Crystal-growth approach of lattice-order simulation and the cluster-variation method

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A method of simulating a lattice-order structure is proposed. The simulation is a new, so far unexploited, application of the physics contained in the cluster-variation method (CVM). Each different size and shape of the basic cluster in the CVM leads to a different level of approximation in the simulation. The method is a modification of the crystal-growth (CG) approach introduced by Welberry and Galbraith in the sense that the CG probability is provided by the CVM. The original derivation of the entropy expressions in the CVM was essentially based on the crystal-growth consideration and thus can be readily modified to derive the CG probability function. The proposed simulation provides the means of connecting the CVM work (which is based on the coordinate space) with the diffraction (which is based on the reciprocal space). Other possible applications of the simulation are discussed.

I. INTRODUCTION

As de Fontaine stated in his review article,[1] there are two useful modes in describing properties of concentrated solid solutions: the wave method and the cluster method. The former has the advantage that it can be closely tied with experimental diffraction data, while the latter can work with atomic interaction models by making use of well-developed entropy expressions. The cluster-variation method (CVM)[2,3] belongs to the latter category, and, except for the simplest case (i.e., the point approximation, also called the Bragg-Williams approximation), it has not been possible to compare results of the CVM treatments with diffraction experiments.

Attempts have been made to bridge the gap between the two modes of approach. The computer simulations done by Gehlen and Cohen[4] and Gragg *et al.*[5] and the probability variation method proposed by Clapp[6,7] use short-range order parameters observed by diffraction experiments and derive atomic distributions in real space.

In this paper, we propose a method somewhat similar in spirit to Cohen's simulation,[4,5] but one which requires much less computer time. We show how to construct a simulation of atomic distributions from computed results of the CVM. Once the simulation has been constructed, it is possible to obtain diffraction patterns from the simulation and thus to compare them with diffraction experiments.

The proposed method is a modified version of Welberry and Galbraith's[8–10] (WG) crystal-growth method. In contrast with WG's method, our method uses the probability function for choosing the species at the growth lattice point in such a way that the probability is consistent with the specific approximation (of the CVM), results of which form the basis of the simulation.

II. CRYSTAL-GROWTH METHOD OF WELBERRY AND GALBRAITH

Welberry and Galbraith construct a simulation of atomic distribution on a crystal lattice by adding an atom at a time. Let us consider a two-dimensional square lattice as an example. The lattice is constructed from the bottom upward and from left to right on a horizontal line; an intermediate stage is illustrated in Fig. 1. Atoms have been placed up to the edge formation j-l-k-m, and i is the next atom to be placed. In this paper, $i,j,k, \ldots$ are used for atomic species and $A,B, \ldots$ are used in indicating lattic points.

The WG method assumes a conditional probability function $P(i;j,l,k,m)$, which we will call the crystal-growth probability (CGP) for short, for placing the

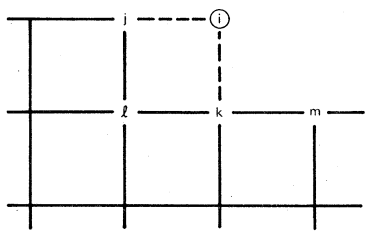

FIG. 1. Intermediate stage of constructing a two-dimensional square lattice.

atomic species i when the surrounding j, l, k, and m are known. They use a random number to choose i so that the probability distribution is satisfied. They repeat the procedure at each lattice point, and when the entire lattice is filled, this is a simulation of the lattice configuration which satisfies the prescribed CGP $P(i;j,l,k,m)$.

When a simulation is thus completed, it can be examined in many different ways. Special features of local atomic groupings can be examined as was done by Gehlen and Cohen[4] and Gragg *et al.*[5] WG mostly worked on two-dimensional lattice simulations and used optical means to obtain diffraction patterns.[8–10] For a three-dimensional simulation, we can construct diffraction patterns using a computer and can compare them with observed diffraction data.

What we are going to do in the rest of the paper is to show what kind of the CGP function $P(i;j,l,k,m, \ldots)$ for placing the ith species at the growth point (when the neighbor configurations $j,l,k,m, \ldots$ are known) is consistent with the CVM formulation. The CGP and the simulation starting from the CVM have the following significance. In the CVM, we start with the basic assumption about the interactions (either pairwise or many-body interactions). By choosing an appropriate basic cluster, we can solve the CVM and hence all the properties for individual configurations of the basic cluster and subclusters and for the system. We previously had stopped the CVM at this point, but now we go further. We construct the appropriate CGP using the cluster probabilities derived by the CVM. After the CGP functions are thus constructed, we can use a procedure similar to that of WG to construct a simulation; then, based on this simulation, we can examine properties (including the diffraction properties) of the lattice not previously examined in the CVM.

The only link missing from the program outlined above is the form of the CGP expression consistent with each CVM approximation formulation. To provide this CGP is the main task of the present paper and is done below.

Although the CGP $P(i;j,l,k,m, \ldots)$ has never been used in the CVM before, its concept is inherently very close to that of the original derivation of the CVM entropy expression. The comparison between Figs. 1 and 2 (the latter is taken from Ref. 2) substantiates this analogy. Actually what we do in the following sections (III–VI) is to modify the method of Ref. 2 and to rederive the CVM entropy expression, a modification in the sense that the derivation starts a step back from that of Ref. 2. The CGP expression turns out to be a natural consequence of the derivation.

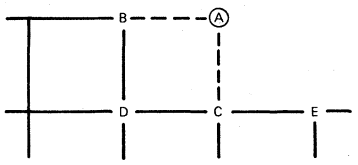

FIG. 2. Intermediate stage of constructing a two-dimensional square lattice (Fig. 3 of Ref. 2).

III. PAIR APPROXIMATION OF CVM

To simplify the presentation, sublattices are not considered here. It is a simple matter to generalize the formulation in case sublattices are needed.

To begin, consider a two-dimensional square lattice. At each lattice point, there is an atom i. Although we call i an atom, it could be a spin; also, the system could be binary, ternary, or multicomponent. Suppose the lattice has been constructed up to the edge formation j-l-k-m in Fig. 1. The last atom placed was j, and the next one to be placed is i.

In the pair approximation, when j was placed, the correlation between j and k (in Fig. 1) was neglected. Therefore, the probability that the diagonal configuration j-k is found in the pair approximation is

$$P_{dg}(j,k) = p_1(j)p_1(k) \ , \tag{3.1}$$

where $p_1(j)$ is the single-state probability for j, and p_{dg} is the diagonal-pair probability.

When the atom is placed, the pair approximation of the CVM requires that the pair configuration j-i appear with the probability distribution $p_2(j,i)$ and simultaneously the pair configuration i-k appear with the given probability distribution $p_2(i,k)$. These two requirements are met if the atom i is placed such that the probability of j-i-k is

$$p_3(j,i,k) = \frac{p_2(j,i)p_2(i,k)}{p_1(i)} \ . \tag{3.2}$$

Note that this expression satisfies

$$\sum_k p_3(j,i,k) = p_2(j,i) \ , \quad \sum_j p_3(j,i,k) = p_2(i,k) \ , \tag{3.3}$$

as required. Expression (3.2), however, has one unpleasant feature: $\sum_i p_3(j,i,k)$ does not reduce to $p_{dg}(j,k)$ in expression (3.1), which is the condition that j and k are uncorrelated. This inconsistency, however, is inherent in the pair approximation, or is the demonstration of the very nature of the approximation, because if such an inconsistency did not exist, the method would be exact.

In formulating the entropy expression in the CVM, we consider an ensemble made of L systems (as explained in detail in Ref. 2). All L systems are built from bottom upward and from left to right, as in Fig. 1. The number of ways G_L of distributing atoms on

the L growth points in the ensemble is written, in the present case, as

$$G_L = \prod_{j,k} [Lp_{dg}(j,k)]! \Big/ \prod_{i,j,k} [Lp_3(j,i,k)]! \ . \tag{3.4}$$

Substituting Eqs. (3.1) and (3.2) into (3.4), taking logarithms of both sides, and using Stirling's approximation yields

$$\ln G_L = L\left[3\sum_i \mathfrak{L}[p_1(i)] - 2\sum_{i,j} \mathfrak{L}[p_2(i,j)] - \mathfrak{L}[1]\right] , \tag{3.5}$$

where the function $\mathfrak{L}[X]$ originates in Stirling's approximation and is defined as

$$\mathfrak{L}[X] \equiv X \ln X - X \ . \tag{3.6}$$

The expression (3.5) is exactly the same as Eq. (B4) of Ref. 2, the pair approximation for the square lattice.

When the coordination number is 2ω, the number of nearest neighbors (of the growth point) that have already been placed is ω, and the probability that $j_1,j_2,\ldots,j_\omega$ appear on these ω points will in general be

$$p_\omega(j_1,j_2,\ldots,j_\omega) = \prod_{k=1}^{\omega} p_1(j_k) \ , \tag{3.7}$$

because these neighbor points are regarded as independent in the pair approximation. Corresponding to expression (3.2), the probability for the configuration $i,j_1,j_2,\ldots,j_\omega$ with the atom i at the growth point is

$$p_{\omega+1}(i,j_1,j_2,\ldots,j_\omega) = \prod_{k=1}^{\omega} p_2(i,j_k) \Big/ [p_1(i)]^{\omega-1} \ . \tag{3.8}$$

In this case, the G_L factor is

$$G_L = \frac{\prod_{j_1,j_2,\ldots,j} [Lp_\omega(j_1,j_2,\ldots,j_\omega)]!}{\prod_{i,j_1,j_2,\ldots,j_\omega} [Lp_{\omega+1}(i,j_1,j_2,\ldots,j_\omega)]!} \ . \tag{3.9}$$

Combining the last three equations yields

$$\ln G_L = L\left[(2\omega-1)\sum_i \mathfrak{L}[p_1(i)] - \omega\sum_{i,j} \mathfrak{L}[p_2(i,j)] - (\omega-1)\mathfrak{L}[1]\right] , \tag{3.10}$$

which is exactly equal to the last equation in Sec. B of Ref. 2.

We have so far derived the G_L expressions of the CVM. Next we turn to CGP, which was discussed in Sec. II. By definition, CGP $P(i;j,k,l,\ldots)$ is the conditional probability of finding the i atom when the configuration of the already-placed neighbor is $j,k,l,\ldots$. Since $p_3(j,i,k)$ in Eq. (3.2) has the meaning of the probability of finding the configuration j-i-k, we can identify CGP as

$$P(i;j,k) = p_3(j,i,k) \Big/ \sum_i p_3(j,i,k) \ . \tag{3.11}$$

In the general case of the coordination number 2ω, we identify

$$P(i;j_1,j_2,\ldots,j_\omega) = p_{\omega+1}(i,j_1,j_2,\ldots,j_\omega) \Big/ \sum_i p_{\omega+1}(i,j_1,\ldots,j_\omega) \ . \tag{3.12}$$

On the right-hand side of these equations, we use Eqs. (3.2) and (3.8), respectively.

IV. SQUARE APPROXIMATION

In the square approximation of the CVM for the two-dimensional square lattice, suppose that the lattice has been built up to the edge formation j-l-k-m in Fig. 1. The formulation of the CVM is based on the ensemble concept. In the square approximation, when the atom j was placed, the angle j-l-k has the right probability distribution[2] within the ensemble. However, when j is placed independent of m, the probability of finding the edge configuration j-l-k-m is

$$p_{ag1}(j,l,k,m) = \frac{p_3(j,l,k)p_2(k,m)}{p_1(k)} \ . \tag{4.1}$$

When i is placed as the next step, the square i-j-l-k and the angle i-k-m must each have the right probability distribution (in the ensemble). Therefore, it follows that

$$p_5(i,j,l,k,m) = p_{sq}(i,j,l,k)p_3(i,k,m)/p_2(i,k) \ . \tag{4.2}$$

Note that p_{sq} and p_{agl} have different geometry. Making use of these two expressions, the G_L factor is written as

$$G_L = \frac{\prod_{j,l,k,m} [Lp_{ag1}(j,l,k,m)]!}{\prod_{i,j,l,k,m} [Lp_5(i,j,l,k,m)]!} \ . \tag{4.3}$$

Use of Stirling's approximation leads to

$$\ln G_L = L\left[2\sum_{i,j} \mathfrak{L}[p_2(i,j)] - \sum_{i,j,k,l} \mathfrak{L}[p_{sq}(i,j,k,l)] - \sum_i \mathfrak{L}[p_1(i)]\right] , \tag{4.4}$$

which is identical with the square approximation in Eq. (C1.5) of Ref. 2. Analogous to the case for the pair approximation, note that $\sum_i p_5(i,j,l,k,m)$ is not equal to $p_{ag1}(j,l,k,m)$, the difference being indicative of the nature of the square approximation.

The CGP $P(i,j,l,k,m)$ is derived from Eq. (4.2) as

$$P(i,j,l,k,m) = p_5(i,j,l,k,m) \Big/ \sum_i p_5(i,j,l,k,m) \ . \tag{4.5}$$

Now we show that we can get the expression of $p_5(i,j,l,k,m)$ from an equation given in Ref. 2. Figure 2 is reproduced from Ref. 2, where it was used in deriving G_L for the square approximation. Note the correspondence between i,j,k,l,m of Fig. 1 and A,B,C,D,E of Fig. 2. When Eqs. (C1.3), (C1.4), and (C1.5) from Ref. 2 are combined, the derivation of G_L is written, based on Fig. 2, as

$$G_L = \frac{\{\text{angle}BDC\}_L \{\text{bond}CE\}_L / \{\text{point}C\}_L}{\{\text{square}ABDC\}_L \{\text{angle}ACE\}_L / \{\text{bond}AC\}_L} \ . \tag{4.6}$$

When A,B, etc., are changed into i,j, etc., following the correspondence of Figs. 2 and 1, and also when the { } notation is changed into p's, the numerator and the denominator of Eq. (4.6) change exactly into $p_{ag1}(j,l,k,m)$ and $p_5(i,j,l,k,m)$. Particularly noteworthy is the fact that $p_5(i,j,l,k,m)$, which forms the basis of CGP $P(i;j,l,k,m)$ in Eq. (4.5) can be derived from the denominator of Eq. (4.6), or to be more specific, from the factors that contain the growth lattice point A. Generalizing this observation leads to the conclusion that the CGP can be derived from those factors of G_L written in Ref. 2 that contain the growth point; since we will make use of this general property in the rest of the paper and in future publications, let us call this property the G_L-CGP relation, for short.

It has been proved before[11] that the four-point square cluster and a three-point angle-shaped cluster of the CVM give identical results when used for the two-dimensional square lattice. For the angle cluster, the intermediate stage of constructing the lattice is drawn in Fig. 3; A,B,C,E are latttice-point names, and i,j,k,m are atomic-species names. The G_L is constructed from Fig. 3 as

$$G_L = \frac{\{\text{pair}EC\}_L \{\text{diagonal pair}CB\}_L / \{\text{point}C\}_L}{\{\text{angle}ECA\}_L \{\text{angle}CAB\}_L / \{\text{pair}CA\}_L} \ . \tag{4.7}$$

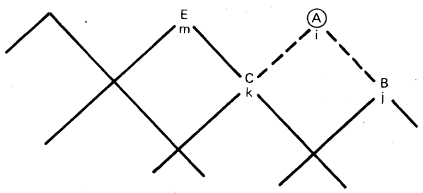

FIG. 3. Intermediate stage of constructing a two-dimensional square lattice for the angle approximation.

This expression is identical with Eq. (I.13) of Ref. 11, which was derived using a different approach. When we use the G_L-CGP relation of the previous paragraph, we compare the A,B,C,E designation with the corresponding species names i,j,k,m in Fig. 3 and change the denominator of Eq. (4.7) into

$$p_4(i,m,k,j) = p_3(m,k,i)p_3(k,i,j)/p_2(k,i) \tag{4.8a}$$

and the CGP is written as

$$P(i;m,k,j) = p_4(i,m,k,j) \Big/ \sum_i p_4(i,m,k,j) \ . \tag{4.8b}$$

This result of the angle treatment is important in applying the CG method in conjunction with the CVM, because the angle expression (4.7) and hence also expression (4.8) are deliberately constructed anisotropically. It was proved in Ref. 11 that the anisotropic construction with the angle is identical with the isotropic construction with the square. It is important to show that the CGP expression (4.8b), which is derived from the anisotropic construction, also gives an isotropic diffraction pattern which is derived from the isotropic treatment based on the square.

The above can be proved as follows. In the square approximation of the CVM, the following relations hold among the square and angle variables:

$$p_{sq}(i,j,l,k) = p_3(j,i,k)p_3(j,l,k)/p_{dg}(j,k) \ . \tag{4.9}$$

This relation looks like a superposition "approximation," but is a rigorous relation, as was proved in Ref. 11. In this expression, $p_{dg}(j,k)$ is a variable for the diagonal pair. When Eq. (4.9) is used in the p_5 expression in Eq. (4.2), we note that the factor $p_3(j,l,k)/p_{dg}(j,k)$ is independent of i and thus drops out when the ratio in Eq. (4.5) is formed. Thus p_5 in Eq. (4.2) can be replaced by

$$p_5(i,j,l,k,m) \rightarrow p_3(j,i,k)p_3(i,k,m)/p_2(i,k) \ , \tag{4.10}$$

which does not contain l and is identical with $p_4(i,m,k,j)$ in Eq. (4.8a).

We can also verify by the actual simulation that the square CVM result and the angle CVM result lead to exactly the same simulation when the conditions are suitably chosen (this is discussed further in Sec. VI).

The fact that the angle cluster simulation, which is superficially anisotropic, gives exactly the same simulation as the square cluster, which is a demonstrably

isotropic simulation, suggests the general property that the seemingly anisotropic simulation (made using a one-dimensionally long cluster) does produce an isotropic simulation.

V. TRIANGLE AND fcc LATTICES

We can use the G_I-CGP relation of Sec. IV to derive CGP's directly from formulas of G_L in Ref. 2. In Ref. 2, Fig. 4 is used to construct the G_L factor for the triangle lattice with the triangle approximation as

$$G_L = \frac{\{\text{bond}BC\}_L \{\text{bond}CD\}_L / \{\text{point}C\}_L}{\{\text{triangle}ABC\}_L \{\text{triangle}ACD\}_L / \{\text{bond}AC\}_L} \quad . \tag{5.1}$$

We write in the corresponding atomic species names i,j,k,l in Fig. 4. Then using the A,B,C,D and i,j,k,l correspondence and collecting terms which contain A, the expression

$$p_4(i,j,k,l) = p_3(i,j,k)p_3(i,k,l)/p_2(i,k) \tag{5.2}$$

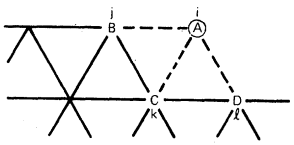

FIG. 4. Intermediate stage of constructing a two-dimensional triangle lattice.

can be derived. Then, using Eq. (5.2), the CGP can be written as

$$P(i,j,k,l) = p_4(i,j,k,l) \Big/ \sum_i p_4(i,j,k,l) \quad . \tag{5.3}$$

For the fcc lattice, G_L for the tetrahedron approximation was calculated in Ref. 2 based on Fig. 5. The atomic species on these points $i,j, \ldots$ are named as listed in Fig. 5. From those terms in the G_L expression, Eq. (H1.1) of Ref. 2, that contain A, we can derive

$$p_7(i,j,k,l,m,n,o) = \frac{p_4(i,n,m,o)p_4(i,k,l,n)p_3(i,j,k)p_3(i,j,m)p_1(i)}{p_2(i,n)p_2(i,k)p_2(i,m)p_2(i,j)} \quad . \tag{5.4}$$

This leads to the CGP as

$$P(i,j,k,l,m,n,o) = p_7(i,j,k,l,m,n,o) \Big/ \sum_i p_7(i,j,k,l,m,n,o) \quad . \tag{5.5}$$

VI. DISCUSSIONS

Examples of the simulation have been made for the Ising model in the two-dimensional square lattice. Several comments are in order.

Since the results of the CVM are being used, we know the occurrence probability of each configuration (e.g., the i-j pair). By counting the number of i-j pairs in the simulation, the reliability of the simulation can be determined. For the square approximation (for which the Curie temperature is $kT_c/\epsilon = 2.42567$), the probability of the $--$ spin pair at $kT/\epsilon = 2.0$ is 0.011 861. Simulations for a 50×50 size crystal gave the values 0.010 829, 0.007 080, 0.016 243, and 0.009 579. Simulations for a 200×200 lattice gave closer, more uniform values: 0.011 060, 0.011 111, 0.010 808, and 0.011 237. WG[8] reported simulations of a 1000×1000 lattice and found that the computer time required was relatively short.

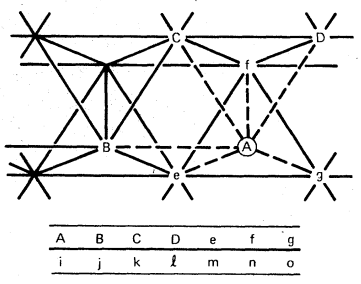

FIG. 5. Intermediate stage of constructing a fcc lattice.

In one simulation, the anisotropy is relatively small. For example, the $+-$ spin pair for the same CVM calculation as above has the probability 0.031 750. A 50×50 simulation gave 0.026 656 (horizontal) and 0.027 489 (vertical), while another simulation gave 0.033 319 (horizontal) and 0.035 402 (vertical).

One possible application of the simulation is to construct the diffraction pattern, as was discussed in the Introduction. A second application is to study correlations beyond the size of the cluster. Although two-dimensonal simulations can be done quickly and with relative ease, how far one can go in three-dimensional simulations is a question of time and the computer memory space.

There is the possibility of another interesting appli-

cation. Usually the random-number generator in a computer has a property that permits the same sequence of random numbers to be generated over and over again when the same starter number is used. As a matter of fact, the identity of the square cluster simulation and the angle cluster simulation as mentioned in Sec. IV was first discovered using the same sequence of random numbers. When we use the same random-number sequence, we can trace the kinetics of processes occurring in the lattice. As an example, in Fig. 6 we show how the "wrong" spin islands shrink in the two-dimensional Ising model as the temperature decreases. This figure was computed using the square approximation of the CVM. The Curie temperature is at 2.425 67. In Fig. 6, we used the same random-number sequence for all T's. It shows that, at $kT/\epsilon = 2.4$, points of all marks are wrong spins and that, as the temperature decreases, wrong spins are gradually converted to right spins to end up with only black circles at $kT/\epsilon = 2.0$. If a different series of random numbers were used for different T's, the spin configurations for T's would be uncorrelated and it would be difficult to assess the shrinkage of spin clusters.

To do the simulation, an equilibrium state of the CVM need not be used. The only requirement is that a consistent set of cluster distribution variables be available. When the path probability methods (PPM)[12] is used in studying kinetics, a series of nonequilibrium states appear as the system develops in time. At each time, the PPM describes the system using a set of nonequilibrium cluster variables. These variables can be used to construct simulations in time series. In so doing, the same random-number sequence mentioned in the preceding paragraph can be used conveniently in following the development of atomic clusters.

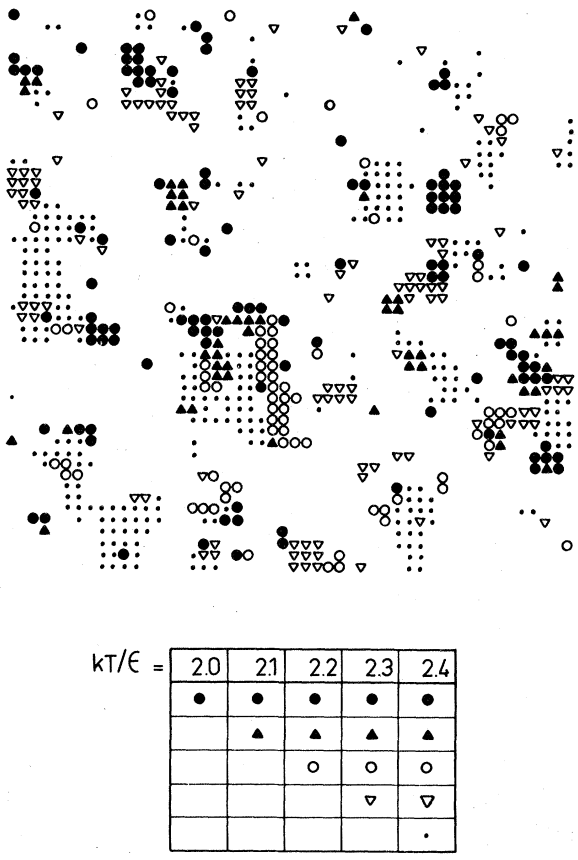

FIG. 6. 50 × 50 simulation of a two-dimensional square-lattice Ising model. It is based on the pair approximation, and shows how "wrong" spin clusters change in temperature.

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