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Scalar Product Method in Statistical Mechanics of Boundary Tension

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Abstract. — The interphase excess free energy $\sigma$ due to an interphase boundary (IPB) is calculated in the Ising model using the Scalar Product (SP) method. Different from the “sum” method calculation of $\sigma$ based on the boundary profile, the SP approach skips the profile and directly evaluates $\sigma$ from the equilibrium properties of the homogeneous phases meeting at the boundary. Using a series of Cluster Variation Method (CVM) approximations of the basic cluster size $n$, a series of $\sigma(n)$ values are calculated. For the 2-D square lattice, the limit of the SP $\sigma(n)$ for $n \to \infty$ is very close to the exact value of Onsager for the $\langle 10 \rangle$ orientation and to that of Fisher and Ferdinand for $\langle 10 \rangle$. Similar extrapolation was done for the 3-D simple cubic lattice. The result agrees well with the known Monte Carlo results. Because the SP approach does not calculate the profile, computational time and labor are much less than those of the sum method.

1. Introduction

The boundary tension or the interphase tension $\sigma$, that is the excess free energy due to the boundary, is of much practical interest. The usual way of calculating $\sigma$ is first to obtain the density profile and the free energy $F$ of the region covering the boundary and then to form the difference between $F$ and the free energy $F_0$ of the homogeneous phase of the same volume [1–3]. The computation for the density profile requires a large number of variables and is lengthy, with one set of variables for each lattice plane position. This kind of calculations of the density profile and $F$ were done applying the Cluster Variation Method (CVM) [4,5]. We will call this approach the “sum” method for short. In addition to the computational labor for the number of planes and for the sufficient numerical accuracy, the sum method contains a still unresolved puzzle on the width of the boundary. Any calculation based on a cluster of a finite size does lead to a finite value for the boundary width, although the size of the system treated by the theory is infinite. It is known, on the other hand, that the width of a boundary diverges with the size of the system. The finite width calculated in approximate theories may still have physical meaning, but it is still not known.

Apart from the sum method, a new approach based on Woodbury’s pioneering work [6–8] had been developed [9,10], which calculated $\sigma$ using the information on the two homogeneous

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phases on the opposite sides of the boundary. This approach was called the Scalar Product (SP) approach. In case the main interest is $\sigma$ rather than the density profile, the computation time is much shorter in the SP than in the sum method of the basic cluster of the same size, and hence approximations with larger size clusters can be performed in the SP. This makes the extrapolation to the rigorous result easier.

In the present paper we report the work on an interphase boundary (IPB) in the Ising model of the 2-dimensional square lattice. Results on the 3-dimensional simple cubic lattice are also reported. In all cases, the calculations are done for the nearest neighbor interactions.

2. Scalar Product formulation

In previous papers [9,10], we proved the following general formula for the nearest-neighbor interactions:

$$\exp(-Na\beta\sigma) = \sum_\nu \left( p^I (\nu) p^{II} (\nu) \right)^{1/2}$$

(1)

where $\sigma$ is the boundary tension, $N$ is the number of lattice points on a plane parallel to the boundary (to be called a “parallel” plane for short), $a$ is the sectional area per lattice point in the plane, $\beta = 1/kT$ is the inverse temperature in the Boltzmann units and $\nu$ indicates a configuration of spins on the entire $N$ points in a parallel plane. In the above equation, $p^I (\nu)$ and $p^{II} (\nu)$ are the probabilities that the configuration $\nu$ appears in the phases I and II, respectively, which meet at the boundary. Equation (1) is the scalar product of two normalized vectors $\left( p^I (\nu) \right)^{1/2}$ and $\left( p^{II} (\nu) \right)^{1/2}$, and leads to the interpretation that the boundary tension $\sigma$ is the measure of the difference between the two bulk phases I and II.

It can be noted that equation (1) has the general structure at the partition function in the sense that an exponential of excess free energy, $Na\beta\sigma$ is obtained as a sum over states of a probability function. Therefore, the generalized CVM procedure can be used to evaluate it. Since the proof of the SP expression (1) has been dormant for the last twenty years [9,10], a brief summary of the proof is presented in Appendix. This appendix supplements the previous proof by adding the finishing touch on the duality puzzle, the explanation of which was not completely satisfactory before.

In equation (1), $\nu$ represents one of the configurations of an entire parallel plane, which is made of a large number $N$ of lattice points. In the practical calculations, we approximate (1) using the CVM with a finite size cluster. When we write a configuration of a chosen cluster as $\alpha$, (1) is approximated as

$$\exp(-Na\beta\sigma) = \sum_\alpha W (\alpha) \left( p^I (\alpha) p^{II} (\alpha) \right)^{1/2}$$

(2)

where $W (\alpha)$ is the number of configurations consistent with the specified set $\{\alpha\}$, and $p^I (\alpha)$ is the probability that one of the configurations among $\{\alpha\}$ occurs in the equilibrium homogeneous phase I. Equation (2) is regarded as a generalization of the ordinary partition function. In the latter, the probability part corresponding to the $p$ factor in (2) is written as the Boltzmann factor, and the weight factor $W (\alpha)$ is written using the CVM entropy formula.

In the following sections we show applications of (2) to 2-dimensional Ising model IPB of the orientations of (10) and (11). We use several approximations of different size clusters in each orientation.
3. \textbf{IPB of (10) and (11) Orientations}

3.1. The (10) Boundary. — We first consider the (10) orientation. A lattice line parallel to the (10) boundary is a chain of nearest-neighbor lattice points. We call a 1-dimensional cluster consisting of \( n + 1 \) consecutive points and containing \( n \) nearest-neighboring pairs an \( n \)-cluster \((n = 0, 1, 2, \ldots)\). When an \( n \) cluster is used as the basic cluster to formulate (2), \( \alpha \) is one of the configurations of the \( n \)-cluster. The \( n = 1 \) case is the pair approximation and was worked out previously [11]. Before using the \( n \)-cluster in (2), we solve the homogeneous 2-dimensional problem using the basic cluster made of two linear \( n \)-clusters placed side by side, namely a ladder-shaped cluster of \( n \) consecutive squares, to be called the \( n \)-square cluster. Because of the dimension-reduction property [12], 1-dimensionally extended clusters like the ladder-shaped clusters of \( n \) consecutive squares are sufficient to calculate an infinitely extended 2-D system.

We consider a certain configuration of +’s and -’s of a 1-dimensional \((n - 1)\)-cluster, and designate such a series of spins as \( i \) in this subsection. Note that an \((n - 1)\)-cluster is defined as made of consecutive \( n \) spins. We write the probability for this configuration as \( \tilde{x}_i \), where a caret indicates that this is the equilibrium value previously calculated for the homogeneous 2-D system for the phase I. The configuration in which a + is placed next to the spin series \( i \) is written as \( i1 \). Similarly, \( i2 \) indicates the configuration in which a - spin comes after the series \( i \). Both \( i1 \) and \( i2 \) are the configurations for the linearly placed \( n + 1 \) spins. The equilibrium probabilities of finding \( i1 \) and \( i2 \) configurations in the homogeneous system are written as \( \tilde{y}_{i1} \) and \( \tilde{y}_{i2} \), respectively. They are solved by the CVM using the \( n \)-square cluster.

Different from \( \tilde{y}_{i1} \) and \( \tilde{y}_{i2} \), we introduce \( y_{i1} \) and \( y_{i2} \), without a caret, to indicate the probabilities of occurrence of the configurations \( i1 \) and \( i2 \) in the 1-D lattice. The \( y \)'s without a caret correspond to \( \{\alpha\} \) in equation (2) and are to be determined in the boundary calculations. Corresponding to \( \tilde{x}_i \), for consecutive \( n \) spins in the bulk, \( x_i \), without the caret is the probability for the same configuration in the boundary and is to be determined.

Since the general structure of equation (2) is similar as the partition function, we can follow the general procedure of the CVM to formulate it. \( W(\alpha) \) corresponds to the entropy part so that the 1-D system, where all CVM entropy coefficients vanish except the \( n \)- and \((n - 1)\)-clusters, we can write:

\[
\frac{1}{N} \ln W = \sum_i L(x_i) - \sum_i (L(y_{i1}) + L(y_{i2}))
\]

where the \( L(x) \) function is derived from the Stirling approximation as

\[
L(x) \equiv x \ln(x) - x.
\]

The probability part \( (p^1 p^{11})^{1/2} \) in (2) corresponds to the Boltzmann factor which can be regarded as the \textit{a priori} probability factor. In writing \( p^1 \) in (2), we can treat \( \tilde{y}_{i1} \) and \( \tilde{y}_{i2} \) as the corresponding \textit{a priori} probability factors for the phase I. Since \( \tilde{y}_{i1}/\tilde{x}_i \) is the conditional probability of finding 1 next to the known series \( i \), we write

\[
\ln(p^1(y_{i1}, y_{i2})) = N \sum_i \left( y_{i1} \ln \left( \frac{\tilde{y}_{i1}}{\tilde{x}_i} \right) + y_{i2} \ln \left( \frac{\tilde{y}_{i2}}{\tilde{x}_i} \right) \right).
\]

In this expression, \( y_{i1} \) and \( y_{i2} \) are the variables, while \( \tilde{y} \) and \( \tilde{x} \) with a caret are constants.

In the Ising model, the second phase II is derived from I by interchanging + and - spins. In the rest of the section we write \( j \) for the \( n \)-cluster configuration which is derived from \( i \) by
interchanging the sign of the spins. Then \( p^{II} (y) \) corresponding to (5) is written as
\[
\ln \left( p^{II} (y_1, y_2) \right) = N \sum_j \left( y_1 \ln \left( \frac{\hat{y}_{1j}}{\hat{x}_j} \right) + y_2 \ln \left( \frac{\hat{y}_{2j}}{\hat{x}_j} \right) \right). 
\]
(6)

Note that \( i \) is associated with \( j \) in (6), and that the variables \( y_1 \) and \( y_2 \) remain the same in both \( p^{I} (y_1, y_2) \) and \( p^{II} (y_1, y_2) \).

Combining (3), (5) and (6), we can write equation (2). Or taking the logarithm of it, we can write the generalized "free energy" as
\[
-\beta a \sigma = \sum_i L (x_i) - \sum_i \left( L (y_1 + L (y_2)) \right)
+ \frac{1}{2} \sum_i \left( y_1 \ln \left( \frac{\hat{y}_{1i} \hat{y}_{2i}}{\hat{x}_i \hat{x}_j} \right) + y_2 \ln \left( \frac{\hat{y}_{2i} \hat{y}_{2i}}{\hat{x}_i \hat{x}_j} \right) \right)
- \beta \lambda \left( 1 - \sum_i \left( y_1 + y_2 \right) \right) 
\]
(7)

where \( a \) is the lattice constant of the square lattice, and the \( \lambda \) term is added for normalization of the \( y \)'s. We can obtain \( \sigma \) as a maximum of (7). This corresponds to replacing the sum over \( a \) in (2) by its maximum term as justified when \( N \) is a large number. When (7) is maximized, we can identify \( \lambda \) as
\[
\beta a \sigma = \beta a \sigma - \sum_i \left( y_1 \frac{\partial (\beta a \sigma)}{\partial y_1} + y_2 \frac{\partial (\beta a \sigma)}{\partial y_2} \right) = \beta \lambda 
\]
(8)
which shows that \( \lambda \) is equal to the excess free energy \( a \sigma \).

Differentiation of (7) leads to
\[
y_1 = x_i \exp (\beta \lambda) \left( \frac{\hat{y}_{1i} \hat{y}_{2i}}{\hat{x}_i \hat{x}_j} \right)^{1/2} 
\]
(9)
\[
y_2 = x_i \exp (\beta \lambda) \left( \frac{\hat{y}_{2i} \hat{y}_{2i}}{\hat{x}_i \hat{x}_j} \right)^{1/2} 
\]
(10)

When we add these two, use the normalization and equation (8), we arrive at the final result:
\[
\beta a \sigma = - \ln \left( \sum_i \left( \left( \frac{\hat{y}_{1i} \hat{y}_{2i}}{\hat{x}_i \hat{x}_j} \right)^{1/2} + \left( \frac{\hat{y}_{2i} \hat{y}_{2i}}{\hat{x}_i \hat{x}_j} \right)^{1/2} \right) \right). 
\]
(11)

Figure 1 plots \( a \sigma (10) / \epsilon \) against the reduced temperature \( T / T_c \) for the 4 kinds of \( n \)-square approximations, \( n = 1, 2, 3 \) and 4. The energy for a \((++\)) pair is chosen as \(-\epsilon\). For comparison, also plotted is the rigorous result of Onsager [13] given as
\[
\tau \equiv \frac{kT}{\epsilon} 
\]
(12)
\[
\frac{a \sigma (10)}{\epsilon} = \tau \ln \left( \frac{\exp \left( \frac{2}{\tau} \right) \tanh \left( \frac{1}{\tau} \right)}{\tau} \right) 
\]
(13a)
\[
\tau^* = \frac{2}{\ln (1 + \sqrt{2})} 
\]
(13b)
2.5
2
1.5
1
0.5
0

Fig. 1. — The IPB tension $\sigma_{(10)}(n)$ calculated by the SP method against the reduced temperature $T/T_c(n)$ for 2D square lattice. $n$ is the number of consecutive squares in the basic clusters used in calculating the homogeneous system. The curves are for $n = 1$, 2, 3, and 4-square approximations from higher to lower. The lowest 5th curve is Onsager’s rigorous result [13].

where $\tau^*$ is the exact Curie temperature of the square lattice.

In Figure 1, the $n = 1$ case is the square approximation for the bulk, and the pair approximation for the line, and was already reported before [11]. The general qualitative features of the four approximations in Figure 1 are the same as the $n = 1$ case. We see in Figure 1 that as $n$ increases, the curves monotonically approach the rigorous curve. We calculate the limit of $n \to \infty$ in the following section.

It may be commented at this point that Onsager [13] calculated his $\sigma_{(10)}$ using the difference between the even and odd circumferences of a cylindrical surface of an antiferromagnetic system, and hence it was not necessary in his method to specify the location and the width of the boundary.

3.2. THE $\langle 11 \rangle$ BOUNDARY. — A lattice line parallel to the $\langle 11 \rangle$ boundary is made of square diagonal pairs. The boundary tension $\sigma_{(11)}$ along this direction can be formulated in practically the same way as for the $\sigma_{(10)}$ case with slight modifications.

In this subsection, we define $i$ as the configuration of an $n$ consecutive diagonal lattice points, and $\hat{x}_i$ is the probability of this configuration in the homogeneous phase. $\hat{y}_{i1}$ and $\hat{y}_{i2}$ are the corresponding probabilities for a line of $n + 1$ diagonal points. In order to obtain such information, we can use a zig-zag form cluster as shown in Figure 2. The long side of this
example cluster contains 4 diagonal pairs, and therefore we will call this example the 4-step cluster.

Figure 3 plots the results of \( \beta a\sigma(11)/\epsilon \) for \( n \)-step clusters for \( n = 1, 2, 3 \) and 4. For comparison, we also draw the rigorous result of Fisher and Ferdinand [14] given by

\[
\frac{a\sigma(11)}{\epsilon} = \sqrt{2} \tau \ln \left( \sinh \left( \frac{2}{\tau} \right) \right).
\]  

(14)

3.3. SP Method and the Sum Method. — It is significant to note the fundamental difference between \( \sigma \) computed by the SP formulation (\( \sigma^{SP} \)) and that by the sum method (\( \sigma^{S} \)). When we treat the (10) IPB using the pair as the basic 2D cluster (instead of an \( n \)-square cluster), the surface tension (\( \sigma^{SP} \)) corresponding to (13) becomes

\[
\frac{a\sigma^{SP}}{\epsilon} = \tau \left( \theta + \ln \left( \frac{1 + \exp(-3\theta)}{1 + \exp(-\theta)} \right) \right) \\
\cosh (\theta) = \frac{\exp (2\beta\epsilon)}{2}
\]  

(15a)  

(15b)

When we can expand \( \sigma^{SP} \) in (15) near its bulk Curie temperature, \( \tau_c = 2/\ln(2) \), we obtain

\[
\lim_{T \to T_c} \frac{a\sigma^{SP}}{\epsilon} \approx \frac{T_c - T}{T_c}
\]  

(16)

which says that the scalar product boundary tension \( \sigma^{SP} \) tends linearly to zero as the temperature goes to the bulk transition temperature \( T_c \). We see in (16) that the mean field critical exponent is 1, which happens to be identical to Onsager’s exact value [13]. We call approximations based on finite size clusters, including the CVM approximations, as the mean field (MF). This critical behavior is different from that of the sum method result \( \sigma^{S} \):

\[
\lim_{T \to T_c} \frac{a\sigma^{S}}{\epsilon} \approx \left( \frac{T_c - T}{T_c} \right)^{3/2}
\]  

(17)

It is unusual that the same physical quantity is formulated in two different ways and the mean field critical exponents are different in two approaches. This difference leads to the significant
computational advantage that \(\sigma^{SP}\) and \(\sigma^S\) calculated by the same cluster bracket the exact solution for \(\sigma\) at all temperatures. In the following we will see examples of this property, which will turn out to be extremely powerful in the 3D case.

3.4. General Geometry. — When we use the CVM for a \(d\)-dimensional \((d \geq 2)\) bulk system, we choose an \((d-1)\)-dimensional cluster \(\alpha_{d-1}\). We consider a “slab”-shaped \(d\)-dimensional cluster \(\alpha_d\) made by two \(\alpha_{d-1}\) clusters placed side by side on two adjacent planes in the \(d\)-dimensional space. In section 3.1, \(\alpha_{d-1}\) is a line of \(n\) pairs, and \(\alpha_d\) is the ladder-shaped cluster of \(n\) squares. For a bulk 3-D cubic lattice, \(\alpha_{d-1}\) can be a 2-D \(n \times n\) square, and \(\alpha_d\) is then a slab made of \(n^2\) cubes placed in a square shape. Because of the dimension reduction property, this \(\alpha_d\) cluster forms the hierarchy of the CVM approximations, which converge to the rigorous limit. In using equation (2) for an IPB inside the \(d\) dimensional system, we use the “planar” \(\alpha_{d-1}\) as the basic cluster, and use the CVM formulation. Equation (2) for the IPB is to be compared with the standard CVM partition function based \(\alpha_{d-1}\)

\[
\exp (-N\beta F (\alpha_{d-1})) = \sum_{\alpha_{d-1}} W (\alpha_{d-1}) \exp (-\beta E (\alpha_{d-1})) .
\] (18)
This shows that \((p^I(\alpha)p^{II}(\alpha))^{1/2}\) in (2) corresponds to the Boltzmann factor in (18), and that both have the meaning of the \textit{a priori} probability. In both cases, each of the \(W(\alpha_{d-1})\) configurations occurs with the same probability. In (2) we have to construct its own \textit{a priori} probability factor, which is different from the Boltzmann shape, and is determined by the equilibrium state calculated by the cluster \(\alpha_d\) for the bulk.

The “free energy” for the \((d - 1)\)-dimensional system in the IPB is written as

\[
F\{\alpha_{d-1}\} = U\{\alpha_{d-1}\} - TS\{\alpha_{d-1}\}. \tag{19}
\]

For the entropy we use the standard CVM form:

\[
-S\{\alpha_{d-1}\} = \sum_{\alpha \subseteq \alpha_{d-1}} a_\alpha \mu_\alpha \sum_{p \in \alpha} \gamma_\alpha(p) P_\alpha(p) \ln (P_\alpha(p)) \tag{20}
\]

where \(a_\alpha\) and \(\mu_\alpha\) are the CVM entropy coefficient and the multiplicity of the subcluster \(\alpha\), respectively. \(P_\alpha(p)\) is the \(p\)th probability of the cluster \(\alpha\) and have a degeneracy factor \(\gamma_\alpha(p)\). The “internal energy” \(U\{\alpha_{d-1}\}\) in (19) is actually the logarithm of the \textit{a priori} probability, and is written as

\[
U\{\alpha_{d-1}\} = -\sum_{\alpha \subseteq \alpha_{d-1}} a_\alpha \mu_\alpha \sum_{p \in \alpha} \gamma_\alpha(p) P_\alpha(p) \ln \left(\frac{P^I_\alpha(p)}{P^{II}_\alpha(p)}\right) \tag{21}
\]

where \(P^I_\alpha(p)\) corresponds to the bulk (phase I) equilibrium probabilities of the same subcluster \(\alpha\). The value of \(\sigma\) is obtained by minimizing (19) with respect to the variables in the cluster \(\alpha_{d-1}\).

### 4. Extrapolation to the Rigorous Limit

We calculate \(\sigma\) using the sequence of three \(n\)-cluster CVM approximations \(n = 1, 2, 3\), and extrapolate them to obtain information of \(\sigma\) in the rigorous calculation. We use both the SP and S methods and compare advantages and disadvantages of the two.

For temperatures close to the critical point, the Coherent Anomaly Method (CAM) of Suzuki [15] provides a simple and powerful tool to determine the exact critical properties of the system by making use of the “canonical” sequence of mean field (MF) approximations. The CAM theory is based on the general property of a series of approximations that, although an individual approximation gives only the “classical” behavior near the critical point, a series of approximations contains information about the rigorous limit. When we consider any physical quantity of interest \(\Phi(T)\), the uniform behavior of the MF approximations of \(\Phi(T)\) mathematically translates in a unique critical exponential \(g(\Phi, \text{MF})\), such that close to the MF critical temperature \(T^*\), \(\Phi(T)\) behaves as

\[
\Phi(T) \approx \hat{\Phi}(T^*) \left(\frac{T - T^*}{T^*}\right)^{g(\Phi, \text{MF})}. \tag{22}
\]

Suzuki called the amplitude factor \(\hat{\Phi}(T^*)\) the coherent anomaly factor and noted that it can be written as

\[
\hat{\Phi}(T^*) \approx \left(\frac{T^*}{T^* - T^*}\right)^{\Delta g(\Phi)}. \tag{23}
\]

The exponent \(\Delta g(\Phi)\) is the difference between the exact critical exponent \(g^*(\Phi)\) associated with \(\Phi\) and the corresponding MF exponent \(g(\Phi, \text{MF})\), while \(T^*\) is the exact critical temperature. When we make use of the above basic equation, CAM allows us to compute both the
Table I. — Critical temperatures and coherent anomaly factors for magnetic susceptibility $\chi$ for the $n$-square approximations for the (10) orientation of 2D square lattice. The CAM estimates for the exact temperature and the magnetic susceptibility critical exponent obtained from this table are $T^*_c = 2.2692 \pm 0.0006$ and $\gamma = 1.748 \pm 0.008$, respectively.

<table>
<thead>
<tr>
<th>$n$</th>
<th>$T_c(n)$</th>
<th>$\bar{\chi}(T_c(n))$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.425666</td>
<td>1.416973</td>
</tr>
<tr>
<td>2</td>
<td>2.376130</td>
<td>1.849774</td>
</tr>
<tr>
<td>3</td>
<td>2.350312</td>
<td>2.250939</td>
</tr>
<tr>
<td>4</td>
<td>2.334538</td>
<td>2.629717</td>
</tr>
</tbody>
</table>

Table II. — Critical temperatures and coherent anomaly factors for magnetic susceptibility $\chi$ for the $n$-step approximations for the (11) of 2D square lattice. The CAM estimates for the magnetic susceptibility critical exponent obtained from this table is $\gamma = 1.789 \pm 0.03$. $T^*_c$ was assumed known at Onsager’s value [13].

<table>
<thead>
<tr>
<th>$n$</th>
<th>$T_c(n)$</th>
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<tr>
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<td>2.425666</td>
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</tr>
<tr>
<td>2</td>
<td>2.364830</td>
<td>1.981231</td>
</tr>
<tr>
<td>3</td>
<td>2.337386</td>
<td>2.538502</td>
</tr>
<tr>
<td>4</td>
<td>2.322445</td>
<td>3.039039</td>
</tr>
</tbody>
</table>

exact critical temperature $T^*$ and the exact critical exponent from $g(\Phi, \text{MF})$ from a sequence of at least three MF approximations, calculable from a CVM sequence.

When the mean field critical temperatures $T^*_c(\text{MF})$ are very close to the exact value $T^*$ we can use (23) in this form. However, in practice $T^*_c(\text{MF})$ deviate significantly from $T^*$, necessitating a modification to (23). For a physical quantity $\Phi$, we write the modified equation corresponding to (23) as

$$\Phi(T_c(n)) = A(T_c(n) - T^*)^{-\Delta \gamma} (1 + B(T_c(n) - T^*)) .$$

(24)

This non-linear equation is solved for $T^*$, $A$, $\Delta \gamma$ and $B$ iteratively. The starting values of the parameters for the iteration are obtained as follows. Considering $T_c(n)$ as a $1/n$ sequence, Neville’s table [16] is constructed, to obtain an estimate of $T^*$. Once knowing the initial values for $T^*$ (which was 2.2728 and 2.2731 for the $n$-square and $n$-step sequences, respectively), the initial values of $A$ and $\Delta \gamma$ follow from a linear least-square fit assigning $B = 0$. Starting with these initial estimates, refined values of the unknowns are obtained. These values are reported in Tables I and II, and are seen to be in fairly good agreement with the exact values. In the $n$-step sequence for the (11) orientation, however, the solution is less satisfactory than for the $n$-square sequence for the (10) orientation, and we found it necessary to use the known exact value for $T^*$ in the $n$-step case, rather than deriving it from the CAM approach.

The same kind of analysis was then applied to determine the exact critical exponent for the surface tension. In Figure 4, we plot $\ln(\sigma_{(10)}^{\text{SP}})$ against $\ln(1 - T/T_c(n))$ for the $n$-square cluster sequence. The slopes of these straight lines correspond to the mean field exponent 1 for $\sigma^\text{SP}$ as in (16), while the intercept with the ordinate axis leads to the coherent anomaly
factor associated with $\sigma$. These factors associated with the 1-, 2-, 3- and 4-squares are 6.4322, 5.7365, 5.4596 and 5.3219, respectively. From these factors and from equation (24), in which we used the exact value for $T^*$, we come to the estimate of the exact critical exponent $\mu$ of 1.0052, which is close to Onsager's exact value $\mu = 1$.  

Away from $T_c$, there is no unique extrapolation procedure. Although it has been proved that the free energy of the $n$-cluster CVM converges to the exact result [17], how it converges is not known. We may consider $T_c(n) - T^*$ as the extrapolation parameter. For a given value of $T/T_{C}(n)$, we may extrapolate polynomial of $\sigma(n)$ using Neville's algorithm [16], or by rational functions. The value of $\sigma$ at the abscissa $T_c(\infty) - T^* = 0$ is an estimate of an infinitely long cluster.  

In Figure 5, we took advantage of the exact $\sigma^T_{(10)}$ value obtained by Onsager [13] and plotted the difference $\sigma_{(10)}(n) - \sigma^T_{(10)}$ as a function of the reduced temperature $T/T_{C}(n)$ for the SP and S formulations. The $\sigma^{SP}$ systematically over-estimates $\sigma^*$ as shown in the four upper curves, while $\sigma^{S}$ under-estimates $\sigma^*$ as in the lower four curves. As $n$ increases in each case, the curves monotonically approach zero. Figure 5 shows that the extrapolated values of $\sigma^{SP}$, which are indicated with error bars, match almost perfectly the exact results of Onsager [13]. In close inspection, we see the fitting is fairly good for $T/T_{C}(n)$ ranging from 0.5 to 0.9, while a systematic deviation occurs for $T$ close to $T_c$. This behavior is interpreted as the cross-over between the MF and the critical regimes. In the latter domain, the polynomial extrapolation
Fig. 5. — The difference between $\sigma_{\langle 10 \rangle}(n)$ and Onsager's exact result $\sigma^*$ [13] against the reduced temperature $T/T_c(n)$ for 2D square lattice. The positive-side curves are the SP method results for $n = 1$, 2, 3- and 4-square approximations, respectively, from the top. The negative-side curves are the sum method results for $n = 1$- and 2- and 3-square approximations, from the bottom. The extrapolated curves are the center two shown with full diamonds. The extrapolated curve for $\sigma^{SP}$ with error bars matches the rigorous curve in a broad range of temperatures.

is necessarily unstable. The fourth curve from bottom in Figure 5 is the extrapolated curve for $\sigma^S$. The extrapolation of $\sigma^S$ is less accurate than the extrapolation of $\sigma^{SP}$, the reason being understood as due to the small number of clusters involved in the sequence.

Figure 6 plots the similar information for the (11) boundary. The extrapolated curve, shown with error bars, is very close to the exact $\sigma^*$ calculated by Fisher and Ferdinand [14].

It is to be noted in Figures 5 and 6 that, using the same cluster of a certain size, the sum method is more reliable than the SP method. The explanation for this observation is left to the future studies. Another noteworthy feature in these plots is that in the same $n$ approximation, $\sigma^{SP}(n)$ and $\sigma^S(n)$ bracket the exact value, and as the approximation improves, the interval between them shrinks. This result suggests another extrapolation scheme based on the simultaneous use of $\sigma^{SP}(n)$ and $\sigma^S(n)$. When we write

$$\bar{\sigma}(n) = \frac{1}{2} (\sigma^{SP}(n) + \sigma^S(n)) \quad \text{and} \quad \tilde{\delta}(n) = \frac{1}{2} (\sigma^{SP}(n) - \sigma^S(n))$$

(25)

we find that the extrapolations of $\sigma^{SP}(n)$ and $\bar{\sigma}(n)$ are the two best estimates of the rigorous value we can achieve based on our four $n$ approximations. The results based on $\bar{\sigma}(n)$ are not shown in Figures 5 and 6 in order not to confuse the plots.
Fig. 6. — The difference between $\sigma_{(11)}(n)$ and the exact result $\sigma^*$ due to Fisher and Ferdinand [14] against the reduced temperature $T/T_c(n)$ for 2D square lattice. The positive-side curves the SP method results for $n = 1$, 2-, 3- and 4-step approximations, respectively, from the top. The negative-side curves are the sum method results for $n = 1$, 2- and 3-step approximations from the bottom. The extrapolated curves are the center two curves. As in Figure 5, the SP extrapolated curve with error bars is in close agreement with the exact solution.

5. Cubic Lattice

The purpose of the study in the previous sections on the 2-D systems was to examine how good the SP method is compared with the known rigorous results. Since these sections have established the reliability of the SP method, we now proceed to the 3-D system.

We need at least three approximations to extrapolate to the limit of infinitely large size cluster, which corresponds to the rigorous limit. The commonly used sum method for IPB is time consuming because different variables are to be assigned to each lattice plane position parallel to the boundary and hence the number of variables becomes too large to obtain sufficient accuracy. Compared with the sum method, the mathematical labor of the SP method is much less, and makes the 3-D calculations tractable to divergent cases.

The three clusters used in the three CVM approximations are shown in Figure 7. (a) is a cube ($n = 1$). (b) is a combination of a cube plus a 10-point clusters. The latter is made of two 5-point crosses placed on adjacent planes. (c) is a combination of a double cube plus a 10-point clusters. Although these three are not on a canonical series in Suzuki’s definition [15], we use them mainly for the mathematical necessity.
Fig. 7. — Clusters used for the present analysis of the 3D simple cubic lattice. (a) is the cube \(n = 1\). (b) is a combination of a cube plus a cross shaped 10-point cluster \(n = 2\). (c) is a combination of a double-cube plus a 10-point cluster \(n = 3\).

The information similar as that for Figures 5 and 6 is plotted in Figure 8 for the \(\langle 100\rangle\) orientation IPB in the simple cubic lattice. For the comparison purposes, the approximate but fairly accurate values of \(\sigma^*\) were taken from tabulated Monte Carlo data [18] (actually twice the listed value). The plotted curves are for (a) and (b) clusters in Figure 7 only, although (c) was also calculated. The values calculated by the approximations are \(T_c(n) = 4.580988(a), 4.560239(b), 4.544872(c)\) and the anomaly coefficients for the magnetic susceptibility are \(\bar{\gamma}(n) = 0.416973(a), 0.453057(b), 0.496270(c)\). Using these data in the CAM formulation, we derived the estimate of \(kT_c/\epsilon = 4.51 \pm 0.01\). Note that different from Figures 5 and 6, the abscissa in Figure 8 is \(\beta \equiv \epsilon/kT\).

In the 3D simple cubic lattice, a plane parallel to the boundary is the 2D square lattice. Therefore, the boundary may itself undergo a phase transition at a temperature \(T\) lower than the bulk Curie temperature [19], the boundary switching from a disordered to an ordered state. Such phase transition occurs in the SP-CVM, although not obvious in Figure 8. Below the transition temperature we follow the stable branch for \(\sigma\). The curves for the 3D case in Figure 8 display the general features we discussed in the 2D case, but the significant difference is that the individual results in the 3D are almost one order of magnitude closer to the rigorous result than those in the 2D cases. The results of the three approximations were extrapolated using Neville’s method.

As was the case in 2D boundaries, \(\sigma^{SP}(n)\) and \(\sigma^{S}(n)\) bracket the exact value, and as the approximation improves the difference between them shrinks. This result is a direct consequence of the difference of behaviors between \(\sigma^{SP}\) and \(\sigma^{S}\) near the Curie temperature as shown in (16, 17). The CAM analysis based on the three approximations (a), (b) and (c) in Figure 7 leads
Fig. 8. — Difference between the CVM approximations for $\sigma$ and Monte Carlo results of the (100) orientation IPB in the simple cubic lattice. The two top (SP-CVM) and the two bottom (S-CVM) curves are for the $n = 1$ and 2 cluster approximations, as defined in Figure 7. The middle curve is for the extrapolation of the arithmetic average of the SP-CVM and S-CVM in (21).

to the coherent anomaly factor $\sigma_{SP}^S(n) = 3.65364(a), 3.33375(b), 3.08290(c)$, and the estimate of the critical exponent for the surface tension as $\mu = 1.239 \pm 0.015$, which interpolate between $\mu_{SP} = 1$ in (16) and $\mu_{S} = 1.5$ in (17). Taking into account this observation, in extrapolating the results of the clusters in Figure 7, we constructed $\bar{\sigma}$ and $\delta$ defined in (25), rather than considering the SP and S surface tensions. The middle curve and the error bars in Figure 8 are the extrapolations of $\bar{\sigma}$ and $\delta$ thus constructed. Figure 8 shows that the extrapolated curve matches well the MC [18] data in the full range of temperature.

6. Summary and Concluding Remarks

Equilibrium properties of IPB's are customarily studied using the sum method (S-CVM) which computes the boundary profile, based on which the excess free energy, or the surface tension, $\sigma$ is derived. When only $\sigma$ is of interest, the Scalar Product method (SP-CVM) can be used instead. The latter calculates $\sigma$ as the scalar product of two vectors representing the two bulk phases which meet at the IPB, and hence almost no extra computational labor is required in addition to calculating the bulk phases. For this reason, SP-CVM can be used in a series of cluster approximations including relatively large size clusters, and their results can be extrapolated to the limit of infinitely large size cluster which corresponds to the rigorous limit.
In Sections 3 and 4, we apply the SP method to the Ising model IPB in a 2-dimensional square lattice to ascertain the reliability of the method. These sections confirm the merit of the SP method by comparing with the known rigorous results of Onsager [13] and Fisher-Ferdinand [14]. We also see that when both SP- and S-methods can be computed, the former overestimates the $\sigma$ value while the latter underestimates it, making their average to arrive at better result than either of the two separately.

In Section 5 we apply the two methods to the 3-dimensional simple cubic lattice Ising model. We calculate the SP- and S-formulations using three finite-size clusters, form their arithmetic averages and extrapolate them to the infinite size cluster. The extrapolated results agree well with the known Monte Carlo results. A noticeable feature of the 3-D calculations is that extrapolations to the rigorous limit are almost an order of magnitude more accurate numerically compared with the 2-D cases.

It is expected that the SP method will be applied to obtaining information of the rigorous values of the boundary tension $\sigma$ of IPB's in wider classes of 3-dimensional problems so far regarded impractical to compute.

Appendix

Proof of the S.P. Equation

A.1 Basic Relations. — The proof of equation (1) for an IPB is rooted in the dimension-reduction idea presented in reference [12]. When the system is one-dimensionally inhomogeneous, as in the present case, the CVM can be rigorously formulated using a cluster made of two adjacent parallel planes ($^1$) (planes parallel to the IPB). Different from the usage in the text, in this appendix we use an integer $n$ to indicate the position of the lattice plane along the gradient direction. The configurations of a parallel plane are denoted by Greek letters $\mu, \nu, \xi, \eta, \text{ etc.}$ Each of them is for a configuration of $N$ lattice points on a parallel plane, $N$ being a macroscopic number. The probability of finding a configuration $\mu$ on a plane at $n$ is written as $p_n(\mu)$, and that for a pair of planes with $\mu$ on $n$ and $\nu$ on $n+1$ is written as $q_{n+h}(\mu, \nu)$, where the subscript $h$ is used for $h \equiv 1/2$ for the sake of brevity, $n+h$ indicating the center position of the plane pair. The interaction energy is written as $\epsilon(\mu, \nu)$ per pair of planes, which may include the intra-plane interactions.

In an inhomogeneous system, we need the continuity relations of the form

$$p_n(\nu) = \sum_\mu q_{n-h}(\mu, \nu) = \sum_\xi q_{n+h}(\nu, \xi). \quad (A.1)$$

Another constraint for $q$'s is the normalization for each pair position:

$$\sum_\mu \sum_\nu q_{n+h}(\mu, \nu) = 1. \quad (A.2)$$

When we minimize the free energy with respect to the pair variable $q$'s, we treat the constraint relations in (A.1) and (A.2) by using Lagrange multipliers $\alpha_n(\nu)$ and $\lambda_{n+h}$, respectively.

($^1$) It may be worthwhile to comment that CVM is exact for one-dimensional system of nearest neighbor interaction when a pair is taken as the basic cluster, however large the number $M$ of species may be. When there are $N$ spins on a parallel plane, we can regard one configuration of the entire parallel plane as one species. Then we are treating a one dimensional system whose lattice point is occupied by one of the $M = 2^N$ (a macroscopic number) species, and the treatment is exact.
The minimization leads to the standard form of the basic equations in the Natural Iteration formulation of the CVM [5,11]:

\[ q_{n+h} (\mu, \nu) = \exp (\beta \lambda_{n+h} - \beta \epsilon (\mu, \nu)) (p_n (\mu) p_{n+1} (\nu))^{1/2} \exp (\alpha_n (\mu) - \alpha_{n+1} (\nu)) . \]  

(A.3)

As is usually the case [5,11], when the free energy \( F \) is a minimum, it can be simplified as

\[ F = \sum_n \lambda_{n+h} \]  

(A.4)

which means \( \lambda_{n+h} \) can be interpreted as the local free energy density per bond.

Since \( p_n (\mu) \) and \( \alpha_n (\mu) \) always appear in a combination, the transformation is simplified when we define

\[ f_n (\mu) \equiv (p_n (\mu))^{1/2} \exp (\alpha_n (\mu)) \]
\[ g_n (\mu) \equiv (p_n (\mu))^{1/2} \exp (-\alpha_n (\mu)) \]
\[ \Gamma (\mu, \nu) = \exp (-\beta \epsilon (\mu, \nu)) \]  

(A.5)

to write (A.3) as

\[ q_{n+h} (\mu, \nu) = \exp (\beta \lambda_{n+h}) f_n (\mu) \Gamma (\mu, \nu) g_{n+1} (\nu) . \]  

(A.6)

It is important to point out in (A.3) that our choice of the Lagrange multiplier \( \alpha_n (\mu) \) is such that the minus sign appears in front of \( \alpha_{n+1} (\nu) \) at \( n + 1 > n + h \). This means in (A.6) the subscript indicating the position of the \( g \) factor is always larger than that of the \( f \) factor.

When we use the equilibrium relation (A.3) in the continuity equation in (A.1), and write it in \( f, g \) and \( \Gamma \), we obtain

\[ f_n (\nu) = \exp (\beta \lambda_{n-h}) \sum_\mu \Gamma (\mu, \nu) f_{n-1} (\mu) \]
\[ g_n (\nu) = \exp (\beta \lambda_{n-h}) \sum_\xi \Gamma (\nu, \xi) g_{n+1} (\xi) . \]  

(A.7)

A.2 Proof. — This proof is based on the same idea as the one presented previously [10], but a significant additional consideration on the duality at the end of the section makes the proof logically complete. We start with the following expression and sum it first over \( \nu \) and then over \( \mu \) to obtain two expressions:

\[ \sum_\mu \sum_\nu f_n (\mu) \Gamma (\mu, \nu) g_{m+1} (\nu) = \]  

(A.8)

\[ = \sum_\mu f_n (\mu) \exp (-\beta \lambda_{m+h}) g_m (\mu) = \sum_\nu f_{n+1} (\nu) \exp (-\beta \lambda_{n+h}) g_{m+1} (\nu) . \]

When we rewrite this as

\[ \sum_\mu f_n (\mu) g_m (\mu) = \exp (-\beta \lambda_{n+h} + \beta \lambda_{m+h}) \sum_\mu f_{n+1} (\mu) g_{m+1} (\mu) \]  

(A.9)

the recurrence nature of this relation can be clearly seen.

In using (A.9), we start with

\[ n = -k \quad \text{and} \quad m = +k \]  

(A.10)
and operate the recurrence relation $M$ times, $M$ being chosen as

$$M \geq 2k. \quad (A.11)$$

Then we arrive at

$$\exp \left( \beta \sum_{n=-k}^{k-1} \sum_{\mu} f_{-k} (\mu) g_k (\mu) \right) = \exp \left( \beta \sum_{n=-k+1}^{k+M} \sum_{\mu} \lambda_{n+h} \right) \sum_{\mu} f_{-k+1+M} (\mu) g_{k+M+1} (\mu). \quad (A.12)$$

In the transformation, some of the $\beta \lambda$ terms cancel because of the condition (A.11).

We note in (A.12) that $M$ appears only on the right-hand side. When we choose $M$ large enough, we can make both of the lattice plane positions $-k + 1 + M$ and $k + M + 1$ lie deep inside the right-hand side phase II, and make $\lambda$'s between these positions be as close as the bulk value $\lambda^{(0)}$. At the same time we choose $-k$ and $k$ so that the phase boundary lies between the two, and also we require that $k$ is also large enough so that $-k$ is deep inside the phase I and $k$ is inside II. Under these conditions, the quantities in (A.12) reduce to

$$\lim_{M \to \infty} \sum_{\mu} f_{-k+1+M} (\mu) g_{k+M+1} (\mu) = \sum_{\mu} f^{II} (\mu) g^{II} (\mu) = 1 \quad (A.13)$$

$$\lim_{k \to \infty} \sum_{\mu} f_{-k} (\mu) g_k (\mu) = \sum_{\mu} f^{I} (\mu) g^{II} (\mu) = \sum_{\mu} (p^I (\mu) p^{II} (\mu))^{1/2} \quad (A.14)$$

$$\sum_{n=-k}^{n=k-1} \lambda_{n+h} \lim_{M \to \infty} \left( \sum_{n=-k+1+M}^{n=k+M} \lambda_{n+h} \right) = \sum_{n=-k}^{n=k-1} \left( \lambda_{n+h} - \lambda^{(0)} \right) = A\sigma. \quad (A.15)$$

In (A.13) and (A.14) we use the fact that the Lagrange multiplier $\alpha$'s vanish in bulk phases. In (A.15), $A$ is the sectional area of the interphasial boundary. Substitution of (A.13), (A.14) and (A.15) in (A.12) results in equation (1) in the text. This completes the proof of (1).

An important comment is in order. In (A.10), we chose $n \leq m$. However, it is equally possible to choose

$$n = +k \quad \text{and} \quad m = -k. \quad (A.16)$$

Then we see that the right-hand side of (A.15) becomes $-A\sigma$, to lead to

$$\exp (+Na\beta\sigma) = \sum_{\nu} \left( p^I (\nu) p^{II} (\nu) \right)^{1/2} \quad (A.17)$$

corresponding to equation (1) in the text. This duality is explained as follows. The basic set of equations in (A.3) is of the standard form of the Natural Iteration Method (NIM) [5] to obtain the equilibrium state corresponding to the minimum of the free energy $F$. When we use the NIM numerically, we can prove that $F$ always decreases [5] and hence the converged solution is for the minimum of $F$. However, when we work on (A.3) analytically as we are doing in this paper, the set of basic equations in (A.3) contains the solutions for both the minimum and the maximum of $F$. In answering the question whether (A.15) is a minimum or a maximum of $F$, we can conclude it is a minimum based on the following reasoning, without calculating the second derivative of $F$. In calculating $\sigma^S$ in the sum method in Figures 5 and 6, either the Newton-Raphson iteration method or the NIM can be used. Since it was proved [5] that the NIM always converges to the stable equilibrium value corresponding to a minimum of $F$, we know the $\sigma^S$ results in Figures 5 and 6 are for a minimum of $F$. The close numerical proximity between $\sigma^S$ and $\sigma^{SP}$ in these figures guarantees that the latter is also a minimum of $F$. 
References