# Correlated-factors theorem for the free energy of anharmonic solids with an application to the $\phi^4$ model

Robert J. Hardy
*Behlen Laboratory of Physics, University of Nebraska, Lincoln, Nebraska 68588-0111*

Michael A. Day, Joseph T. Souders, Ignacio Birriel, and Tavio C. D'Angelis
*Department of Physics, Lebanon Valley College, Annville, Pennsylvania 17003-0501*
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The correlated-factors theorem states that the harmonic average of a product of factors is given exactly by the result of a differential operator $e^W$ acting on the product of the averages of the factors. The theorem is true both classically and quantum mechanically. It is proved and the form of the operator $W$ is found. The theorem suggests an approximation for calculating the free energy of anharmonic solids. As an example, the approximate free energy is used to calculate the specific heat, magnetization, susceptibility, and the dependence of the phase-transition temperature on the coupling constant for the $\phi^4$ model on a square lattice. By comparing with Monte Carlo results, this approximation is found to be significantly more accurate than the correlated Einstein model, self-consistent phonon theory, and mean-field theory.

## I. INTRODUCTION

The purpose of this paper is to present the correlated-factors theorem and to give an example of how it can be used to obtain approximations for determining the free energy of anharmonic solids. The correlated-factors theorem is an exact result for harmonic averages, which states that

$$\left\langle \prod_I f_I \right\rangle_0 = e^W \prod_I \langle f_I \rangle_0 , \tag{1}$$

where the operator $e^W$ accounts for the correlations between the different factors $f_I$, which are functions of the canonical coordinates. The detailed form of the differential operator $W$ is quite simple and is given at the end of Sec. II. The theorem is valid both classically and quantum mechanically.

Our main interest is in real crystalline solids. However, to simplify the presentation the theorem will be illustrated here by applying it to the $\phi^4$ model. This model, sometimes referred to as the $S4$ model,[1,2] is commonly used an an example in the study of ferromagnetic and ferroelectric phase transitions.[3,4] It is a continuous spin variation of the Ising model with the Hamiltonian

$$H=\sum_{i=1}^{N}[\phi(s_i)-Bs_i]-\sum_{1\le j<k\le N} Ja_{jk}s_j s_k , \tag{2}$$

where $s_i$ is the spin coordinate of the $i$th particle and $-\infty<s_i<\infty$. The double-well potential

$$\phi(s)=\varepsilon[(s/\sigma)^2-1]^2 \tag{3}$$

is used. It has a maximum of height $\varepsilon$ between minima at $\pm\sigma$. $B$ is proportional to the strength of the external field, $J$ is the nearest-neighbor coupling constant, and $a_{jk}$ equals 1 when particles $j$ and $k$ are nearest neighbors and equals zero otherwise. We consider a two-dimensional square lattice of $N$ particles with periodic boundary conditions. The $\phi^4$ model is essentially classical. Since $H$ has no kinetic energy term, its free energy is

$$F=-\frac{1}{\beta}\ln\left[\frac{1}{\sigma^N}\int d^N s\, e^{-\beta H}\right] , \tag{4}$$

where $(1/\sigma^N)$ is introduced to make the argument of the logarithm dimensionless, $(1/\beta)=k_B T$, and $k_B$ is Boltzmann's constant.

The pertinence of the correlated-factors theorem to free-energy calculations can be seen by considering the relationship

$$F=F_0-\frac{1}{\beta}\ln\langle e^{-\beta(H-H_0)}\rangle_0 , \tag{5}$$

which is exact for classical systems. Here, $F_0$ and the canonical average $\langle\cdots\rangle_0$ are formed with $H_0$. Let the Hamiltonian $H_0$ be harmonic. When both the true Hamiltonian $H$ and the harmonic Hamiltonian $H_0$ are given as sums of terms, the Boltzmann factor can be written as a product of factors:

$$e^{-\beta(H-H_0)}=\prod_I f_I . \tag{6}$$

By substituting this into Eq. (5) and using the correlated-factors theorem, one obtains

$$F=F_0-\frac{1}{\beta}\ln\left\langle\prod_I f_I\right\rangle_0=F_0-\frac{1}{\beta}\ln\left[e^W\prod_I\langle f_I\rangle_0\right] . \tag{7}$$

As an example of Eq. (6), consider the $\phi^4$ model. For it we use the harmonic Hamiltonian

$$H_0=\sum_i(\tfrac{1}{2}Ks_i^2-\Gamma s_i)-\sum_{j<k}J_0 a_{jk}s_j s_k , \tag{8}$$

where $K$ is a spring constant and $\Gamma$ is a constant force.

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$K$, $\Gamma$, and $J_0$ are adjustable parameters. With this and Eq. (2) for $H$, the exponential $e^{-\beta(H-H_0)}$ becomes

$$e^{-\beta(H-H_0)}=\prod_{I=1}^{N} f_I(s_i)\prod_{I=N+1}^{3N} f_I(s_j,s_k)\ , \tag{9}$$

where

$$f_I(s_j,s_k)=e^{-\beta(J_0-J)s_j s_k}\ , \tag{10}$$

$$f_I(s_i)=e^{-\beta\Delta\phi(s_i)}\ , \tag{11}$$

and

$$\Delta\phi(s_i)=[\phi(s_i)-Bs_i]-(\tfrac{1}{2}Ks_i^2-\Gamma s_i)\ . \tag{12}$$

It is convenient to set $I=i$ in the different one-particle factors $f_I(s_i)$. Also, since each particle in a square lattice has four nearest-neighbor bonds and each bond is shared by two particles, there are $2N$ different two-particle factors $f_I(s_j,s_k)$. The different $I$ values from $N+1$ to $3N$ must be set into one to one correspondence with the values of $j$ and $k$ that identify different nearest-neighbor pairs.

The usefulness of Eq. (7) for determining the free energy follows from the presence of the operator $e^W$, which facilitates the forming of series expansions and approximations. One simple example is the following expansion in powers of the artificially introduced ordering parameter $\lambda$:

$$\ln\left[e^{\lambda W}\prod_I\langle f_I\rangle_0\right]=\sum_I\ln\langle f_I\rangle_0+\lambda Z_1+\frac{\lambda^2}{2}Z_2+\cdots\ . \tag{13}$$

In many applications the adjustable parameters in the harmonic Hamiltonian can be chosen so that both the first- and second-order terms in this vanish, that is, so that the following *zeroing conditions* are satisfied:

$$Z_1=\left[W\prod_I\langle f_I\rangle_0\right]\Big/\left[\prod_I\langle f_I\rangle_0\right]=0\ , \tag{14}$$

$$Z_2=\left[W^2\prod_I\langle f_I\rangle_0\right]\Big/\left[\prod_I\langle f_I\rangle_0\right]-Z_1^2=0\ . \tag{15}$$

By using this expansion, satisfying the zeroing conditions, and neglecting terms of third order and higher, Eq. (7) gives the approximation

$$F=F_0-\frac{1}{\beta}\sum_I\ln\langle f_I\rangle_0\ , \tag{16}$$

which can be both accurate and easily evaluated.

This approximation can also be obtained by replacing the average of the product $\langle\prod_I f_I\rangle_0$ in Eq. (7) by the product of the averages, $\prod_I\langle f_I\rangle_0$. Since such a replacement neglects the correlations between the factors in the anharmonic part to the free energy, it will be called the *uncorrelated-factors approximation,* or UFA. The effects of correlations on the anharmonic part are partially accounted for by satisfying both zeroing conditions. Doing so causes the UFA to be accurate through second order in $\lambda$.

Two different approximations that are special cases of the UFA have been considered in the past. In the uncorrelated pairs approximation[5] (UPA) only the first zeroing condition, Eq. (14), was satisfied. The harmonic spring constants were determined in the traditional manner by setting them equal to the second derivatives of the potential energy. Jones and Hardy[6] obtained accurate predictions for the properties of solid argon from absolute zero to the melting temperature with this approximation and the Barker-Fisher-Watts potential, which includes three-body forces. In the correlated Einstein model[7] (CEM) both zeroing conditions were satisfied, but the harmonic Hamiltonian was of the Einstein type, which has no interparticle coupling terms. By including third-order terms in a series expansion similar to Eq. (13), the CEM gave results that were in excellent agreement with available Monte Carlo (MC) estimates for both the hard-sphere solid[8] and the classical Lennard-Jones solid.[9]

A general proof of the correlated-factors theorem is given in Sec. II. Then, in Sec. III the equations that determine the free energy for the $\phi^4$ model in the UFA are developed. Both zeroing conditions are satisfied and the harmonic Hamiltonian, Eq. (8), is used. In Sec. IV accurate predictions are obtained for the specific heat, magnetization, and susceptibility for a wide range of temperatures. The UFA is accurate at all temperatures except those very close to the critical point and gives good predictions for the dependence of the phase-transition temperature on the coupling constant $J$. It is not, however, the type of approximation that can be expected to describe critical behavior correctly.

The predictions of the UFA are compared with those of three other analytic approximations: the CEM, self-consistent phonon theory[10] (SCP), and mean-field theory[11] (MFT). The word "analytic" is used to distinguish these approximations from the statistical approximations produced by MC and molecular-dynamics methods. In their simpler forms, the statistical methods give estimates for the averages of phase functions for small finite classical systems, and their accuracy is limited only by the size of the statistical sample used. Consequently, they are very useful for testing the accuracy of analytic approximations. By comparing with MC estimates we find that the UFA and the CEM are significantly more accurate than SCP or MFT, and that the UFA is more accurate than the CEM. Also, preliminary results on the Lennard-Jones solid show that the UFA gives predictions that are in excellent agreement with the quantum effective-potential Monte Carlo estimates of Liu and co-workers.[12]

Although the emphasis here is on determining the free energy, the correlated-factors theorem can also be applied to the determination of phase averages. The CEM has already been used to obtain a representation for the radial distribution function $g(r)$ of a hard-sphere solid,[8] and this representation has been utilized in a density-functional treatment of melting.[13]

## II. CORRELATED-FACTORS THEOREM

To utilize the correlated-factors theorem to determine the free energy, the Boltzmann factor $e^{-\beta(H-H_0)}$ must be

expressed as a product of factors. In general each factor $f_I$ will be a function with several arguments $s_i$, each of which may be either a canonical coordinate or a linear function of the canonical coordinates. For example, in Eqs. (10) and (11) for the $\phi^4$ model each factor has one or two of the canonical coordinates $s_1,\ldots,s_N$ as arguments, and each $s_i$ occurs in several different factors. In general the harmonic Hamiltonian $H_0$ may contain both linear and quadratic functions of the coordinates, and there will be kinetic energy terms in both $H_0$ and $H$ that cancel in $H-H_0$.

For the three-dimensional solids considered in the UPA and CEM papers the true Hamiltonian had the form[5,7]

$$H=\sum_i \frac{|\mathbf{p}_i|^2}{2m}+\sum_{j<k}\phi(|\mathbf{R}_j-\mathbf{R}_k+\mathbf{s}_j-\mathbf{s}_k|)\ , \tag{17}$$

where $\mathbf{p}_i$ is the momentum of the $i$th particle and $\phi(r)$ is a pair potential. The canonical coordinates are the components of the displacements $\mathbf{s}_i$ of the particles from their lattice sites $\mathbf{R}_i$. In the UPA it was convenient to consider factors that were functions of the "pair displacements" $\mathbf{q}_p=\mathbf{s}_j-\mathbf{s}_k$, which are linear combinations of the canonical coordinates, so that each factor was a function with one vector argument:

$$f_p(\mathbf{q}_p)=\exp-\beta[\phi(|\mathbf{R}_p+\mathbf{q}_p|)-(\mathbf{q}_p\cdot\overleftrightarrow{\phi}_p\cdot\mathbf{q}_p/2-\boldsymbol{\Gamma}_p\cdot\mathbf{q}_p)] \tag{18}$$

Here, $\mathbf{R}_p=\mathbf{R}_j-\mathbf{R}_k$, and the parameters $\overleftrightarrow{\phi}_p$ and $\boldsymbol{\Gamma}_p$ were introduced in the harmonic Hamiltonian. In the CEM it was necessary to consider such factors as functions with two vector arguments: $f_{jk}(\mathbf{s}_j,\mathbf{s}_k)$.

In the rest of this section the $\phi^4$ model is used to illustrate the proof of the correlated-factors theorem. After developing some notation the proof begins by using Fourier transform theory and the cumulant expansion to express the harmonic average $\langle\prod_I f_I\rangle_0$ as a collection of exponentials of averages. Then, a simple relationship for the derivative of the exponential function allows several of the Fourier transform operations to be inverted and the terms that correlate the factors $f_I$ to be placed into a differential operator $e^W$. The resulting theorem and the explicit form for the operator $W$ are given by Eqs. (31) and (32).

A function $f_I(s_i)$ and its Fourier transform $\tilde{f}_I(k_{Ii})$ are related by

$$f_I(s_i)=\frac{1}{\sqrt{2\pi}}\int dk_{Ii}\,e^{ik_{Ii}s_i}\tilde{f}_I(k_{Ii}) \tag{19}$$

and

$$\tilde{f}_I(k_{Ii})=\frac{1}{\sqrt{2\pi}}\int ds_{Ii}\,e^{-ik_{Ii}s_{Ii}}f_I(s_{Ii})\ . \tag{20}$$

Combining these gives

$$f_I(s_i)=\frac{1}{2\pi}\int dk_{Ii}\,e^{ik_{Ii}s_i}\int ds_{Ii}\,e^{-ik_{Ii}s_{Ii}}f_I(s_{Ii})\ . \tag{21}$$

Capital letter subscripts label quantities associated with different factors, while lower-case subscripts label quantities associated with different arguments, i.e., different canonical coordinates or linear combinations of canonical coordinates. Each canonical coordinate or linear combination of canonical coordinates, $s_i$, may be an argument of several different factors. It is important to note the distinction between $s_i$ and the transform variable $s_{Ii}$. It is the $s_i$ that are averaged.

By applying Eq. (21) to every argument in every factor in $\langle\prod_I f_I\rangle_0$ and by moving the harmonic-average brackets so they only enclose quantities that depend on the canonical coordinates, one obtains

$$\left\langle\prod_I f_I\right\rangle_0=\frac{1}{(2\pi)^P}\left[\prod_I\prod_i^{(I)}\int dk_{Ii}\right]\left\langle\exp\left[+i\sum_i\sum_i^{(I)}k_{Ii}s_i\right]\right\rangle_0\left[\prod_I\prod_i^{(I)}\int ds_{Ii}\right]\exp\left[-i\sum_I\sum_i^{(I)}k_{Ii}s_{Ii}\right]\left[\prod_I f_I(s_{Ii},\cdots)\right]\ , \tag{22}$$

where $P$, the power of $2\pi$, equals the total number of arguments in all factors. $\prod_i^{(I)}$ indicates a product of quantities with the values of $i$ that label the arguments of the $I$th factor $f_I$. The sum $\sum_i^{(I)}$ is defined analogously to the product $\prod_i^{(I)}$. For example, if the 9th factor had arguments $s_2$ and $s_3$, i.e., if $f_9(s_2,s_3)$ were one of the factors, then $\sum_i^{(9)}$ would indicate a sum of two terms, one with $i=2$ and one with $i=3$. In the $\phi^4$ model on a square lattice there is only one term in the sum $\sum_i^{(I)}$ when $1\le I\le N$, while there are two terms in each sum when $N<I\le 3N$. Thus, while $\sum_I$ alone implies a sum of $3N$ terms, $\sum_I\sum_i^{(I)}$ implies a sum of $5N$ terms, and $P$ equals $5N$.

Next, the cumulant expansion is used. When applied to a harmonic average of $e^{iL}$, where $L$ is any linear functions of the canonical coordinates, all cumulants of third order and higher vanish, so that

$$\langle e^{iL}\rangle_0=\exp\left[i\langle L\rangle_0-\tfrac{1}{2}\left\langle(L-\langle L\rangle_0)^2\right\rangle_0\right]\ . \tag{23}$$

This result is valid for both classical and quantum harmonic averages.[14] For the classical canonical averages considered here its proof is straightforward. After transforming the integration coordinates, or variables, in the averaging process to normal coordinates, it becomes an exercise in completing the square and changing variables in integrals of exponentials of a linear plus a quadratic function.

By using the cumulant expansion, the harmonic average in Eq. (22) becomes

$$\left\langle \exp\left[+i\sum_I \sum_i^{(I)} k_{Ii}s_i\right]\right\rangle_0 = \exp\left[+i\sum_I \sum_i^{(I)} k_{Ii}\langle s_i\rangle_0\right]\exp\left[-\frac{1}{2}\sum_I \sum_i^{(I)}\sum_J \sum_j^{(J)} \Lambda_{ij}k_{Ii}k_{Jj}\right], \tag{24}$$

where

$$\Lambda_{ij} = \langle \Delta s_i \Delta s_j \rangle_0 \tag{25}$$

and

$$\Delta s_i = s_i - \langle s_i \rangle_0 . \tag{26}$$

The sums over $I$ and $J$ in Eq. (24) can be separated into a single sum over $I$ with $I=J$ and a double sum $\sum'_{IJ}$, where the prime indicates that terms with $I=J$ are excluded. By substituting Eq. (24) into Eq. (22) and by changing several of the sums in the exponents of exponentials to products of exponentials, one obtains

$$\langle \prod_I f_I \rangle_0 = \frac{1}{(2\pi)^P}\left[\prod_I \prod_i^{(I)} \int dk_{Ii}\right]\exp\left[-\frac{1}{2}\sum'_{IJ}\sum_i^{(I)}\sum_j^{(J)} \Lambda_{ij}k_{Ii}k_{Jj}\right]$$
$$\times \prod_I \left[\exp\left[-\frac{1}{2}\sum_i^{(I)}\sum_j^{(I)} \Lambda_{ij}k_{Ii}k_{Ij}\right]\left[\prod_i^{(I)} \int ds_{Ii}\right]\exp\left[-i\sum_i^{(I)} k_{Ii}(s_{Ii}-\langle s_i\rangle_0)\right] f_I(s_{Ii},\ldots)\right] . \tag{27}$$

When the same procedures used to obtain the above are applied to the average of a single factor, one obtains

$$\langle f_I(s_i,\ldots)\rangle_0 = \frac{1}{(2\pi)^\nu}\left[\prod_i^{(I)} \int dk_{Ii}\right]$$
$$\times \exp\left[-\frac{1}{2}\sum_i^{(I)}\sum_j^{(I)} \Lambda_{ij}k_{Ii}k_{Ij}\right]\left[\prod_i^{(I)} \int ds_{Ii}\right]\exp\left[-i\sum_i^{(I)} k_{Ii}(s_{Ii}-\langle s_i\rangle_0)\right] f_I(s_{Ii},\ldots) , \tag{28}$$

where the variables being averaged are explicitly indicated and $\nu$ is the number of arguments in $f_I$. Note that the same quantities appear at the end of both Eqs. (27) and (28).

To be able to use Eq. (28) to simplify Eq. (27) the exponential containing the double sum $\sum'_{IJ}$ in Eq. (27) needs to be exchanged with the integrations over the $k_{Ii}$. This is done by considering the exponential containing the sum to be a power series and using the identity

$$k_{Ii} = -i(\partial/\partial x_{Ii})e^{ik_{Ii}x_{Ii}}\Big|_{x=0} \tag{29}$$

to replace each $k_{Ii}$ with $(-i(\partial/\partial x_{Ii})$. The new variable $x_{Ii}$ is to be differentiated before it is set to zero. The differentiations $(\partial/\partial x_{Ii})$ can be exchanged with the integrations over the $k_{Ii}$. The needed factors of $e^{ik_{Ii}x_{Ii}}$ are obtained by changing the functions $f_I(s_i)$ in Eq. (28) to $f(s_i+x_{Ii})$ [see Eq. (21)], which gives

$$\langle f_I(s_i+x_{Ii},\ldots)\rangle_0 = \frac{1}{(2\pi)^\nu}\left[\prod_i^{(I)} \int dk_{Ii}\right]\exp\left[-\frac{1}{2}\sum_i^{(I)}\sum_j^{(I)} \Lambda_{ij}k_{Ii}k_{Ij}\right]\left[\prod_i^{(I)} \int ds_{Ii}\right]$$
$$\times \exp\left[-i\sum_i^{(I)} k_{Ii}(s_{Ii}-\langle s_i\rangle_0 - x_{Ii})\right] f_I(s_{Ii},\ldots) . \tag{30}$$

By combining the above results, Eq. (27) can be rewritten as

$$\langle \prod_I f_I(s_i,\ldots)\rangle_0 = \left[e^W \prod_I \langle f_I(s_i+x_{Ii},\ldots)\rangle_0\right]\Big|_{x=0} , \tag{31}$$

where

$$W = \frac{1}{2}\sum'_{IJ}\sum_i^{(I)}\sum_j^{(J)} \Lambda_{ij}(\partial/\partial x_{Ii})(\partial/\partial x_{Jj}) . \tag{32}$$

This is the *correlated-factors theorem*. It is valid for a wide range of systems, and not just the $\phi^4$ model. The essential conditions for its validity are (a) that each of the arguments of the factors $f_I$ is a linear function of the canonical coordinates and (b) that the harmonic Hamiltonian is a sum of linear and quadratic functions of the canonical coordinates. Since the cumulant expansion, Eq. (23), is valid for both classical and quantum harmonic averages, the correlated-factors theorem is valid both classically and quantum mechanically.

## III. UNCORRELATED-FACTORS APPROXIMATION $\phi^4$ MODEL

The essential equations for determining the free energy for the $\phi^4$ model in the UFA are given below by Eqs. (35)–(38) and Eqs. (44), (46), and (47). The double-well potential is given by Eq. (3).

The first simplification to make when applying the UFA to the $\phi^4$ model is to set the adjustable parameter $J_0$ in $H_0$ equal to the nearest-neighbor coupling constant $J$ in the true Hamiltonian $H$. It then follows from Eq. (10) that $f_I(s_i,s_j)=1$. Because of this, only the one-particle factors $f_I(s_i)$ given by Eq. (11) are needed. The reason for initially having $J_0 \neq J$ was to illustrate the generality of the proof in the previous section.

For the UFA to be accurate through second order, the adjustable parameters $K$ and $\Gamma$ in the harmonic Hamiltonian must be chosen so that the zeroing conditions, Eqs. (14) and (15), are satisfied. The differential operator $W$ is a sum of terms, each of which operates on two *different* factors, $f_I$ and $f_J$. Consequently, no factor is differentiated more than once in Eq. (14) and no factor is differentiated more than twice in Eq. (15). As a result, one can satisfy both zeroing conditions by requiring that

$$\langle \partial f_I(s_i)/\partial s_i \rangle_0 = 0 \tag{33}$$

and

$$\langle \partial^2 f_I(s_i)/\partial s_i^2 \rangle_0 = 0 \ , \tag{34}$$

where $I=i$. By taking the indicated derivatives, using Eqs. (11) and (12) for $f_I(s_i)$, and rearranging terms, one can show that

$$\Gamma = B - \left\langle \frac{e^{-\beta\Delta\phi(s_i)}}{\langle e^{-\beta\Delta\phi(s_i)}\rangle_0} \left[ \frac{\partial\phi(s_i)}{\partial s_i} - Ks_i \right] \right\rangle_0 \tag{35}$$

and

$$K = \left\langle \frac{e^{-\beta\Delta\phi(s_i)}}{\langle e^{-\beta\Delta\phi(s_i)}\rangle_0} \left[ \frac{\partial^2\phi(s_i)}{\partial s_i^2} - \beta \left[ \frac{\partial\phi(s_i)}{\partial s_i} - Ks_i + \Gamma - B \right]^2 \right] \right\rangle_0 . \tag{36}$$

In addition to the explicit dependence on $K$ and $\Gamma$ in the above, there is an implicit dependence that comes in through the harmonic averages.

Because of the symmetry of the Hamiltonians, the harmonic averages have the same values for all particles, i.e., for all $i$, so that there are just two independent zeroing conditions. The form of the zeroing conditions in Eqs. (35) and (36) is particularly convenient for the iterative determination of $K$ and $\Gamma$. Once these parameters have been found, the UFA value for the free energy per particle is calculated with

$$F(T,B)/N = F_0(T,B)/N - k_B T \ln\langle e^{-\beta\Delta\phi(s_i)}\rangle_0 \ , \tag{37}$$

which follows from Eqs. (16) and (11). Other thermal properties can be obtained by differentiating $F(T,B)$.

A useful formula for evaluating the harmonic averages needed in Eqs. (35), (36), and (37) can be deduced from Eq. (28). For factors with a single argument there is only one factor in the product $\prod_i^{(I)}$, and the one term included in the sums $\sum_i^{(I)}\sum_j^{(I)}$ has $i=I=j$. By taking the integral over $k_{Ii}$, which is equivalent to taking the inverse Fourier transform of $e^{-1/2\Lambda_{ii}k_{Ii}^2}$, one obtains

$$\langle g(s_i)\rangle_0 = \int ds \frac{e^{-(s-\langle s_i\rangle_0)^2/(2\Lambda_{ii})}}{\sqrt{(2\pi\Lambda_{ii})}} g(s) \ , \tag{38}$$

where $g$, instead of $f_I$, has been used to indicate that the formula is valid for any one-particle function $g(s)$. The width of this Gaussian probability density is proportional to the square root $\Lambda_{ii}$. It follows from Eq. (25) that $\Lambda_{ii}$ is the mean value (or, variance) of the spin coordinate of particle $i$:

$$\Lambda_{ii} = \langle (\Delta s_i)^2 \rangle_0 \ . \tag{39}$$

Before the above formula can be used, the dependence of $\langle s_i\rangle_0$ and $\Lambda_{ii}$ on the adjustable parameters $\Gamma$ and $K$ in $H_0$ must be determined. To find this dependence it is convenient to introduce barred coordinates defined by

$$\bar{s}_i = s_i - \Gamma/(K - N_{nn}J) \ , \tag{40}$$

where $N_{nn}=\sum_j a_{ij}$ is the number of nearest neighbors. For a square lattice $N_{nn}=4$. Introducing the barred coordinates into Eq. (8) for $H_0$ gives

$$H_0 = \frac{1}{2}\sum_i \sum_j M_{ij}\bar{s}_i\bar{s}_j + C \ , \tag{41}$$

where

$$M_{ij} = K\delta_{ij} - Ja_{ij} \ , \tag{42}$$

and $C$ is a constant. The harmonic average of the $n$th power of a barred coordinate is

$$\langle \bar{s}_i^n \rangle_0 = \left(\int d^N\bar{s}\, e^{-\beta H_0}\bar{s}_i^n\right)/\left(\int d^N\bar{s}\, e^{-\beta H_0}\right) . \tag{43}$$

From this and from the absence of any terms linear in the $\bar{s}_i$ in $H_0$, it follows that $\langle \bar{s}_i\rangle_0$ is zero. This with Eq. (40) implies that

$$\langle s_i\rangle_0 = \Gamma/(K - N_{nn}J) \ . \tag{44}$$

By using Eqs. (25), (26), and (40) and introducing the

transformation that diagonalizes the matrix $M_{ij}$, it can be shown that

$$\Lambda_{ii}=\langle \bar{s}_i^2 \rangle_0=(k_B T/N)\sum_k (1/m_k) , \tag{45}$$

where the $m_k$ are the eigenvalues of $M_{ij}$. A more detailed analysis for a square lattice gives

$$\Lambda_{ii}=\frac{k_B T}{\pi}\int_0^{\pi} d\theta \frac{1}{\sqrt{(K-2J\cos\theta)^2-(2J)^2}} , \tag{46}$$

where the limit $N\to\infty$ has been taken. Similarly, the harmonic free energy per particle becomes

$$\frac{F_0(T,B)}{N}=-\frac{\Gamma^2}{2(K-4J)}+\frac{1}{2}k_B T\ln\left[\frac{\sigma^2}{2\pi k_B T}\right]+\frac{k_B T}{2\pi}\int_0^{\pi} d\theta \ln\left[\tfrac{1}{2}\left[(k-2J\cos\theta)+\sqrt{(K-2J\cos\theta)^2-(2J)^2}\right]\right] . \tag{47}$$

## IV. CALCULATIONS

The specific heat per particle $c_B$, the magnetization per particle $m$, and the isothermal susceptibility $\chi_T$ can be obtained by differentiating the free energy:

$$c_B=-\frac{T}{N}(\partial^2 F/\partial T^2)_B , \tag{48}$$

$$m=-\frac{1}{N}(\partial F/\partial B)_T , \tag{49}$$

$$\chi_T=(\partial m/\partial B)_T=-\frac{1}{N}(\partial^2 F/\partial B^2)_T . \tag{50}$$

In exact theory the magnetization $m$ equals $\langle s_i \rangle$, the average of the spin coordinate formed with the true Hamiltonian. In the UFA the magnetization equals the harmonic average $\langle s_i \rangle_0$.

Results for the $\phi^4$ model on a square lattice with $\epsilon=\sigma=1$ and $B=0$ are presented in Figs. 1–4. For comparison the predictions of the CEM, SCP, and MFT are presented along with those of the UFA. All values for $c_B$, $m$, and $\chi_T$, were obtained by numerically differentiating approximate free energies.

The CEM results were obtained by modifying the methods developed in Ref. 7 to apply when the true Hamiltonian is given by Eq. (2). The Einstein-type harmonic Hamiltonian used is

$$H_0=\sum_i (\tfrac{1}{2}Ks_i^2-\Gamma s_i) , \tag{51}$$

which has no interparticle terms.

Both MFT and SCP can be obtained with the Gibbs-Bogoliubov inequality[15]

$$F\le F_0+\langle H-H_0 \rangle_0 . \tag{52}$$

To obtain MFT one introduces the approximate Hamiltonian

$$H_0=\sum_i [\phi(s_i)-(B+\hat{B})s_i] , \tag{53}$$

which is not harmonic, and adjusts the mean-field $\hat{B}$ to minimize the right-hand side of the Gibbs-Bogoliubov inequality. To obtain SCP one uses the harmonic Hamiltonian, Eq. (8), for the approximate Hamiltonian and ad-

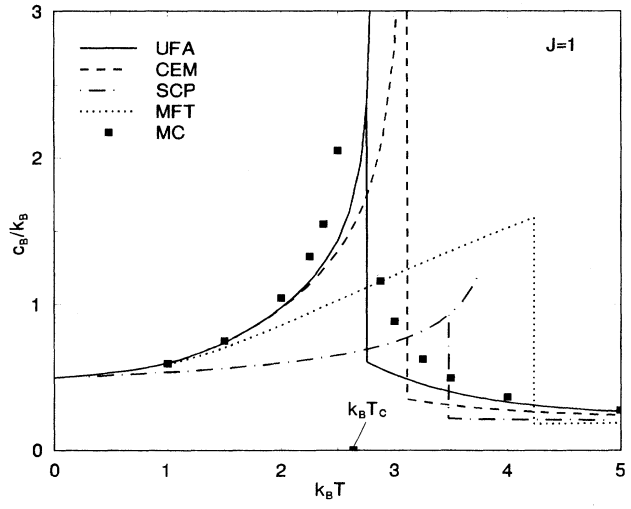


FIG. 1. Specific heat per particle as a function of temperature at $B=0$ for the $\phi^4$ model with $J=1$ and $\epsilon=\sigma=1$. Results for several different approximations are given. See text for details.

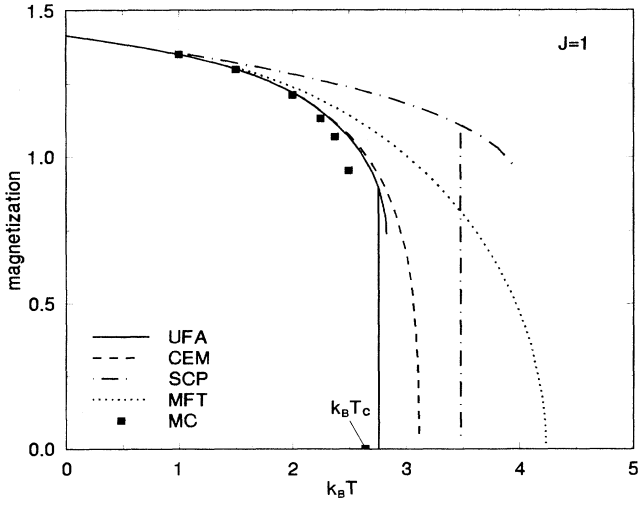


FIG. 2. Magnetization per particle as a function of temperature at $B=0$ for the $\phi^4$ model with $J=1$ and $\epsilon=\sigma=1$.

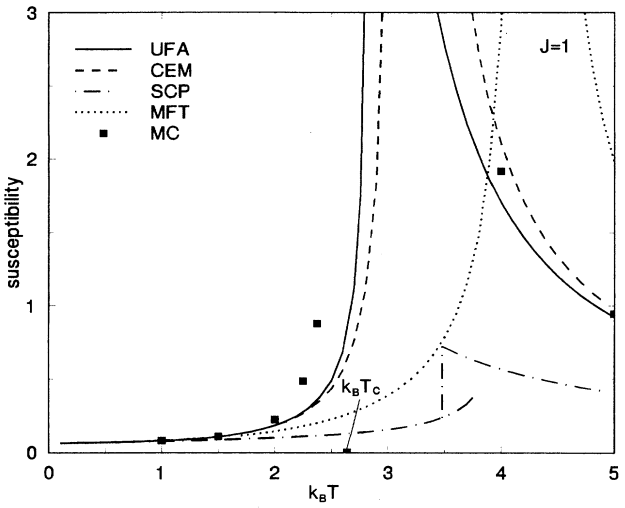


FIG. 3. Isothermal susceptibility as a function of temperature at $B=0$ for the $\phi^4$ model with $J=1$ and $\epsilon=\sigma=1$.

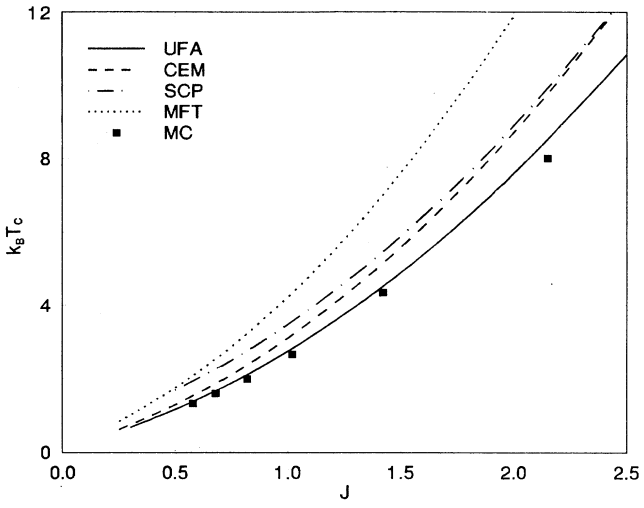


FIG. 4. Dependence of the phase-transition temperature on the coupling constant $J$ for the $\phi^4$ model at $B=0$ with $\epsilon=\sigma=1$.

justs the parameters $K$ and $\Gamma$.

The equations for determining the free energy with SCP are quite similar to those for the UFA. The conditions that must be satisfied to minimize the right-hand side of the Gibbs-Bogoliubov inequality are

$$\Gamma=B-\langle \partial\phi(s_i)/\partial s_i - Ks_i \rangle_0 \tag{54}$$

and

$$K=\langle \partial^2\phi(s_i)/\partial s_i^2 \rangle_0 , \tag{55}$$

which are similar to the zeroing conditions, Eqs. (35) and (36). The free energy per particle is given by

$$F(T,B)/N=F_0(T,B)/N+\langle \Delta\phi(s_i) \rangle_0 , \tag{56}$$

which is similar to Eq. (37). Equations (38), (44), (46), and (47) apply to SCP without modification.

The MC estimates presented in Figs. 1, 2, and 3 for temperatures away from the phase transition were calculated for a $20\times20$ square lattice with periodic boundary conditions. Each data point was obtained with a run of $25\times10^6$ steps after an initialization run of $4\times10^6$ steps. No extrapolation to the thermodynamic limit was made. The MC values for $k_BT_c$ given on the horizontal axes in Figs. 1, 2, and 3 and in Fig. 4 were obtained from Milchev, Heermann, and Binder.[2]

A vertical line in Figs. 1, 2, or 3 locates the transition temperature $T_c$ predicted by the indicated approximation. $T_c$ equals 2.64, 2.76, 3.11, 3.48, and 4.23, respectively, for MC, UFA, CEM, SCP, and MFT. The CEM (when $J>0.421$) and MFT give second-order phase transitions, while the UFA and SCP (and the CEM when $J<0.421$) give first-order transitions. The transition temperatures for the first-order transitions are the temperatures at which the free energies of the two phases are equal.

## V. CONCLUSIONS AND DISCUSSION

It is clear from the figures that the UFA and the CEM are significantly more accurate than SCP or MFT and that the UFA is more accurate than the CEM. Although none of these four approximations can be expected to predict critical behavior correctly, it is interesting that the two approaches utilizing independent sites in their development, the CEM and MFT, predict second-order phase transitions, while the two approaches utilizing normal modes, the UFA and SCP, predict first-order transitions. Presumably, the second-order prediction is the correct one.[3] Thus, as one would expect from the more general type of harmonic Hamiltonian used in the UFA, it is generally more accurate than the CEM, but the latter approximation gives the better prediction for the order of the transition.

In their application to the $\phi^4$ model the UFA, the CEM, and SCP use two adjustable parameters, $K$ and $\Gamma$, while MFT uses only one, the mean-field $\hat{B}$. Because of this, it is not surprising that the UFA and CEM are more accurate than MFT, but one must look elsewhere to understand the relatively low accuracy of SCP. A discussion of the shortcomings of SCP and of a possible route for overcoming them has recently been given by Morris and Gooding.[16]

The equations for determining the free energy in SCP can be viewed as approximations to the equations in the UFA that apply in the limit of weak anharmonicity: To see this, note that the strength of the anharmonicity can be considered to be proportional to $\Delta\phi$. Then, if one expands Eq. (37) for the free energy in powers of the explicitly appearing $\Delta\phi$ and keeps only the lowest power nonvanishing terms, one obtains the SCP result, Eq. (56). If one similarly expands the UFA zeroing conditions Eqs. (35) and (36), one obtains the SCP conditions Eqs. (54) and (55). When doing this, one must remember that the derivatives of $\phi(s_i)$ and the associated terms containing

$K$, $\Gamma$, and $B$ in Eqs. (35) and (36) came from differentiating $\Delta\phi$, and thus should be considered to be proportional to $\Delta\phi$.

The modulating factors $e^{-\beta\Delta\phi}/\langle e^{-\beta\Delta\phi}\rangle_0$ in the harmonic averages in Eqs. (35) and (36) are a characteristic feature of approximations based on the correlated-factors theorem. Similar factors appear in the UPA and CEM, but not in SCP. In exact theory a low probability density is associated with regions of configuration space where the potential energy is high. This low probability density is better accounted for by harmonic averages with modulating factors than by harmonic averages without them. To see why, note that the potential $\phi(s_i)$ can become significantly greater than the other terms in $\Delta\phi(s_i)$. [See Eqs. (12).] This causes $\Delta\phi(s_i)$ to become large, which causes the modulating factor to become exponentially small.

As a final comment we point out an interesting interpretation of the zeroing conditions. By transferring the differentiations in Eqs. (33) and (34) from $f_I(s_i)$ to the Gaussian $\exp(-\frac{1}{2}(s_i-\langle s_i\rangle_0)^2/\Lambda_{ii})$ in the harmonic average [see Eq. (38)], one can show that

$$\langle s_i\rangle_0=\langle e^{-\beta\Delta\phi(s_i)}s_i\rangle_0/\langle e^{-\beta\Delta\phi(s_i)}\rangle_0 \tag{57}$$

and

$$\langle \Delta s_i^2\rangle_0=\langle e^{-\beta\Delta\phi(s_i)}\Delta s_i^2\rangle_0/\langle e^{-\beta\Delta\phi(s_i)}\rangle_0 . \tag{58}$$

These equations state that in the UFA the adjustable parameters in $H_0$ are chosen so that the harmonic average of the spin coordinate is equal to its modulated-harmonic average, and similarly for the variance.

## ACKNOWLEDGMENTS

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