ranged interactions. Further, we may use them to clearly demonstrate how one builds up a system layer by layer through repeated operations with $\underline{K}$. Let us define $\vec{Z}_L$ by

$$\vec{Z}_L = \underline{K}^L \cdot \vec{W}_1 ; \tag{3.11}$$

then the components of $\vec{Z}_L$ are the partition functions $Z_L(\alpha)$ for a system with the $(L+1)$th layer restricted to its αth configuration. Definition (3.11) implies the following fundamental recursion:

$$\vec{Z}_{L+1} = \underline{K} \cdot \vec{Z}_L . \tag{3.12}$$

With $Z_{L,W}$ given by $\vec{W}_{L+1}^{\dagger} \cdot \vec{Z}_L$, (3.12) explicitly specifies how to perform this layer-by-layer construction.

We are now in a position to derive transfer-matrix formulas for the expectation values of observable quantities. A simple, correct definition of the average of an observable $\underline{A}(n)$ in the nth layer is the following. The average of $\underline{A}(l)$ is given by its value, $A(l, \alpha)$ in the αth configuration, times the probability $p(l, \alpha)$ that the lth layer is in its αth configuration, summed over all configurations α:

$$\langle \underline{A}(l) \rangle = \sum_{\alpha=1}^{\bar{N}} A(l, \alpha) p(l, \alpha) . \tag{3.13}$$

The probability $p(l, \alpha)$ is just the ratio of the partition function for a system in which the lth layer is constrained to be in its αth configuration, to the full partition function. For the case of end walls, we have

$A(l, \alpha) p(l, \alpha)$

$$= \frac{A(l,\alpha)}{Z_{L,W}} \sum_{\alpha_1} \cdots \sum_{\alpha_{l-1}} \sum_{\alpha_{l+1}} \cdots \sum_{\alpha_{L+1}} W_1(\alpha_1) W_{L+1}(\alpha_{L+1}) \times \prod_{t=1}^{L} e^{-\beta \mathcal{E}(\alpha_t, \alpha_{t+1})} . \quad (3.14)$$

Let us introduce a projection matrix which filters out all but the αth configuration. We label this matrix $\underline{P}(\alpha)$. Since a layer is specified by the totality of its configurations, these projection matrices satisfy a completeness relation:

$$\sum_\alpha \underline{P}(\alpha) = \underline{I} , \quad (3.15)$$

where $\underline{I}$ is the $\bar{N} \times \bar{N}$ identity matrix. Also, since $\underline{A}(l)$ is an observable for our systems,

$$\underline{A}(l)\underline{P}(\alpha) = \underline{P}(\alpha)\underline{A}(l) = A(l,\alpha)\underline{P}(\alpha) . \quad (3.16)$$

Using (3.14) and (3.16), we can write $A(l,\alpha)p(l,\alpha)$ as

$$A(l,\alpha)p(l,\alpha) = Z_{L,W}^{-1} \{ W_{L+1}^{\dagger} \cdot \underline{K}^{L-l} \cdot \underline{P}(\alpha) \cdot \underline{A}(l) \cdot \underline{K}^{l} \cdot \vec{W}_1 \} . \quad (3.17)$$

Then using (3.13), (3.15), and (3.17) we may write the average of $\underline{A}(l)$ as

$$\langle \underline{A}(l) \rangle_W = Z_{L,W}^{-1} \{ \vec{W}_{L+1}^{\dagger} \cdot \underline{K}^{L-l} \cdot \underline{A}(l) \cdot \underline{K}^{l} \cdot \vec{W}_1 \} . \quad (3.18)$$

By an entirely analogous derivation, the joint expectation of the observable $\underline{A}(l)$ in layer l and the observable $\underline{B}(l+R)$ in layer $l+R$ is found to be

$$\langle \underline{A}(l)\underline{B}(l+R) \rangle_W = Z_{L,W}^{-1} \{ \vec{W}_{L+1}^{\dagger} \cdot \underline{K}^{L-R-l} \cdot \underline{B}(l+R) \cdot \underline{K}^{R} \cdot \underline{A}(l) \cdot \underline{K}^{l} \cdot \vec{W}_1 \} . \quad (3.19)$$

However, these arguments have been independent of the boundary conditions, so we may immediately write the related formulas in the cyclic case as

$$\langle \underline{A}(l) \rangle_C = Z_{L,C}^{-1} \operatorname{Tr}[\underline{A}(l)\underline{K}^{L}] , \quad (3.20)$$

$$\langle A(l)B(l+R) \rangle_C = Z_{L,C}^{-1} \operatorname{Tr}[\underline{K}^{L-R} \underline{B}(l+R)\underline{K}^{R}\underline{A}(l)] . \quad (3.21)$$

Before proceeding further, it is convenient to introduce a more abstract notation. From the theory of linear vector spaces, we know that $\underline{K}$ forms a representation of an abstract operator, also denoted $\underline{K}$, and further that $\vec{W}_1$ and $\vec{W}_{L+1}$ are the components of abstract vectors $|W_1\rangle$ and $|W_{L+1}\rangle$ in this representation. Having recalled these facts, we see that our fundamental equations may be rewritten

$$Z_{L,W} = \langle W(L+1) | \underline{K}^{L} | W(1) \rangle , \quad (3.22a)$$

$$Z_{L,C} = \operatorname{Tr}\{\underline{K}^{L}\} , \quad (3.22b)$$

$$|Z(L)\rangle = \underline{K} |Z(L-1)\rangle , \quad (3.22c)$$

$$\underline{P}(\alpha) = |\alpha\rangle\langle\alpha| , \quad \sum_\alpha |\alpha\rangle\langle\alpha| = \underline{I} , \quad (3.22d)$$

$$\langle \underline{A}(l)\underline{B}(R+l) \rangle_W = \langle W(L+1) | \underline{K}^{L-R-l} \times \underline{B}(R+l)\underline{K}^{R}\underline{A}(l)\underline{K}^{l} | W_1 \rangle Z_{L,W}^{-1} , \quad (3.22e)$$

$$\langle \underline{A}(l)\underline{B}(l+R) \rangle_C = Z_{L,C}^{-1} \operatorname{Tr}[\underline{K}^{L-R}\underline{B}(R+l)\underline{K}^{R}\underline{A}(l)] . \quad (3.22f)$$

In order to treat the case with explicitly layer-dependent interlayer and intralayer interactions, all we need realize is that the transfer matrix $\underline{K}$ then retains an explicit dependence upon which layer it is adding to the system. Because matrices are noncommutative, we must replace iterates of $\underline{K}$ by ordered products $\underline{K}_1\underline{K}_2 \cdots \underline{K}_m\underline{K}_{m+1} \cdots$. For example, the cyclic partition function becomes

$$Z_{L,C} = \operatorname{Tr}(\underline{K}_L \underline{K}_{L-1} \cdots \underline{K}_2\underline{K}_1) . \quad (3.23)$$

This additional complication may make trivial problems difficult, and difficult problems insoluble—the reason being that noncommuting operators cannot be simultaneously diagonalized.

Our abstract notation is sufficiently general to treat such problems as the $S=\infty$ or classical Heisenberg model and the classical gas in the grand-canonical ensemble for which there are continuous infinities of configurations available to a layer. Here instead of matrix representations, the representations of $\underline{K}$ will be the kernels of suitable integral operators.[19]

Having completed our introduction to the transfer-matrix formalism, we go on in the next subsection to discuss general properties of the eigenvalue spectrum when the layer is finite in size. For a lattice system, the size of a layer is defined as follows: Let $N_1, N_2, \ldots, N_{d-1}$ be the number of sites to each of the $d-1$ intralayer directions; then the layer size N is given by $N_0 N_1 \cdots N_{d-1}$, where N_0 is the number of lattice planes in a layer thickness. For a continuum system we may use the same definition for N, where now, for example, N_j is the (dimensionless) extension of the layer in the jth direction, measured, say, in hard-core diameters. At finite N, we show that the limit as the number of layers L tends to infinity is well behaved and considerably simpler than the problem with L finite. The asymptotic decay of correlation is expressed in terms of the spectrum of the transfer matrix $\underline{K}$.

B. Eigenvalue Spectrum, Infinite Limit, and Asymptotic Decay of Correlation Functions

Generally even for a lattice system with discrete degrees of freedom, the transfer matrix will be real but not symmetric. Hence, we cannot always expect its eigenvectors to form a maximally

linearly independent set, i.e., the spectrum of $\underline{K}$ will not, in general, be complete. However, $\underline{K}$ must have a Jordan normal form[21]; and as noted previously,[19] this is just as good for our purposes as the completeness property.

Our matrices $\underline{K}$ all have non-negative elements, and our integral operators are positive semidefinite since the energy function is real. However, for infinitely repulsive interactions, some elements may be zero. On the other hand, we can expect generally that there will be an iterate $\underline{K}^n$, for sufficiently large n, which will have positive-definite elements. This simply corresponds to the fact that sufficiently separated layers should be compatible in the sense that the joint probabilities $\{P(l, \alpha; l+R, \beta)\}$ should be nonzero for arbitrary α and β for large enough R. Indeed under very general conditions, $\underline{K}^2$ will be positive (no zero elements)—physically any state of layer n is compatible with *any* state of layer $n+2$ via some state in the $(n+1)$th layer. (This follows from our assumption that only neighboring layers interact with each other.) Given this physically reasonable assumption, we may employ the Perron-Fröbenius theorem.[22] This important theorem states that if $\underline{K}$ is positive semidefinite and has a positive iterate with positive-definite elements, then $\underline{K}$ has a unique, simple, and positive largest eigenvalue λ_0. Further, the eigenvector of this largest eigenvalue will have non-negative entries. So, not only is λ_0 nondegenerate, but also there are no eigenvalues λ_t with modulus $|\lambda_t|$ equal to λ_0.

We now express $\underline{K}$ in its Jordan normal form.[23] Let $\underline{K}' = \underline{T}^{-1}\underline{K}\,\underline{T}$ be the Jordan form of $\underline{K}$. Then $\underline{K}'$ is a block diagonal matrix, the dimensions of its blocks being the degeneracies of its eigenvalues. Assume that there are n eigenvalues, $\lambda_0 > \lambda_1 > \lambda_2 > \lambda_3 \cdots > \lambda_{n-1}$, with associated degeneracies $J_0 = 1$, $J_1, J_2, \ldots, J_{n-2}, J_{n-1}$. Since the sum of the multiplicities must equal the dimension of the transfer matrix, we have

$$\sum_{p=0}^{n-1} J_p = \bar{N} . \tag{3.24}$$

We write $\underline{K}'$ as

$$\underline{K}' = \begin{bmatrix} \lambda_0 & & & & \\ & \underline{L}_{J_1}(\lambda_1) & & & \\ & & \underline{L}_{J_2}(\lambda_2) & & \\ & & & & \\ & & & & \underline{L}_{J_{n-1}}(\lambda_{n-1}) \end{bmatrix}_{\bar{N}\times\bar{N}} , \tag{3.25}$$

with

$$L_J(\lambda) = \begin{bmatrix} \lambda & 1 & & & & & \\ & \lambda & 1 & & & & \\ & & \lambda & 1 & & & \\ & & & \ddots & \ddots & & \\ & & & & \ddots & \ddots & \\ & & & & & \lambda & 1 \\ & & & & & & \lambda \end{bmatrix}_{J\times J}$$

Since $(\underline{K}')^m = \underline{T}^{-1}\underline{K}^m\underline{T}$, it suffices to examine $(\underline{K}')^m$ in order to investigate the spectrum of $\underline{K}^m$. It follows from (3.25) that $(\underline{K}')^m$ is block diagonal with the n blocks $[\underline{L}_{J_t}(\lambda_t)]^m$, $t = 0, 1, \ldots, n-1$.

Let us now consider the structure of $[\underline{L}_J(\lambda)]^m$:

$$[\underline{L}_J(\lambda)]^m = [\lambda\underline{I} + \underline{J}_J^-]^m , \tag{3.26}$$

where $\underline{I}$ is the $J\times J$ identity matrix, and $\underline{J}_J^-$ is a representation of a so-called lowering operator in a space of dimension J. It is named in analogy with the operator $\underline{J}^-$ familiar from the theory of angular momentum in quantum mechanics.[24] Consider the J states $\{|h\rangle\}$ defined through their column vector representation:

$$\varphi(h) = \begin{bmatrix} 0 \\ \vdots \\ 1 \\ \vdots \\ 0 \\ \vdots \\ 0 \end{bmatrix} , \quad h = 1, 2, \ldots, J , \tag{3.27}$$

the 1 being in the hth place. Then clearly we have

$$\begin{aligned} \underline{J}_J^-|h\rangle &= \begin{cases} |h-1\rangle , & h = 2, 3, \ldots, J \\ 0 , & h = 1 \end{cases} \\ \langle h|\underline{J}_J^- &= \begin{cases} \langle h+1| , & h = 1, 2, \ldots, J-1 \\ 0 , & h = J . \end{cases} \end{aligned} \tag{3.28}$$

Equation (3.28) implies the following representation for $\underline{J}_J^-$:

$$\underline{J}_J^- = \sum_{h=1}^{J-1} |h\rangle\langle h+1| . \tag{3.29}$$

Hence,

$$[\underline{J}_J^-]^m = \begin{cases} \sum_{l=1}^{J-m} |l\rangle\langle l+m| , & m < J \\ 0 , & m \geq J . \end{cases} \tag{3.30}$$

We use (3.30) together with a binomial expansion of (3.26) to see that

$$[\underline{L}_J(\lambda)]^m = \sum_{p=0}^{\{m, J\}} \binom{m}{p} \sum_{l=1}^{J-p} |l\rangle\lambda^{m-p}\langle l+p| , \tag{3.31}$$

where $\{m, J\}$ is the minimum of m and $J-1$. We can write each $\{\underline{L}_{J_t}(\lambda)\}^m$ in the form (3.31). Since the associated vectors are orthonormal—$\langle \lambda_t, l | \lambda_s, r \rangle = \delta_{st}\delta_{lr}$—we may simply write $(\underline{K}')^m$ as the sum of these orthonormal operators. That is, we consider each $[\underline{L}_{J_t}(\lambda_t)]^m$ to be an operator in the full $\bar{N}$-dimensional space, all of whose entries except for the tth block are zero. Then, we have

$$(\underline{K}')^m = \sum_{t=0}^{n-1} \sum_{p=0}^{\{m, J_t\}} \binom{m}{p} \sum_{l=1}^{J_t - p} |\lambda_t, l\rangle \lambda_t^{m-p} \langle \lambda_t, l+p| . \tag{3.32}$$

This result is of fundamental importance in the theory of the transfer matrix. Using it we may derive general results for the free energy, the asymptotic decay of correlations, correlations near surfaces, etc.

The associated vectors $\{|\lambda_t, l\rangle\}$ form a complete set since they are orthonormal and since there are exactly $\bar{N}$ of them. They are referred to as generalized eigenvectors of $\underline{K}'$ of rank l and eigenvalue λ_t. This is because they have the following properties:

$$(\underline{K}' - \lambda_t \underline{I})^m |\lambda_t, l\rangle = 0 , \quad m \geq l \tag{3.33a}$$

$$(\underline{K}' - \lambda_t \underline{I})^m |\lambda_t, l\rangle \neq 0 , \quad m \leq l . \tag{3.33b}$$

This is easily seen because, in the tth block, subtracting $\lambda_t \underline{I}$ from $\underline{K}'$ leaves only $\underline{J}_{J_t}^-$, and $(\underline{J}_{J_t}^-)^m$ has the property that all the entries of its first m columns are zero!

In order to study the thermodynamic limit ($L \to \infty$) and the asymptotic decay of correlations, we substitute the Jordan form for $\underline{K}^m$ into the formulas of Sec. III A. The transformed states $|W_1'\rangle$ and $|W_{L+1}'\rangle$ are defined by

$$|W_1'\rangle = \underline{T}^{-1} |W_1\rangle , \quad \langle W_{L+1}'| = \langle W_{L+1}| \underline{T} \tag{3.34a}$$

and the transformed observable $\underline{A}'(l)$ by

$$\underline{A}'(l) = \underline{T}^{-1} \underline{A}(l) \underline{T} . \tag{3.34b}$$

With these definitions at hand we see that all the results of Sec. III A hold also if all the unprimed variables are replaced by primed variables. Again, this is obvious from linear-vector-space theory—expectation values are invariant under similarity transformations.

For simplicity we shall first consider the case with cyclic boundaries and then consider the differences induced by end walls. In what follows, the layer size N is kept finite; thus our matrices are finite, and the Perron-Fröbenius theorem applies. We use (3.10) and (3.32) to write the cyclic partition function in the $\{|\lambda_t, l\rangle\}$ basis as

$$Z_{L,C} = \sum_{t=0}^{n-1} \sum_{q=1}^{J_t} \langle \lambda_t, q | \left[\sum_{s=0}^{n-1} \sum_{p=0}^{\{L, J_s\}} \binom{L}{p} \sum_{l=1}^{J_s - p} |\lambda_s, l\rangle \lambda_s^{L-p} \langle \lambda_s, l+p| \right] |\lambda_t, q\rangle , \tag{3.35}$$

or more simply,

$$Z_{L,C} = \lambda_0^L \left[1 + \sum_{t=1}^{n-1} J_t (\lambda_t/\lambda_0)^L\right] \qquad (J_0 = 1) . \tag{3.36}$$

We can determine all bulk thermodynamic properties from the (general) free energy per layer given by

$$-\beta F_c \equiv \lim_{L \to \infty} (1/L) \ln(Z_{L,C}) . \tag{3.37}$$

Using (3.36), the free energy is written

$$-\beta F_c = \ln\lambda_0 + \lim_{L \to \infty} (1/L) \ln\left[1 + \sum_{t=1}^{n-1} J_t (\lambda_t/\lambda_0)^L\right] . \tag{3.38}$$

The last term on the right-hand side of (3.38) is seen to be majorized by

$$(1/L)\ln[1 + \bar{N}(\lambda_1/\lambda_0)^L] \approx (\bar{N}/L)(\lambda_1/\lambda_0)^L \to 0 \quad \text{as } L \to \infty . \tag{3.39}$$

Thus the cyclic free energy per layer is completely determined by the largest eigenvalue of $\underline{K}$:

$$-\beta F_c = \ln\lambda_0 . \tag{3.40}$$

It should be emphasized that F_c is the free energy per layer and as such is still proportional to N, the layer size. Ultimately in calculating bulk thermodynamics, one takes the further thermodynamic limit $N \to \infty$. Thus the free energy per site f is to be calculated

$$-\beta f_c \equiv \lim_{N \to \infty} \lim_{L \to \infty} \frac{1}{NL} \ln(Z_{L,C}) = \lim_{N \to \infty} \frac{1}{N} \ln(\lambda_0(N)) . \tag{3.41}$$

Evidently a finite free energy per site will imply that $\lambda_0(N) \approx \mu_0^N [1 + o(e^N)]$ as N tends to infinity. In the formal part of this work we do not consider this latter thermodynamic limit. However, in the application to the Ising model, f will be calculated via perturbation theory and found to be finite. (Under suitable conditions, it may be shown very generally that f exists and is finite.[25])

We now calculate the expectation value of an observable $\underline{A}(l)$ in the lth layer. We shall find that if $\underline{A}(l)$ has no explicit dependence upon layer index, the result is independent of the layer:

$$\langle \underline{A}(l) \rangle_c = Z_{L,C}^{-1} \sum_{r=0}^{n-1} \sum_{q=0}^{J_r} \langle \lambda_r, q | \left[\sum_{t=0}^{n-1} \sum_{p=0}^{\{L, J_t\}} \binom{L}{p} \right.$$

$$\times \sum_{l=1}^{J_t-p} |\lambda_t, l\rangle \lambda_t^{L-p} \langle \lambda_t, l+p| \Big] \underline{A}'(l) |\lambda_r, q\rangle \ . \tag{3.42}$$

Or, as L tends to infinity, we have

$$\langle \underline{A}(l) \rangle_c = \sum_{t=0}^{n-1} \sum_{p=0}^{J_t-1} \sum_{l=1}^{J_t-p} \frac{\langle \lambda_t, l+p | \underline{A}'(l) | \lambda_t, l \rangle}{\lambda_0^p} \times \binom{L}{p} \left(\frac{\lambda_t}{\lambda_0}\right)^{L-p} . \tag{3.43}$$

Now suppose that $\langle \lambda_0 | \underline{A}'(l) | \lambda_0 \rangle$ is nonzero, then

$$\langle \underline{A}(l) \rangle_c = \langle \lambda_0 | \underline{A}'(l) | \lambda_0 \rangle \ . \tag{3.44}$$

However, if the right-hand side of (3.44) is zero, so also is that of (3.42). [This is because the remaining terms in (3.42) are majorized by $O(\lceil \lambda_1/\lambda_0 \rceil^L)$ which tends to zero as L tends to infinity.] Thus (3.44) is correct for an infinite system. Then, as claimed above, if $\underline{A}'(l)$ does not depend upon l, neither does its expectation.

The derivation of the joint expectation value of $\underline{A}(l)$ and $\underline{B}(l+R)$ is only slightly more complicated and yields in the limit as $L \to \infty$:

$$\langle \underline{A}(l) \underline{B}(l+R) \rangle_c = \langle \underline{A}(l) \rangle_c \langle \underline{B}(l+R) \rangle_c + \langle \delta \underline{A}(l) \delta \underline{B}(l+R) \rangle_c \ , \tag{3.45}$$

where

$$\langle \delta \underline{A}(l) \delta \underline{B}(l+R) \rangle_c = \sum_{t=1}^{n-1} \sum_{p=0}^{\{R, J_t\}} \binom{R}{p} \sum_{l=1}^{J_t-p} \frac{\lambda_t^{R-p}}{\lambda_0^R} \times \langle \lambda_0 | \underline{B}' | \lambda_t, l \rangle \langle \lambda_t, l+p | \underline{A}' | \lambda_0 \rangle \ . \tag{3.46}$$

Using (3.46) we are able to calculate the decay of net pair-correlation functions as $R \to \infty$.

Suppose that (for N finite) the matrix element $\langle \lambda_0 | \underline{B}' | \lambda_1, l \rangle \langle \lambda_1, l+p | \underline{A}' | \lambda_0 \rangle$ is nonzero for at least some l and p. Then as R tends to infinity the contributions from λ_1 in (3.46) are exponentially greater than those from any other eigenvalue and determine the ultimate decay of correlation. We define an inverse range of correlations κ through[5]

$$\kappa \equiv \lim_{R \to \infty} \left(-\frac{1}{R} \ln | \langle \delta \underline{A}(l) \delta \underline{B}(R+l) \rangle_c | \right) . \tag{3.47}$$

Then if κ is nonzero, we know that the net correlation function (3.46) decays as $e^{-\kappa R}$ as R tends to infinity. But note that definition (3.47) is sufficiently general that it includes, for example, functions which decay like $P(R; n)e^{-\kappa R}$, where $P(R; n)$ is a polynomial of degree n in both R and R^{-1}.

As R tends to infinity, (3.46) becomes

$$\langle \delta \underline{A}(l) \delta \underline{B}(l+R) \rangle_c \approx \left(\frac{\lambda_1}{\lambda_0}\right)^R \sum_{p=0}^{J_1-1} \binom{R}{p} \times \sum_{l=1}^{J_1-p} \frac{\langle \lambda_0 | \underline{B}' | \lambda_1, l \rangle \langle \lambda_1, l+p | \underline{A}' | \lambda_0 \rangle}{\lambda_1^p} \ . \tag{3.48}$$

Then κ defined by (3.47) is

$$\kappa = \ln(\lambda_0 / |\lambda_1|) \ . \tag{3.49}$$

This may be taken as a proof on the basis of the Perron-Fröbenius theorem that in systems with finite-size layers and with discrete degrees of freedom, net pair correlations will always decay exponentially with decay specified by the largest and next-largest level. Now the formulas we have derived above are true for $1 \ll R \ll L$ even if L is finite. Thus, the layer size N, given by $N_0 N_1 N_2 \cdots N_{d-1}$ will still be finite if we take N_j to be L for every $j \geq 1$. Then our formulas will be true for the decay of correlations in the layering direction of a large but finite hypercube. If the system has strictly short-range forces, the layering direction is arbitrary. Hence, for such a system the correlation function will decay exponentially in *all* directions.

At this point one may ask to what extent we can apply these results to a system with continuous degrees of freedom (so that the transfer "matrix" is now an operator in an infinite-dimensional space). For example, one could ask whether the Perron-Fröbenius theorem extends to such systems. In its full generality this question goes beyond the level of this work and will not be considered herein. However, as noted previously[19] for a positive completely continuous operator one can use the Jentzch and Hopf theorems[26] which then replace the Perron-Fröbenius theorems.

For the systems with continuous degrees of freedom which we consider (e.g., the classical Heisenberg model or a classical fluid), the "transfer operators" will be completely continuous since they can be derived from limiting sequences of bounded finite-dimensional operators. Further, as in the discrete case, they will be nonnegative but not necessarily positive definite. However, as pointed out above, $\underline{K}^2$ will be positive under very general circumstances and thus will have a positive unique eigenvalue of largest modulus. This suffices to prove that a net pair correlation function defined on such a system decays exponentially under the conditions noted above in the discrete case.

It is often most convenient to employ periodic boundary conditions. However, in order to justify their use, we must convince ourselves that these simplified boundary conditions do justice to the bulk thermodynamics of a system with end walls. One expects this to be the case because the number of "end-wall" interactions is proportional to N, whereas there are $O(NL)$ bulk interactions. Then as L tends to infinity these surface terms should have a negligible effect upon such bulk properties as the free energy or the decay of correlation functions far from either end. On the other hand, we know that periodic boundary conditions are inad-

equate to treat such interesting effects as surface tension, scattering from surface states, and the decay of correlations near a surface. In addition, when a system is ordered, order induced by a pinned surface might well propagate throughout the system, affecting both bulk expectation values and the decay of correlation functions within the bulk. Therefore, we shall treat the case of end-wall boundary conditions in order to justify the use of cyclic boundary conditions for bulk properties and to enable us to treat surface properties.

The weight vectors $|W_1'\rangle$ and $\langle W_{L+1}'|$ defined in (3.34a) may be expanded in the $\{|\lambda_t, q\rangle\}$ basis:

$$|W_1'\rangle = \sum_{t=0}^{n-1} \sum_{q=1}^{J_t} W_1(t, q)|\lambda_t, q\rangle ,$$
$$\langle W_{L+1}'| = \sum_{t=0}^{n-1} \sum_{q=1}^{J_t} W_{L+1}(t, q)\langle \lambda_t, q| . \tag{3.50}$$

Using (3.22a) (in the primed representation), (3.32), and (3.50), the end-wall partition function is seen to be

$$Z_{L,w} = \sum_{t=0}^{n-1} \sum_{p=0}^{\{L-1,J_t\}} \binom{L}{p} \sum_{l=1}^{J_t-p} W_1(t, l+p)\, W_{L+1}(t, l)\lambda_t^{L-p} . \tag{3.51}$$

When L tends to infinity, if the weights $W_1(0,1)$ and $W_{L+1}(0,1)$ are nonzero, the dominant contribution to the partition function is $W_1(0,1)W_{L+1}(0,1)\lambda_0^L$. Then the free energy per layer is given by

$$-\beta F_w = \ln\lambda_0 , \tag{3.52}$$

which is in exact agreement with the free energy calculated in the case of cyclic boundaries. Thus, except in the unusual case that the end walls are such that $W_1(0,1)W_{L+1}(0,1)$ is identically zero, we have shown that the bulk free energy is independent of the boundary conditions imposed upon the end surfaces.

The calculation of expectation values is somewhat more cumbersome. Consider the expectation of $\underline{A}(l)$:

$$\langle \underline{A}(l)\rangle_w = \sum_{t_1}^{n-1} \sum_{t_2=0}^{n-1} \sum_{p_1=0}^{\{l-1,J_{t_1}\}} \sum_{p_2=0}^{\{L-l-1,J_{t_2}\}} \binom{l}{p_1}\binom{L-l}{p_2} \sum_{s_1=1}^{J_{t_1}-p_1} \sum_{s_2=1}^{J_{t_2}-p_2} \frac{W_1(t_1, p_1+s_1)W_{L+1}(t_2, s_2)}{Z_{L,w}}$$
$$\times (\lambda_{t_1})^{l-p_1}(\lambda_{t_2})^{L-l-p_2}\langle \lambda_{t_2}, p_2+s_2|\underline{A}'|\lambda_{t_1}, s_1\rangle . \tag{3.53}$$

We take the "thermodynamic limit," L tending to infinity, with l fixed. Then

$$\langle \underline{A}(l)\rangle_w = \sum_{t=0}^{n-1} \sum_{p=0}^{\{l-1,J_t\}} \binom{l}{p} \sum_{s=1}^{J_t-p} \frac{W_1(t, p+s)}{W_1(0,1)} \times \frac{\lambda_t^{l-p}}{\lambda_0^l}\langle \lambda_0|\underline{A}'|\lambda_t, s\rangle . \tag{3.54}$$

For sufficiently large l, we see that all the terms in (3.54) except $\langle\lambda_0|\underline{A}'|\lambda_0\rangle$ are majorized by $O(|\lambda_1/\lambda_0|^l)$. Hence, for large l, we have

$$\langle \underline{A}(l)\rangle_w = \langle\lambda_0|\underline{A}'|\lambda_0\rangle + O(\{\lambda_1/\lambda_0\}^l) . \tag{3.55}$$

Generally, we measure a bulk density $\bar{A}$ defined by

$$\bar{A} \equiv \lim_{L\to\infty} \frac{1}{L} \sum_{l=1}^{L+1} \langle \underline{A}(l)\rangle_w . \tag{3.56}$$

There will exist a positive number p such that for l greater than p, $\langle \underline{A}(l)\rangle_w$ is given by (3.55). For the p terms in (3.56) with l less than or equal to p, it suffices to replace the summand by $O(1)$. Then $\bar{A}$ may be written

$$\bar{A} = \lim_{L\to\infty} (1/L) \sum_{l=p+1}^{L} [\langle\lambda_0|\underline{A}'|\lambda_0\rangle + O(|\lambda_1/\lambda_0|^l)] + O(p/L) . \tag{3.57}$$

As L tends to infinity we may allow p to become infinite, as long as p/L tends to zero. Then (3.57) becomes, very simply,

$$\bar{A} = \langle\lambda_0|\underline{A}'|\lambda_0\rangle . \tag{3.58}$$

Formulas (3.55) and (3.58) reproduce (3.44) for the cyclic expectation value of $\underline{A}(l)$.

Thus, bulk expectation values are unaffected by the end-wall boundary conditions. Similar considerations to those above show that the joint expectation of $\underline{A}(l)$ and $\underline{B}(l+R)$ becomes independent of boundary conditions when L, l, and $L-l-R$ tend to infinity. That is, for fixed R,

$$\langle \underline{A}(l)\underline{B}(l+R)\rangle_w = \langle \underline{A}(l)\underline{B}(l+R)\rangle_c , \quad L\to\infty , \quad l\to\infty , \quad L-R-l\to\infty . \tag{3.59}$$

In particular, the decay of pair correlation functions remains exponential with the same inverse range of correlation κ defined above.

It should be noted that were λ_0 allowed to be degenerate, expectation values need *not* become independent of boundary conditions even within the bulk of the system. The result is explicitly dependent upon the weights $\{W_1(0, q);\ W_{L+1}(0, q')\}$ assigned to the degenerate largest eigenvectors in the first and last layers. However, the free en-

ergy F would still be given by (3.52), as is seen by (3.36) and (3.51) with J_0 not equal to one.

To simplify our considerations, we shall now assume that $\underline{K}$ has a complete spectrum $\{|\lambda_t, q)\}$ and that the vectors $|W(1)\rangle$ and $|W(L+1)\rangle$ can be written in this representation as

$$|W(1)\rangle = \sum_{t=0}^{n-1} \sum_{q=1}^{J_t} W_1(t,q)|\lambda_t, q) ,$$
$$\langle W(L+1)| = \sum_{t=0}^{n-1} \sum_{q=0}^{J_t} W_{L+1}(t,q)(\lambda_t, q| . \tag{3.60}$$

With the completeness property, $\underline{K}^m$ may be expressed as

$$\underline{K}^m = \sum_{t=0}^{n-1} \sum_{q=0}^{J_t} |\lambda_t, q)\lambda_t^m(\lambda_t, q| . \tag{3.61}$$

Then (3.18) for the expectation of $\underline{A}(l)$ may be written

$$\langle \underline{A}(l) \rangle_w = \frac{\sum_{q=1}^{J_0} \sum_{p=0}^{J_0} W_1(0,q) W_{L+1}(0,p)(\lambda_0, p|\underline{A}'|\lambda_0, q)}{\sum_{q=1}^{J_0} W_1(0,q) W_{L+1}(0,q)} , \tag{3.62}$$

with $L \to \infty$, $l \to \infty$, and $L - l \to \infty$. Note that although this expectation value is independent of the layer l, it still depends upon the weights assigned to the end walls—this despite the fact that l corresponds to a layer within the bulk! With degenerate largest level, the analogous cyclic expectation becomes, as L tends to infinity,

$$\langle \underline{A}(l) \rangle_c = \frac{1}{J_0} \sum_{q=1}^{J_0} (\lambda_0, q|\underline{A}|\lambda_0, q) . \tag{3.63}$$

Even in cases where the cyclic expectation (3.63) is zero—such as the cyclic expectation of the magnetic moment of an Ising ferromagnet below its critical temperature—the end-wall expectation (3.62) need not be zero. Thus, for a system with a degenerate largest level, the expectation value of an observable quantity depends upon the boundary conditions imposed. Such a situation is indicative of the existence of *long-range order* in the system. For no matter how far we choose our layer from the walls, expectations of quantities defined within the layer will explicitly depend upon the configurations of the end walls. Such long-range order is found to arise below the ordering temperature of a system exhibiting a continuous phase transition. For such systems there exists an *order parameter*: a physical variable whose expectation value is strictly zero above the ordering temperature, but whose value ranges over a finite interval of values, depending upon boundary conditions, below the ordering temperature.[27] Examples of such order parameters are the spontaneous magnetization of a ferromagnet, the difference in density between the liquid and gaseous phases of a liquid-vapor system, and the superfluid density of He II. Thus we have confirmed the intimate link between the existence of such long-range order and the degeneracy of the largest eigenvalue of the transfer matrix.[6,13]

Now, of course, for finite cross section N, we know that the Perron-Fröbenius theorem requires that λ_0 be nondegenerate. But, as N tends to infinity, λ_0 and λ_1 may become asymptotically degenerate in the sense that[6,13,20]

$$\lambda_1/\lambda_0 \approx 1 + O(e^{-\beta N\sigma}), \quad N \to \infty. \tag{3.64}$$

Thus, in the full thermodynamic limit there may exist a range of temperature $(0, T_c)$ over which the system exhibits long-range order. Equation (3.64) is the basis for a very simple calculation due to Fisher[19] of the surface tension at the phase boundary between two coexisting phases. The basic notion is that we can determine the surface tension by a comparison of the partition function with the ends weighted for different phases, to the partition functions for a system in which the ends are weighted for the same phase. Weighting the end walls for the two phases presents no difficulty, since at low temperatures, by the Perron-Fröbenius theorem, the largest eigenvector is a symmetric combination of the two phases, whereas evidently the next largest eigenvector is the corresponding antisymmetric combination. The resulting formula for the surface tension is

$$-\beta\sigma(1,2) = \lim_{N\to\infty} N^{-1} \ln\{\ln[\lambda_0(N)/\lambda_1(N)]\} . \tag{3.65}$$

Concerning the nature of long-range order, one should note that although external fields may induce "order" in a system in the sense, for example, that the spin-correlation function $\langle S^z(0)S^z(R)$ does *not* decay to zero as R tends to infinity in a magnetic field, H; there is no true propagation of order *throughout* the system. In fact, for a ferromagnet, a finite field will break the degeneracy (or quasi-degeneracy) of λ_0 and λ_1, thereby destroying the ordered state. We have emphasized this point to make clear the difference between true long-range order, evidenced by $\lambda_0 \approx \lambda_1$ and externally induced "order" or alignment.

To conclude this section, we present a few general remarks of Fisher[19] about the asymptotic decay of correlations. Since the transfer matrix is positive semidefinite, its characteristic polynomial $K(\lambda)$ has all real coefficients. Thus, the eigenvalues must either be real or appear in complex-conjugate pairs (λ_t, λ_t^*). This being the case, we may list the possibilities for the second-largest eigenvalue λ_1: (i) λ_1 is real, positive, and no other eigenvalue has equal modulus; (i′) λ_1 is also simple (nondegenerate); (ii) λ_1 is negative, real, or (λ_1, λ_1^*) are a complex-conjugate pair; (iii) λ_1 is

positive, real, and there are other eigenvalues of equal modulus.

Let $G(\vec{R})$ be the net correlation function of interest. In case (i), $G(\vec{R})$ decays exponentially. Generally, λ_1 will be degenerate, and we will find

$$G_{(i)}(\vec{R}) \approx P_n(\vec{R})\, e^{-\kappa R} \quad \text{as } R \to \infty, \tag{3.66}$$

where $P_n(\vec{R})$ is a polynomial of degree n equal to one plus the degeneracy of λ_1. In case (i′), λ_1 is also simple (nondegenerate). Then n will be zero, and the decay will be a pure exponential:

$$G_{(i')}(\vec{R}) \approx A\, e^{-\kappa R} \quad \text{as } R \to \infty. \tag{3.67}$$

For real, negative λ_1, we find that

$$G_{(ii)}(\vec{R}) \approx A\, e^{-\kappa R}[(-1)^{R\nu} P_n(\vec{R})] \quad \text{as } R \to \infty, \tag{3.68}$$

where ν is a positive constant and $n = 1 + J_1$. That is, in case (ii), $G(\vec{R})$ ultimately oscillates in sign. In the complex case (ii), we have

$$\lambda_1 = |\lambda_1|\, e^{i\theta} \text{ and } \lambda_1^* = |\lambda_1|\, e^{-i\theta}.$$

Hence, we have

$$G_{(ii)}(\vec{R}) \approx P_n(R) \cos R\theta\, e^{-\kappa R} \text{ as } R \to \infty. \tag{3.69}$$

In case (iii), we have a general combination of the other two cases:

$$G_{(iii)}(\vec{R}) \approx [P_n(R) + Q_p(R)(-1)^{\nu R} + \textstyle\sum_i A_i \cos R\theta_i] e^{-\kappa R}. \tag{3.70}$$

Whether or not this last correlation eventually does not change sign depends upon the relative amplitudes of the monotone and oscillatory components. In any case, this correlation function will always contain an oscillatory component.

IV. SUMMARY

In this work we have reviewed the phenomenological prediction (1.4) for the decay of correlation in many-body systems, extended it to treat the decay of correlation near surfaces, and contrasted this prediction with the exactly known results for the two-dimensional zero-field Ising model. In order to reconcile the differences between the phenomenological and Ising results, we consider in the following papers of this series the decay of correlation in d-dimensional Ising models with arbitrary magnetic fields, away from the critical point.

Our study of the decay of correlation in Ising systems is based on a general transfer-matrix method,[19] which we have developed in sufficient detail herein to form a basis for the remaining papers of this series.

The general formulas of use are (3.22a)–(3.22f) for the partition function and for expectation values of physical quantities both for cyclic and for "end-wall" boundary conditions in the layering direction. Equation (3.22) is a general formula for a positive iterate of an arbitrary matrix. Equations (3.40) and (3.44) determine the bulk-free energy and the expectation of bulk quantities, respectively, while the inverse range of correlations defined in (3.47) is given by (3.49). The decay of correlations is given by (3.48). (Note, however, that this result is for finite cross section N. As N tends to infinity, the eigenvalues immediately below λ_1 may close up to form a band[1,5,6] with leading edge λ_1. Then the contributions from the eigenvalues at this band edge are not damped with respect to that from λ_1 as R tends to infinity. Therefore, in such circumstances we need integrate over the leading edge of this band.) From (3.62) we can calculate the expectation of, for example, the order parameter (e.g., spontaneous magnetization) of an ordered system, that is, a system for which the two largest eigenvalues of the transfer matrix are asymptotically degenerate. Equation (3.64) yields the surface tension at a phase boundary below the ordering temperature of an ordering system. Finally, formulas (3.66)–(3.70) depict the various kinds of asymptotic decay possible depending upon the reality, positivity, and simplicity—or lack thereof—of λ_1, the second-largest eigenvalue.

ACKNOWLEDGMENTS

Thanks are due M. N. Barber for his comments on a draft of this work and to N. S. Gillis for useful discussions and helpful criticism.

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*Work supported by the U. S. Atomic Energy Commission, the National Science Foundation, and the Advanced Research Projects Agency through the Materials Science Center at Cornell University.

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$$(1/\Omega)\int_\Omega dR \int_\Omega dR'\; G_\epsilon(\vec{R}-\vec{R}').$$

Additionally, κ for the slab must be nonzero at the bulk T_λ. However, this objection is not as serious as those above. In the light of these objections, agreement between his results and experiment seems fortuitous.

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