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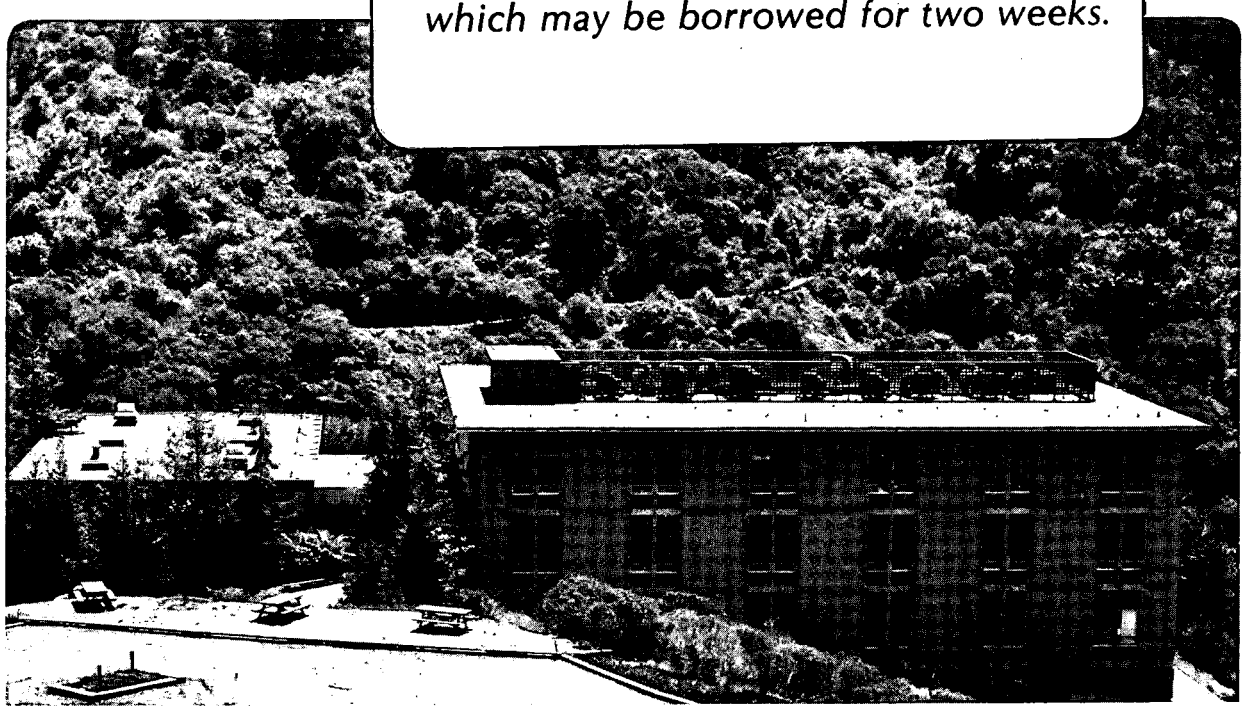

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AN EXACTLY-SOLUBLE MODEL FOR {001} ANTIPHASE BOUNDARIES IN BINARY ORDERING ALLOYS

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ABSTRACT

An *exactly soluble* model which mimics the properties of {001} antiphase boundaries in the face-centered-cubic substitutional alloys (Ising antiferromagnets) with only nearest-neighbor interactions is developed. The three-dimensional model is extended to any dimension, including one- and two-dimensional systems. For three-dimensional systems, it is proven that, in the thermodynamic limit, antiphase boundaries are unstable at all temperatures. It is postulated that antiphase boundaries are unstable for all thermodynamic systems with dimension greater than one. In one dimension, where antiphase boundaries can be defined mathematically, the concentration of antiphase boundaries is one half at both zero and infinite temperatures, but at all temperatures in between, the concentration is less than one half. Antiphase boundaries are found at equilibrium in higher-dimensional systems with small sizes, the order of those used in Monte Carlo simulations of the Ising model. The implications of this unusual size effect are discussed.

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I. Introduction

The definitive theory of the ordering face-centered-cubic *(fcc)* substitutional alloys is yet to be found.[1] Ultimately, the theory must incorporate a description of both the electronic and the thermodynamic properties of the alloy, but the extreme complexity of the problem usually requires simplification, commonly achieved by considering one of the two properties[2].

The most common approach to developing a theory for the thermodynamic properties of the ordering alloys makes use of the similarities between the simple binary substitutional alloy and the antiferromagnetic Ising model in the presence of a magnetic field. In this approach, an A-B binary alloy is mapped onto the Ising model: an atom of type A (B) is equivalent to an up (down) spin. The chemical potential difference between atoms of different types is equivalent to an external magnetic field. The energy is then written:

$$E = \sum_{ij} J_{ij}\ \sigma_i \sigma_j - h \sum_i \sigma_i$$

where σ_i is an Ising spin at site i which can take on the values ± 1, J_{ij} is the interaction energy between spins at sites i and j, and h is the external magnetic field. (The

particular model under consideration here is defined in an *fcc* lattice and such that $J_{ij} = J > 0$ for i and j nearest-neighbors, and $J_{ij} = 0$ for all other pairs).

Real alloys are significantly more complex than the simple Ising model analogy. In particular, many body effects[3], atomic-size,[4] and fermi-surface[5,6] properties are all expected to play important roles in determining the true phase stability. It is unlikely that these effects can all be reduced to pairwise interactions. The Ising model, however, does provide a good starting point for understanding the thermodynamic properties of alloys, and the model can be made more realistic by successive inclusion of some of the neglected effects. In addition, the Ising model provides an important means for assessing the effects of approximations contained in theories, for any theory which solves the more complicated real alloy problem must be able to solve the simpler Ising model.

Exact solutions to the Ising model are known only for one and two dimensions. Solutions for three-dimensional systems are known only through approximate methods. The effects of the approximations must be clearly understood and great care must be taken to insure that the results of any calculation truly represent the physics of the system, and not the shortcomings of the approximation.

Thus far, approximate methods have resulted in a widely accepted topology[7] for the phase diagram of the nearest-neighbor *fcc* Ising antiferromagnet, but some discrepancies still remain. The thermodynamic calculations for this Ising system fall into three categories: small cluster variational techniques, numerical simulations, and low- and high-temperature expansions. The results of the different methods are often compared among themselves, for consistency, and also compared with experimental results believed to reflect Ising-like behavior (e.g. the Cu-Au alloys).

One early small-cluster calculation on the *fcc* binary alloys was due to Shockley[8], who calculated the Cu-Au phase diagram using a mean-field approach. The agreement with the experimentally known Cu-Au phase diagram was not satisfactory: the

calculated phase diagram was topologically different from that of the experiments. The following years brought the development and application of the quasi-chemical method[9], and later the cluster variation method[10–13] (CVM). The latter led to qualitatively good agreement with the experimentally determined phase diagrams, and the agreement with experiment was improved even further with the inclusion of "many-body" effects[14]. In addition, CVM results produced the currently accepted topology of the nearest-neighbor *fcc* Ising antiferromagnet's phase diagram.

One drawback of the small cluster variational techniques is that the finite size of the cluster imposes conditions on which phases can be examined. The cluster size is selected for the investigation of the particular phases believed to appear in the phase diagram, and this requires some previous knowledge of the phase diagram. Another shortcoming is that the number of states can only be counted approximately.

As an alternative to the small cluster approach, many investigators have resorted to numerical calculations utilizing Monte Carlo methods. Unlike the small cluster variational methods, Monte Carlo methods require no prior knowledge of the phase diagram, but interpretation of the results is often difficult, and finite-size effects are not always entirely understood.

The initial Monte Carlo results of Binder[15] and Phani et. al.[14] for the *fcc* binary alloy with only nearest-neighbor interactions disagreed with those of CVM, which necessitated reexamination of both results[17–20]. The conflict centered on the exact location of the triple-point [the point where the disordered, the $L1_0$ (AB-type), and the $L1_2$ (AB_3-type) phases are in equilibrium]. While the calculated transition temperatures of the stoichiometric compounds were not too different (the Monte Carlo calculations gave slightly lower transition temperature for all compositions of the alloy), Binder's Monte Carlo results placed the triple-point at $T = 0$, and CVM placed the triple-point temperature at a nonzero value, of the order of the pair-interaction energy[9–12].

One source of this discrepancy arises from the frustration present in the *fcc* lattice. The frustration may lead to the appearance of {001} antiphase boundaries, which are explicitly excluded in CVM, and difficult to interpret in Monte Carlo studies. A {001} antiphase boundary in the $h = 0$, $T = 0$ case is depicted in figure 1, using a description similar to Kikuchi and Sato's[21]. The configurations of the four possible (001) planes for the perfectly ordered case are shown. Each dark symbol (either square or circle) represents an up spin (Cu atom), and the lighter symbols represent down spins (Au atom). The $L1_0$ phase is constructed by stacking the planes in one of four configurations: (...AaAaAaAa...), (...AbAbAbAb...), (...BaBaBaBa...) or (...BbBbBbBb...). An antiphase boundary is introduced by a slip of one half of the lattice by $[a/2, a/2, 0]$ where a is the cubic lattice spacing. This is the equivalent of going from (...AaAaAaAa...)-type stacking to (...AaAaBbBb...)-type stacking. (In the definition of antiphase boundary used here, it extends throughout the entire crystal; domains separated by antiphase boundaries are not considered). The dashed boxes in the figure contain one nearest-neighbor tetrahedron of the face-centered-cubic lattice, with two atoms from each of the planes. Each of these tetrahedra has two up spins and two down spins, the minimal energy configuration, for both Ba and Bb stacking order. This is also true for Aa and Ab stacking. It therefore costs no energy to stack the planes in a random order (...ZzZzZzZz...) where each Z (z) is a plane of type A (a) or B (b). The system has an infinitely degenerate ground state. An infinitesimal next-nearest-neighbor interaction, however, removes this degeneracy.

Antiphase boundaries are present in the Monte Carlo calculations[18,-20], as revealed by studies of the triple point region. The presence of antiphase boundaries in the Monte Carlo results raises important issues. In Binder's calculations, one antiphase boundary would result in a state with no long-range order, but, physically the system still has a large degree of long-range order, at least in two dimensions, and is very different from the random, disordered configuration. With a more precise definition of

order (which accounts for the long-range order still present in the antiphased state), the Monte Carlo calculations yield a nonzero triple-point temperature[18–20]. The puzzle is not completely solved, however, for the triple-point temperature in the Monte Carlo results is roughly two-thirds of the triple-point temperature predicted by the best available CVM results[7]. In addition, the transition temperatures predicted by the Monte Carlo methods are still consistently lower than those of CVM.

It is not yet clear whether or not antiphase boundaries appear in the true phase diagram of the nearest-neighbor *fcc* Ising antiferromagnet. There are reasons to expect that the boundaries might be present. Antiphase boundaries cost no energy, but there is an entropy associated with their presence. This entropy is generally neglected. In the thermodynamic limit, the free energy is of order n^3 [where n^3 is the number of spins (atoms) in the system], and the contribution from antiphase boundaries is of order n, hence negligible.

This argument suggests that the antiphase boundaries are present even as $T \rightarrow 0$, but do not affect the thermodynamic properties of the system. Clearly, the system with antiphase boundaries is considerably different from the system without them, regardless of their influence on the free energy, and so it is important to determine whether or not antiphase boundaries exist at a given temperature.

Slawny[22] made significant progress in this direction when he suggested that the one-dimensional structure of this system does directly influence its thermodynamics. Slawny noted that the excitation spectrum of a particular ground state is extremely sensitive to its one-dimensional structure. Since the excitation spectrum determines a particular ground state's thermodynamic properties, the one-dimensional disorder has a dramatic influence on the thermodynamics of the system. Slawny's exact arguments apply to a class of systems satisfying three criteria: the system must have a *finite* number of degenerate, *periodic* states in the ground-state manifold which all meet the *Peierls' condition*[23]: that there be an energy gap between the ground state and the first

excited state. For these systems, the "true" ground state is the state which admits the largest number of low-lying excitations.

The nearest-neighbor *fcc* Ising antiferromagnet clearly violates the first two of these conditions. The ground-state manifold contains an *infinite* number of *not necessarily periodic* states. Slawny introduces interactions into the model which insure long-range order in three dimensions so that the conditions of his theorem are met, and then considers the limit as these interactions go to zero. He concludes that antiphase boundaries do not appear in the low temperature expansion for the nearest-neighbor *fcc* Ising antiferromagnet. Based on Slawny's arguments, Mackenzie and Young[24], and later, Lebowitz et al.[25] calculated low-temperature expansions about the "true" ground state: the ordered $L1_0$ phase *without* antiphase boundaries. This is a somewhat surprising result: the "true" ground state of the system is "selected" based solely on entropic contributions, and the result of this "selection" is the completely ordered state.

Slawny's conclusions most probably apply to the *fcc* Ising system under consideration here, but there is some danger in his approach. The infinite one-dimensional degeneracy of the model only exists in one point of parameter space. The fact that an infinitesimal next-nearest-neighbor interaction removes the infinite degeneracy suggests that limiting processes may not be applicable.

Assuming that Slawny's conclusions are correct, there is still more work to be done. It is of interest to understand the behavior of the Ising model at temperatures for which low-temperature expansions are no longer valid. Slawny's arguments do not indicate whether or not antiphase boundaries appear at higher temperatures.

The purpose of this paper is to investigate, in greater detail, whether or not antiphase boundaries appear in the equilibrium phase diagram of the nearest-neighbor *fcc* Ising antiferromagnet (and by analogy, in the simple binary substitutional alloy). The approach chosen is the construction and solution of an exactly soluble model for cubic {001} antiphase boundaries which violates the first two Slawny criteria. This violation

is of the kind encountered in the nearest-neighbor *fcc* Ising antiferromagnet. The insight gained by solution of this simple model can be applied to the more difficult Ising problem, and to understand the role of antiphase boundaries in more complex real alloys.

Section II of this paper develops the model, which is subsequently solved in section III. Analysis of the results comprises section IV, and section V contains the conclusions.

II. The Model

The excitation spectra of each state in the ground-state manifold of the nearest-neighbor *fcc* Ising antiferromagnet are characterized by a set of common low-lying excitations. State dependent differences in the spectra appear at the third-level of excitation[26]. This difference is directly related to the antiphase structure. For zero external field (chemical potential difference), the state with the highest number of third-level excitations is the $L1_0$ phase, and this number decreases as the number of antiphase boundaries increases.

The model constructed here mimics these properties as closely as possible while still allowing a simple exact solution for the thermodynamic properties. Similarly to the nearest-neighbor *fcc* Ising antiferromagnet, the model below has an *infinite* ground state degeneracy in which the states are *not necessarily periodic*. The antiphase dependence of the excitation spectra is very similar in the two systems. Each state in the ground-state manifold of the constructed model admits a common set of lowest-lying excitations, but the number of second-level excitations is determined by the antiphase structure of the state: a state with more antiphase boundaries has fewer second-level excitations.

The model system is composed of n planes, each of which contains N sites. The planes are indexed by the subscript k, and each site within a plane is indexed by the

subscripts i and j. The thermodynamic variables are defined to be σ_{ijk} and Σ_k, both of which can assume the values ± 1. A configuration is designated by $\{\sigma, \Sigma\}$ and the internal energy is:

$$E(\{\sigma, \Sigma\}) = \varepsilon \left\{ \sum_{ijk} (1 + \sigma_{ijk}) + (1/4) \sum_{ijk} (1 + \sigma_{ijk})(1 + \sigma_{ij(k+1)})(\gamma_0 - \gamma \Sigma_k \Sigma_{(k+1)}) \right\}$$

where the indices run over the entire system, and periodic boundary conditions are *not* assumed. The first term accounts for the elementary excitations of the sites; they have energy 2ε (The energy scale is set by the value of ε.). The second sum represents an antiphase-structure dependent interaction between excitations on adjacent planes. An antiphase boundary in the model occurs at a plane k such the $\Sigma_k \Sigma_{(k+1)} = -1$. The factors containing the σ's impose the restriction that both sites i, j, k and $i, j, (k+1)$ must be excited. The parameters γ_0 and γ are positive dimensionless constants such that $\gamma < \gamma_0$. The γ_0 term in the interaction is antiphase-structure independent, but the γ term is not. The energy of two juxtaposed excitations is $(4 + \gamma_0 - \gamma)\varepsilon$ in the normal state, and $(4 + \gamma_0 + \gamma)\varepsilon$ in the antiphased state.

The partition function of this system, which contains nN sites, is then written:

$$Z_{nN} = \sum_{\{\sigma,\Sigma\}} e^{-\beta E(\{\sigma,\Sigma\})}$$

where $\beta = 1/k_B T$, k_B is Boltzmann's constant, and T is the temperature.

III. The Solution of the Model

Let μ_i denote the number of sites in plane i which are excited, and ν_i the number of these for which the equivalent site in plane $(i+1)$ is also excited. The number of ways configurations for a two plane system is

$$C_N^{\mu_1} C_{\mu_1}^{\nu_1} C_{N-\mu_1}^{\mu_2 - \nu_1} \tag{1}$$

where C_N^M is the binomial coefficient:

$$C_N^M = \frac{N!}{(N-M)!\,M!}.$$

The first coefficient in (1) is the number of ways to choose the μ_1 sites on plane 1, the second, the number of ways to choose the ν_1 sites on plane 2 which are juxtaposed with an excitation on plane 1, and the last, the number of ways to place the remaining excitations on plane 2. There are restrictions on the values for μ_1, ν_1, and μ_2. All physically allowed configurations of the planes are included by summing over all terms for which expression (1) is defined.

The analysis above is easily extended to the case of n planes. The energy in terms of the μ_i and ν_i is

$$E = 2\varepsilon \sum_{i=1}^{n} \mu_i + \varepsilon \sum_{i=1}^{n-1} \nu_i(\gamma_0 - \gamma\Sigma_i\Sigma_{i+1}). \tag{2}$$

The partition function is

$$Z_{nN} = \sum_{\{\Sigma\}} \sum_{\mu_1} \cdots \sum_{\mu_n} \sum_{\nu_1} \cdots \sum_{\nu_{n-1}} \left\{ C_N^{\mu_1} \prod_{i=1}^{n-1} C_{\mu_i}^{\nu_i} C_{N-\mu_i}^{\mu_{i+1}-\nu_i} \right\} \left\{ \prod_{i=1}^{n-1} x_i^{\nu_i} \right\} (w)^{\sum_{i=1}^{n}\mu_i} \tag{3}$$

where $\sum_{\{\Sigma\}}$ is a sum over all configurations of the antiphase boundaries, the remaining sums run over all physical values of μ_i and ν_i, $w = e^{-2\beta\varepsilon}$ and $x_i = e^{-\beta\varepsilon(\gamma_0 - \gamma\Sigma_i\Sigma_{i+1})}$.

The terms involving ν_{n-1} and μ_n reduce to

$$\sum_{\nu_{n-1}} \sum_{\mu_n} C_{\mu_{n-1}}^{\nu_{n-1}} C_{N-\mu_{n-1}}^{\mu_n - \nu_{n-1}} x_{n-1}^{\nu_{n-1}} w^{\mu_n} = (1+w)^{N-\mu_{n-1}} (1 + x_{n-1}w)^{\mu_{n-1}}.$$

If the variable y_k is defined by the following (descending index) mapping:

$$y_k = w \frac{(1 + x_k y_{k+1})}{(1 + y_{k+1})}, \qquad y_n = w, \tag{4}$$

then the partition function is then given by

$$Z_{nN} = \sum_{\{\Sigma\}} \prod_{k=1}^{n} (1 + y_k)^N. \tag{5}$$

The sum over all configurations of the antiphase boundaries, which is not performed analytically, is complicated because each y_k depends on the antiphase structure of all the layers $\geq k$. (The sum has been calculated numerically for small n.) The apparent asymmetry of this solution is caused by the method of solution; it can be demonstrated (analytically for small n, numerically for larger n) that the expression for a given configuration is independent of the end from which the mapping (4) is begun.

IV. Analysis

Expression (5) can be used to prove that in the thermodynamic limit, the free energy of the three-dimensional system is exactly the free energy of one of the two states without antiphase boundaries. Slawny's conclusions that only one of the many states of the ground-state manifold should appear in the low temperature expansions is indeed applicable to this system. Even more importantly, in the thermodynamic limit antiphase boundaries have zero concentration at any finite temperature.

The free energy of the d-dimensional model system (i.e. a system where $N \simeq n^{d-1}$) is proportional to the natural logarithm of the partition function

$$F = -k_B T \ln \left\{ \sum_{\{\Sigma\}} \prod_{k=1}^{n} (1 + y_k)^{n^{d-1}} \right\}. \tag{6}$$

The two states without antiphase boundaries contribute the largest terms to the sum, and the next largest terms are from configurations with just one antiphase boundary. This makes physical sense, because each antiphase boundary replaces approximately n^{d-1} second-lowest-lying excitations by slightly higher ones. The result of this replacement is a reduction in the value of the product over k. The free energy can be written

$$F = -k_B T \ln S_{\max} - k_B T \ln \left\{ 2 + 1/S_{\max} \sum_{\{\Sigma'\}} \prod_{k=1}^{n} (1 + y_k)^{n^{d-1}} \right\} . \tag{7}$$

where $S_{\max}$ is the largest term in the sum over configurations in (6), i.e. that

corresponds to the two perfectly ordered states, and the sum over $\{\Sigma'\}$ includes all configurations except those two corresponding to $S_{\max}$. The first term in (7) is proportional to n^d. For the last term of expression (7) to contribute to the free energy, it must also be proportional to n^d. The second largest terms in the sum over antiphase configurations differ from the largest for some $m < n$ of the y_k. Define α to be the geometric mean of the ratio of these altered terms to their corresponding values in the product for the system with no antiphase boundaries:

$$\alpha = \prod_{j=1}^{m} \left\{ \frac{1 + y_j}{1 + y_{\max j}} \right\}^{1/m} < 1 \quad .$$

If the number of configurations with only one antiphase boundary is taken to be 2^n -- obviously an overestimate since 2^n is the *total* number of configurations -- then the last term in equation (9) is less than or equal to

$$-k_B T \ln \left\{ 2 + 2^n \alpha^{n^{d-1} m} \right\} = -k_B T \ln \left\{ 2 + (2^{n^{2-d}/m} \alpha)^{n^{d-1} m} \right\} \quad . \tag{8}$$

The only way in which (8) can be of order n^d is if $(2^{n^{2-d}/m} \alpha) > 1$, which is possible only if $n^{2-d}/m > 0$. Since $1 \leq m < n$, antiphase boundaries do not appear[27] in the free energy for $d > 2$.

For $d > 2$, it can be proven explicitly that the antiphase boundaries themselves do not appear. Assume that the second largest terms in the sum arise from configurations with approximately n antiphase boundaries, and that there are 2^n of these configurations. With arguments similar to those developed above for the free energy, the contribution from these terms to the concentration of antiphase boundaries is found to be zero:

$$\lim_{n \to \infty} (2^{n^{2-d}/m} \, n^{n^{1-d}/m} \, \alpha)^{n^{d-1} m} = 0 \quad , \quad d > 2 \quad . \tag{9}$$

This is physically reasonable since it has been argued that, if present, antiphase boundaries must affect the obversable thermodynamic properties of the system. In this

situation, the absence of antiphase boundaries in the free energy is indicative of their zero concentration.

While antiphase boundaries cost no energy in the ground state, there is an energy associated with their creation at any nonzero temperature. The energy of one boundary is proportional to the "antiphase excitation gap", $2\gamma\epsilon$, multiplied by the necessarily finite number of juxtaposed excitations which scales with the area of the planes, n^{d-1}. In the thermodynamic limit, the energy cost becomes infinite (for $d > 1$). This argument suggests that antiphase boundaries have zero concentration in any version of this system with dimension larger than one, and that antiphase boundaries appear only for $d = 1$. [A seemingly unphysical one-dimensional antiphase boundary is defined *mathematically* by setting $d = 1$ in expression (6).]

For $d > 1$ it is possible to write down the complete partition function of the model in a compact form, which can then be used to calculate all the thermodynamic functions. Since no antiphase boundaries appear, the partition function is determined entirely by the period-one fixed point of the mapping (4). (For the case with no antiphase boundaries, the x_k of (4) becomes a constant, $x_\infty = e^{-\beta\epsilon(\gamma_0-\gamma)}$, independent of k). The partition function is

$$Z_{n^d} = (1 + y)^{n^d} \quad , \quad d \geq 2 \tag{10}$$

where y is the period-one fixed point of the mapping (5) with x_∞ substituted for x_k:

$$y = 1/2 \left\{ x_\infty w - 1 + [\,(x_\infty w - 1)^2 + 4w\,]^{1/2} \right\} . \tag{11}$$

(Surface effects are neglected).

The free energy is easily calculated from equations (10) and (11). In the limit $\gamma_0 = \gamma = 0$, the free energy is that expected for an assembly of n^d non-interacting two-state systems. (Strictly speaking, in this limit antiphase boundaries appear, but since they do not alter the excitation spectra of the various states, their contribution to

the free energy is strictly one dimensional and vanishes in the thermodynamic limit. The concentration of antiphase boundaries is exactly one half for all temperatures.) For $\gamma_0 \neq \gamma = 0$, the boundaries (which are again decoupled from the system) appear but, the two-state systems are now correlated. With $\gamma_0 \neq 0$, $\gamma \neq 0$, the system has no antiphase boundaries; the sites are, however, still correlated. The heat capacity per site for $d = 3$ (figure 2), which displays a Schottky anomaly, shows that the correlated system is still very similar to a collection of isolated two-state systems.

In one dimension, the antiphase boundaries can be defined mathematically and are expected to occur. The entire expression (5) must be used to calculate the thermodynamic properties. The partition function is calculated for periodic one-dimensional systems containing up to sixteen sites, and the concentration of antiphase boundaries is computed. This concentration is plotted as a function of $\beta\varepsilon/(1 + \beta\varepsilon)$ in figure 3 for $\gamma_0 = 0.8$, and (a) $\gamma = 0.1$, (b) $\gamma = 0.3$, and (c) $\gamma = 0.6$. (The abscissae are zero at infinite temperature, and one at zero temperature.) The results are not very sensitive to the number of sites: there is no perceptible difference between the four- and sixteen-site calculations. At very low temperatures (right side of figure 3), the concentration of antiphase boundaries is one half, exactly the value expected from averaging over all of the ground states. The physical difference between the three curves is the antiphase excitation gap, $2\gamma\varepsilon$, which increases from curves (a) to (c). As the temperature increases from zero, the concentration of antiphase boundaries decreases; the system becomes *more ordered,* with respect to antiphasing, as the temperature is *increased.* (In this situation, "order" is proportional to the concentration of antiphase boundaries; the boundaries themselves do not form an ordered structure but are distributed randomly over the sites of the system). The physics behind this unusual behavior is quite clear. The system begins to order so that the number of excitations available to it at lower temperatures actually increases, just as in the three-dimensional case. The apparent ordering actually results in an *increase* in entropy. As the temperature

increases further, the concentration of antiphase boundaries increases towards its infinite temperature value of one half.

Whereas antiphase boundaries have zero concentration in the infinite three-dimensional model, they do appear *with nonzero concentration at equilibrium* in finite-sized clusters with periodic boundary conditions. These are precisely the type of systems used in the Monte Carlo calculations. It is therefore possible that these results reflect the presence of antiphase boundaries which are unstable in the thermodynamic limit. Figure 4 is a plot of the concentration of antiphase boundaries (for $d = 3$) versus the same function of $\beta\varepsilon$ used in figure 3, for $\gamma_0 = 0.5$ and $\gamma = 0.2$, for systems with up to $16^3 = 4096$ sites. (The Monte Carlo calculations are often performed on systems containing on the order of 6000 sites[18–20]). Figure 5 is the same type of plot for the parameters $\gamma_0 = 0.8$ and $\gamma = 0.6$.

As in the one-dimensional case, the concentration of antiphase boundaries is one half for very low temperatures. For a finite range of temperatures an increase in temperature reduces the concentration of antiphase boundaries. Unlike the one-dimensional case, these results depend on the size of the system. For larger systems, the concentration of antiphase boundaries decreases more rapidly as the temperature increases. This makes physical sense, since the energy cost of a nonzero temperature antiphase boundary scales as n^2. In the thermodynamic limit, the concentration of antiphase boundaries is zero everywhere except at $T = 0$ and $T = \infty$. The actual value of the minimum is also a function of the antiphase excitation gap.

It is very likely that the nearest-neighbor *fcc* Ising antiferromagnet behaves similarly. Further insight is gained by analyzing how Ising model maps onto the model solved here. The most notable feature is that the effective value of the antiphase excitation gap for the Ising model is magnetic field dependent. The gap actually decreases as the triple-point field is approached, suggesting that antiphase boundaries are more likely to appear, as is observed in the Monte Carlo studies[18–20,28]. It seems unlikely,

however, that the effective value of γ can ever be identically zero, which is a necessary condition to have a nonzero concentration of antiphase boundaries in the thermodynamic limit.

The connection between complete disorder and and the appearance of antiphase boundaries needs to be carefully examined. Clearly, an antiphase boundary is not definable in the disordered state. If, however, there is any amount of long-range order, the concept of an antiphase boundary is meaningful and it is then important to understand the relationship between the three-dimensionally disordered state and the one-dimensionally disordered state. It is conceivable that, near the transition temperature, three-dimensional disorder could couple to (and reduce the value of) the antiphase excitation gap, resulting in an increase of the number of antiphase boundaries.

This analysis may explain the depression of the transition temperatures found in Monte Carlo methods relative to CVM results. The appearance of antiphase boundaries near the order-disorder transition may be interpreted as complete disorder, resulting in the observed depression. Furthermore the relative depression of the transition temperature would be largest near the triple point because of the further reduction in the effective value of γ due to the magnetic-field (chemical-potential) dependence. This is the observed behavior (figure 6).

The role of in-plane direct correlations in the Ising system, which are completely neglected in the model developed here, must be evaluated more carefully. In the Ising model, a large number of excitations in a plane can result in a plane which is "antiphased". Hence, antiphase boundaries could arise from this mechanism.

V. Conclusion

The model developed and solved here is a considerably simplified version of the nearest-neighbor *fcc* Ising antiferromagnet which mimics its ground state properties. The model provides a unique insight into some of the characteristics of the more

complicated Ising system.

The simplified model is analyzed for consistency with the predictions of Slawny. As Slawny conjectured, the "true" thermodynamic ground states of the three- and two-dimensional versions of this system are in fact the states with the largest number of low-lying excitations -- the ordered states without antiphase boundaries. Furthermore, in the thermodynamic limit, antiphase boundaries have zero concentration at any finite temperature.

In the (mathematically defined) one-dimensional system, antiphase boundaries do appear. Their concentration at zero and infinite temperatures is equal to one half, and is less than one half at intermediate temperatures. There is a range of temperatures for which *increasing* the temperature results in a *more ordered* antiphase structure. The degree to which the system orders is determined by the antiphase excitation gap, $2\gamma\varepsilon$. Larger degrees of order correspond to larger values of γ.

The behavior of the model for systems with sizes on the order of those used in the Monte Carlo calculations was investigated. It was found that for all finite-sized d-dimensional systems antiphase boundaries will appear *at equilibrium with nonzero concentration.* The antiphase boundaries are more likely to appear in smaller systems, and systems in which the antiphase excitation gap is small.

The model can be used to infer properties of the more complicated nearest-neighbor *fcc* Ising antiferromagnet and, additionally, suggests a possible resolution of the discrepancies between Monte Carlo and CVM results. In the nearest-neighbor *fcc* Ising antiferromagnet, the effective antiphase excitation gap is magnetic-field dependent. As the triple-point field is approached, the gap decreases, and antiphase boundaries appear in the Monte Carlo calculations. Furthermore, as the planes become more and more disordered, the effective energy cost of a nonzero temperature antiphase boundary may decrease. It is then possible that near the transition temperature, the concentration of antiphase boundaries might rapidly increase (for finite-sized

systems). Since the order-disorder transition is known to be first order, it is unlikely that the energy cost per unit area of an antiphase boundary can ever be identically zero at finite temperature below the transition.

The role of in-plane direct correlations in the Ising model needs to be assessed more carefully. The chance that a significant number of excitations can "create" an antiphase boundary leaves open the possibility that the boundaries may be stable in the infinite three-dimensional Ising system. The density of excitations required for the "creation" of an antiphase boundary is quite high. This information, combined with the knowledge that the phase transition is first-order, suggests that the nearest-neighbor *fcc* Ising model completely disorders before an antiphase boundary is "created". It is therefore plausible that complete {001} antiphase boundaries do not appear in the true equilibrium phase diagram of the nearest-neighbor *fcc* Ising antiferromagnet.

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26 The excitations of the nearest-neighbor *fcc* Ising antiferromagnet form a discrete energy spectrum. A third-level excitation is then defined as any excitation which has the third lowest excitation energy.

27 Antiphase boundaries naturally appear for the case in which $x_k = 1$. Physically, this corresponds to all states in the ground-state manifold having identical excitation spectra. Hence for this case, one clearly needs to include all possible configurations in the low-temperature expansion for the partition function. The contribution of the antiphase boundaries, however, is thermodynamically negligible, and the concentration of antiphase boundaries is one half for all temperatures.

28 From the calculations presented here, it seems plausible that antiphase boundaries would appear in Monte Carlo systems even for systems with very small next-nearest-neighbor interactions, and one would not expect any kind of discontinuous behavior in the Monte Carlo results as the next-nearest-neighbor interaction is allowed to go to zero. There is also some question concerning the role of the superdegenerate point in the phase diagram. There does not seem to be any evidence for a disordered-type phase stemming from this point in the phase diagram. Rather, the phase diagram seems to contain only the $L1_0$, $L1_2$, and the disordered phases. See reference 25 for more details.

Figure Captions

Figure 1 The four possible (001) planes of the perfectly ordered $h = 0$, $T = 0$ case. Each dark (light) symbol represents an up (down) spin. The planes labeled Ba and Bb are the configurations produced by placing planes a and b, respectively, on top of plane B. The dashed boxes contain one of the nearest-neighbor tetrahedra which compose the *fcc* lattice. Each of these tetrahedra is in the minimal energy configuration, containing two up spins

and two down spins. The planes can be stacked in any order: (...ZzZzZzZz...), where each Z (z) is a plane of type A (a) or B (b), and the energy is still minimal.

Figure 2 The heat capacity per site, $\partial u/\partial\tau$, where u is the internal energy and $\tau = \beta^{-1}$, for a three-dimensional system for both correlated and uncorrelated systems plotted versus β. The correlated system has parameters $\gamma_0 = 0.7$ and $\gamma = 0.2$ While the correlated system is considerably more complex than the collection of non-interacting two-state systems, the heat capacity still displays the characteristic Schottky anomaly.

Figure 3 The concentration of antiphase boundaries plotted as a function of $\beta\varepsilon/(1 + \beta\varepsilon)$ for the one-dimensional system for three values of the parameters: (a) $\gamma_0 = 0.8$ and $\gamma = 0.1$; (b) $\gamma_0 = 0.8$ and $\gamma = 0.3$; and (c) $\gamma_0 = 0.8$ and $\gamma = 0.6$. The abscissae are zero at $\beta = 0$ and one at $\beta = \infty$. [Antiphase boundaries are defined mathematically in one dimension by putting $d = 1$ in expression (6).] The curves display a minimum in the concentration of antiphase boundaries at some intermediate temperature. For some range of temperatures, the antiphase structure actually becomes *more ordered* as the temperature is *increased*. The depth of the minimum is strongly dependent on the antiphase excitation gap, $2\gamma\varepsilon$, which determines the energy difference between excitations involving an antiphase boundary and those which do not. The minimum is deeper for the larger values of γ.

Figure 4 The concentration of antiphase boundaries plotted as a function of $\beta\varepsilon/(1 + \beta\varepsilon)$ for three-dimensional systems of finite size n^3 for $\gamma_0 = 0.5$ and $\gamma = 0.2$. The abscissae are zero at $\beta = 0$ and one at $\beta = \infty$. The curves all display a minimum in the concentration of antiphase boundaries at some intermediate temperature. The depth of the minimum is strongly

dependent on the size of the sample and is deeper for larger samples. The depth of the minimum also depends on γ.

Figure 5 The concentration of antiphase boundaries plotted as a function of $\beta\varepsilon/(1 + \beta\varepsilon)$ for three-dimensional systems of finite size n^3 for $\gamma_0 = 0.8$ and $\gamma = 0.6$. The abscissae are zero at $\beta = 0$ and one at $\beta = \infty$. The curves display a minimum in the concentration of antiphase boundaries at some intermediate temperature. The depth of the minimum is strongly dependent on the size of the sample. The minima of the curves are deeper in this plot than they are for their counterparts in figure 4 because of the larger value of γ. The $n = 16$ case displays a considerable range of temperature for which the concentration of antiphase boundaries is numerically negligible. In the thermodynamic limit, $n \rightarrow \infty$, the concentration of antiphase boundaries is zero over the entire range of β (except the endpoints $\beta = 0$ and $\beta = \infty$).

Figure 6 The equilibrium phase diagrams of the nearest-neighbor *fcc* Ising antiferromagnet predicted by the CVM[17] (dashed line) and Monte Carlo[19] (solid line) methods. The transition temperature predicted by the Monte Carlo results is depressed relative to those predicted by CVM. The model constructed here suggests that the Monte Carlo results are influenced by the presence of antiphase boundaries which do not appear in an infinite system.

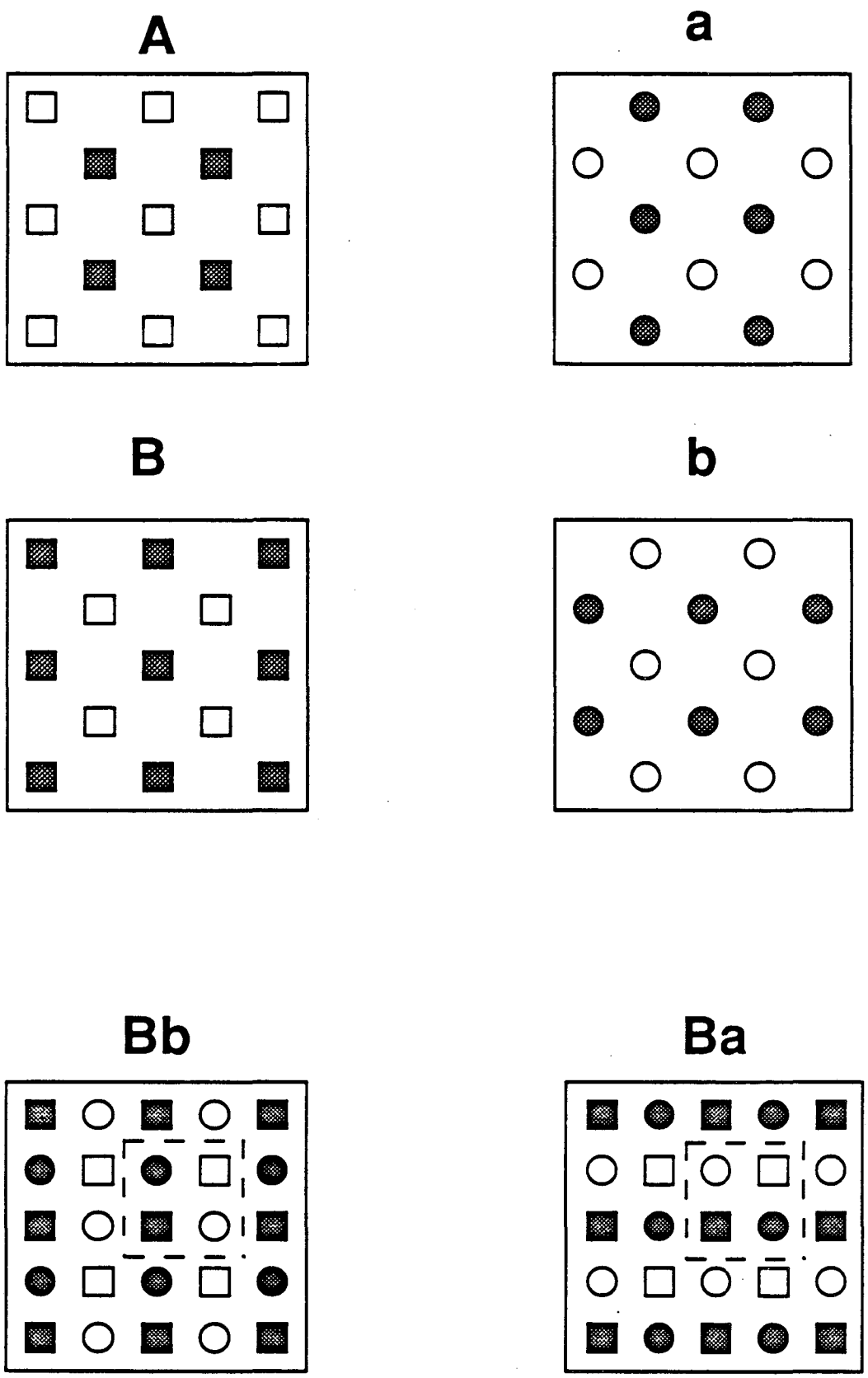


Figure 1

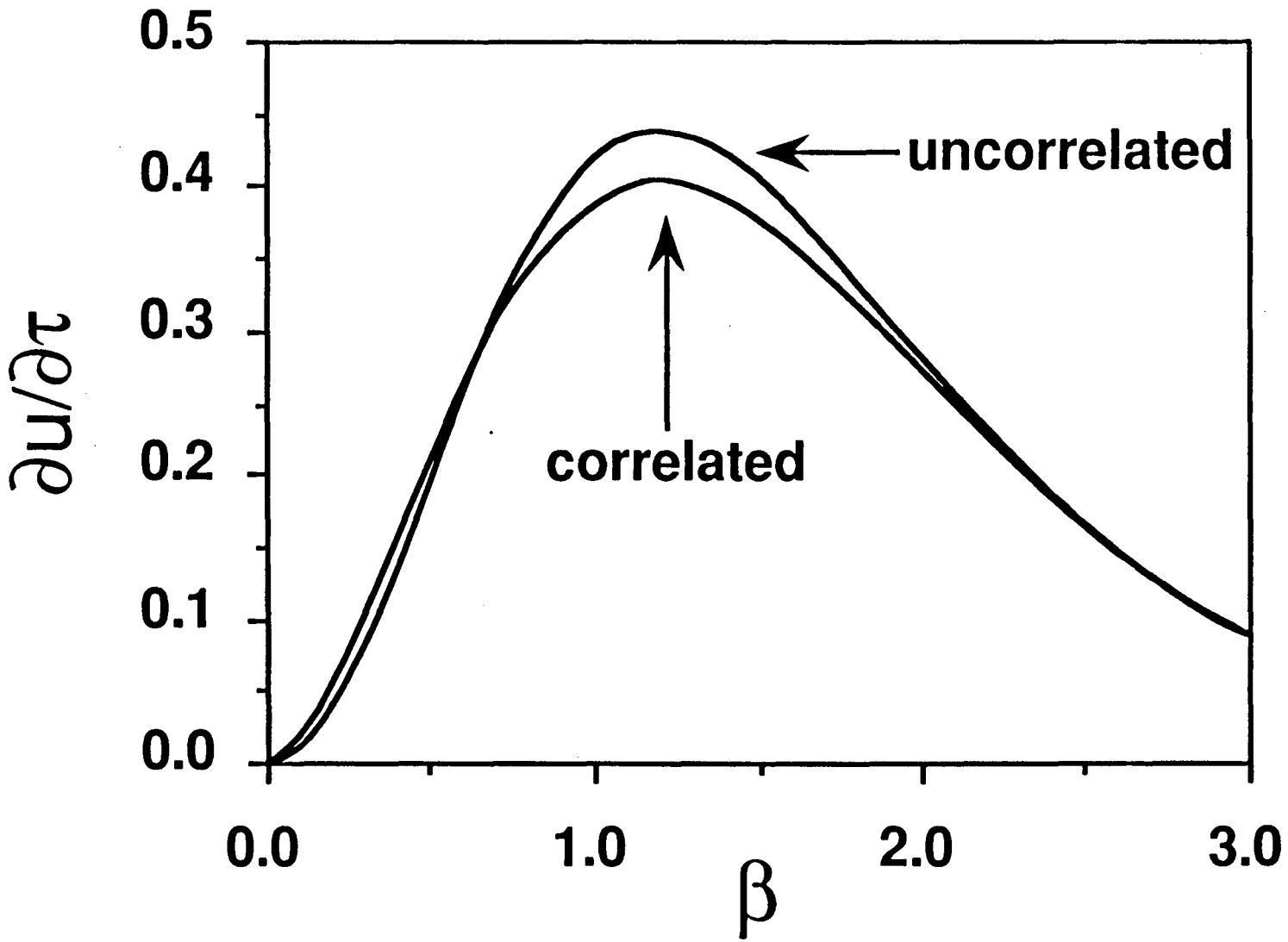


Figure 2

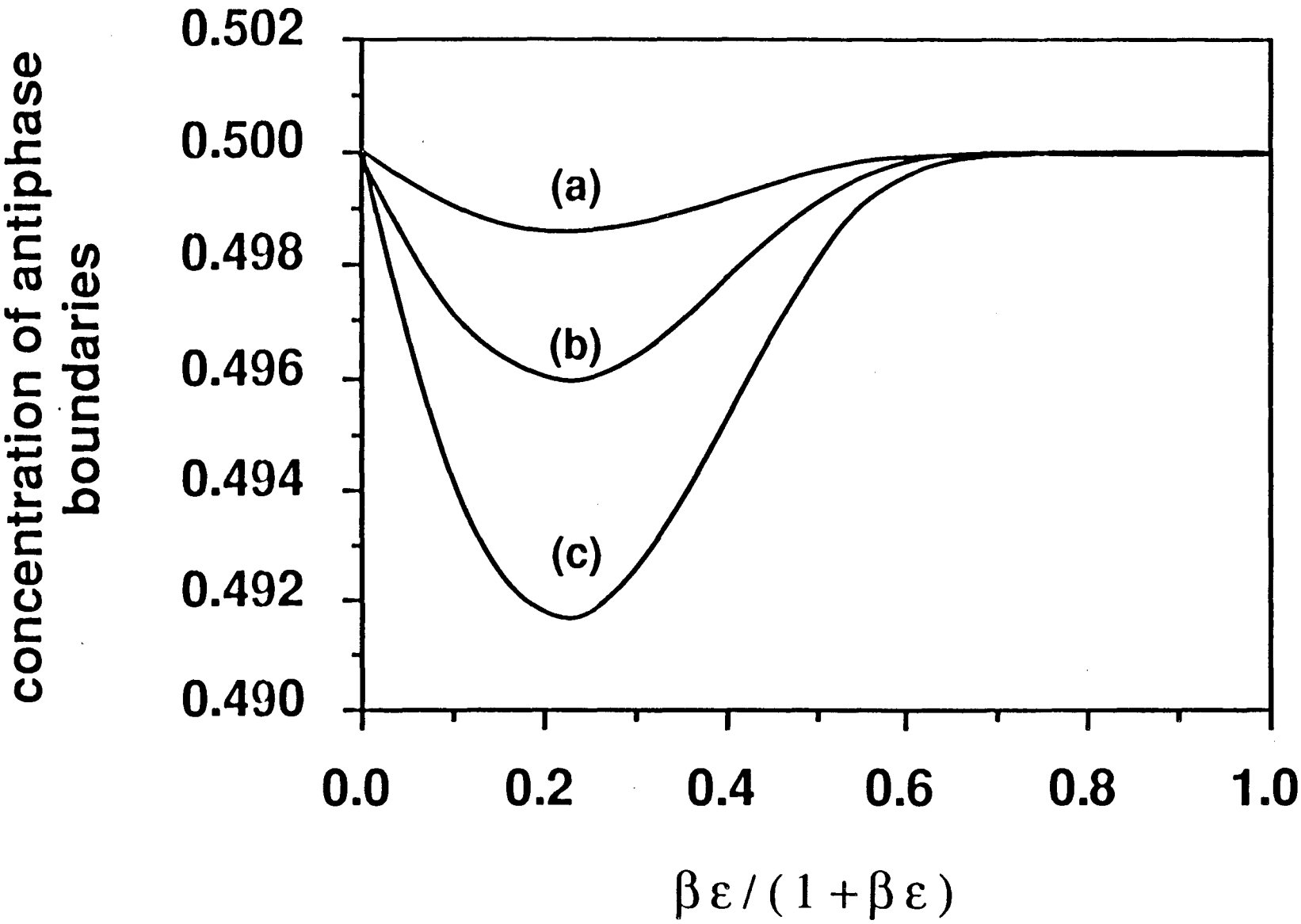

concentration of antiphase boundaries
0.502
0.500
0.498
0.496
0.494
0.492
0.490
(a)
(b)
(c)
0.0
0.2
0.4
0.6
0.8
1.0
βε/(1+βε)

Figure 3

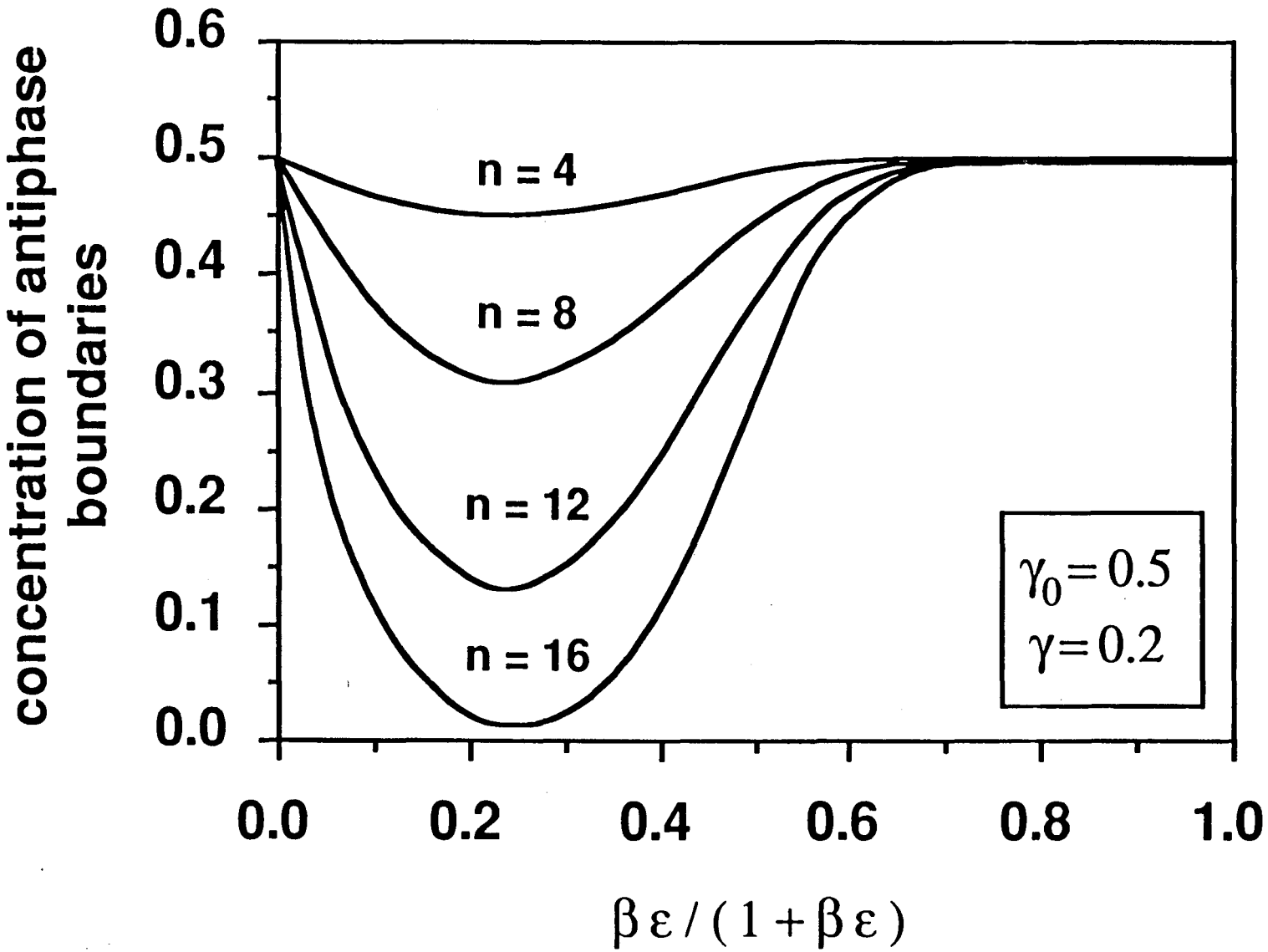
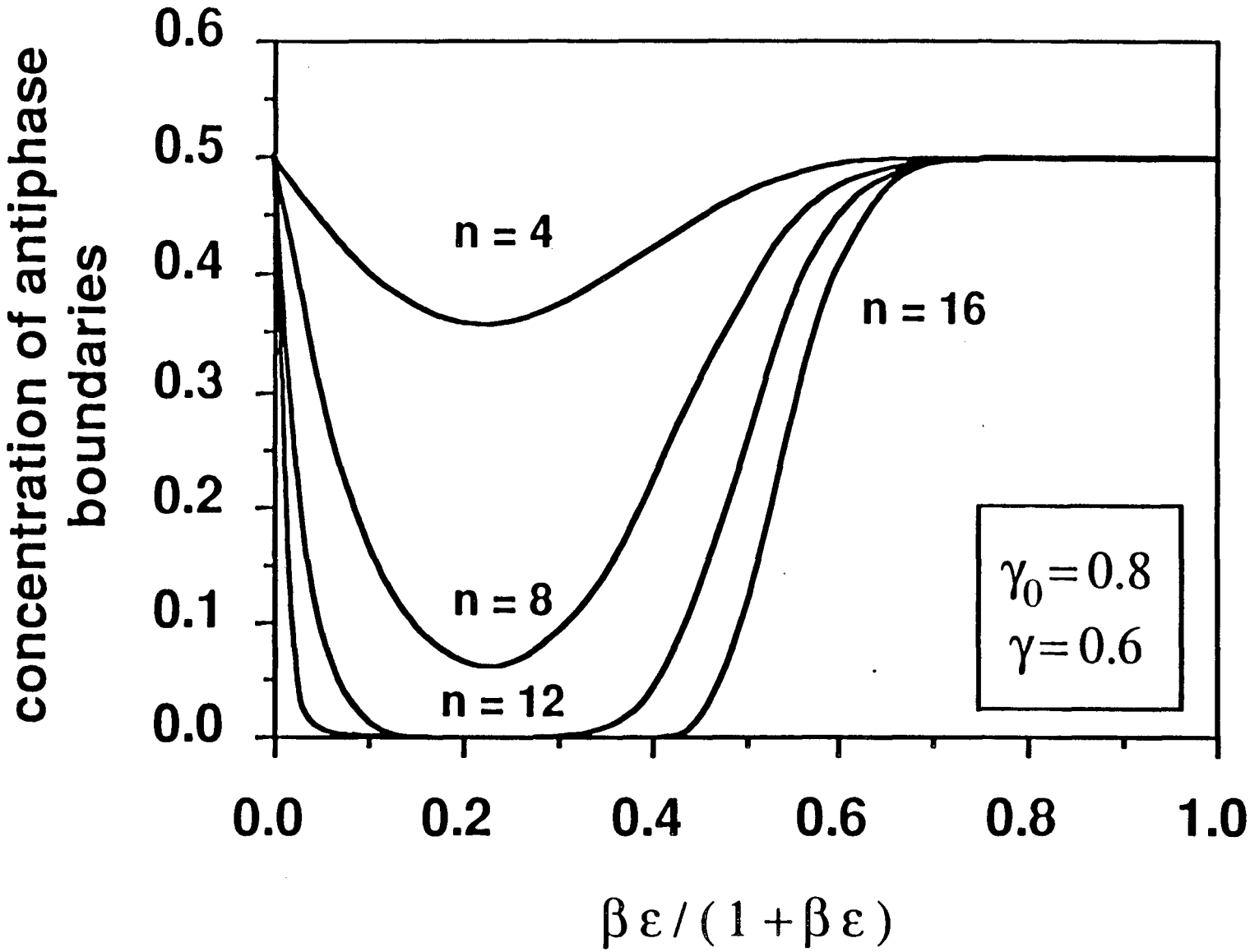

concentration of antiphase boundaries
0.6
0.5
0.4
0.3
0.2
0.1
0.0
n = 4
n = 8
n = 12
n = 16
$\gamma_0 = 0.5$
$\gamma = 0.2$
0.0
0.2
0.4
0.6
0.8
1.0
$\beta\varepsilon/(1+\beta\varepsilon)$

Figure 4


concentration of antiphase boundaries
0.6
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n = 4
n = 8
n = 12
n = 16
$\gamma_0 = 0.8$
$\gamma = 0.6$
0.0
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0.4
0.6
0.8
1.0
$\beta\varepsilon/(1+\beta\varepsilon)$

Figure 5

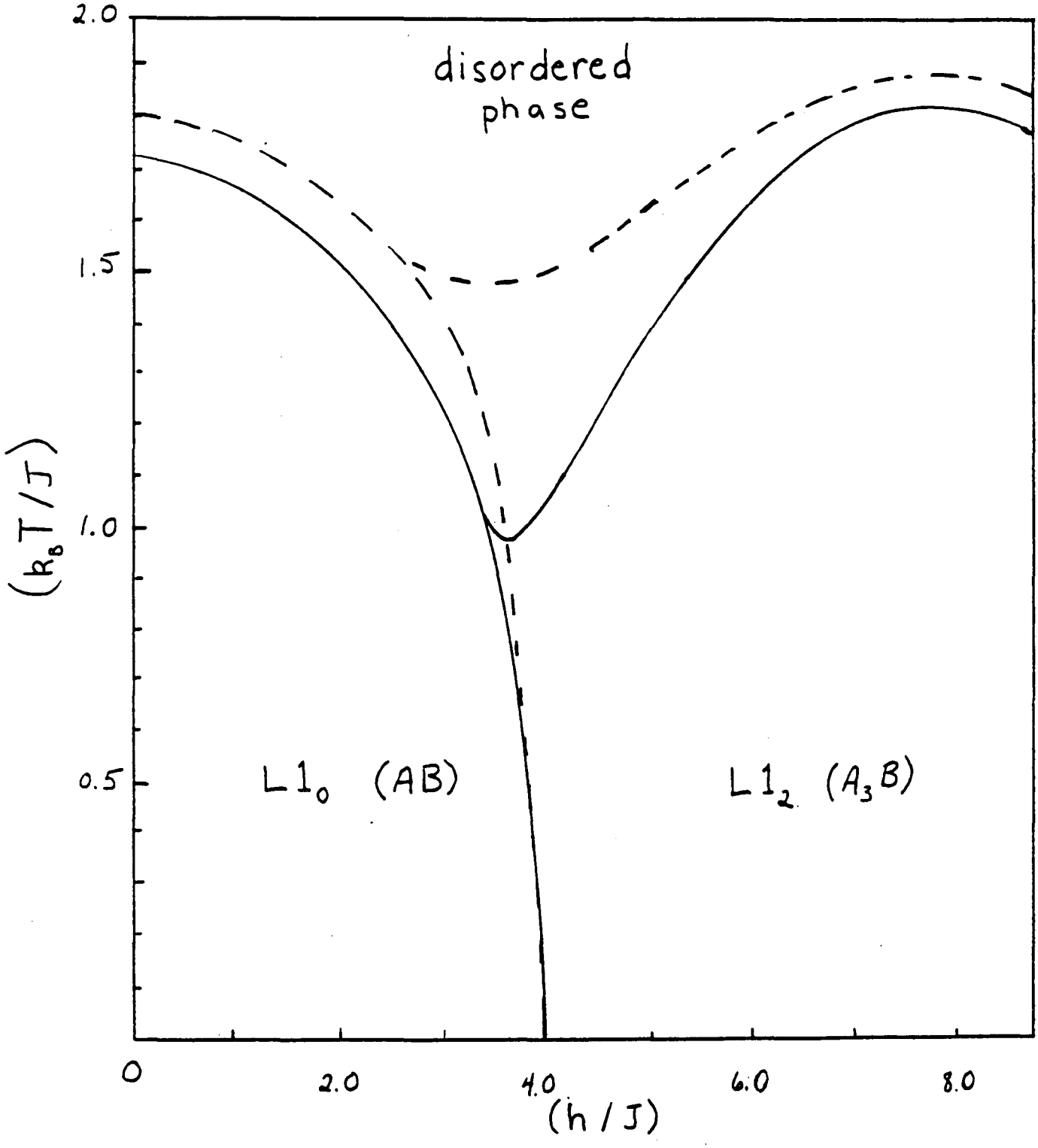

Figure 6

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