Diffusion Enhances Chirality Selection

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Abstract

Diffusion effect on chirality selection in a two-dimensional reaction-diffusion model is studied by the Monte Carlo simulation. The model consists of achiral reactants A which turn into either of the chiral products, R or S, in a solvent of chemically inactive vacancies V. The reaction contains the nonlinear autocatalysis as well as recycling process, and the chiral symmetry breaking is monitored by an enantiomeric excess ϕ.

Without dilution a strong nonlinear autocatalysis ensures chiral symmetry breaking. By dilution, the chiral order ϕ decreases, and the racemic state is recovered below the critical concentration c_c. Diffusion effectively enhances the concentration of chiral species, and c_c decreases as the diffusion coefficient D increases. The relation between ϕ and c for a system with a finite D fits rather well to an interpolation formula between the diffusionless (D = 0) and homogeneous (D = ∞) limits.

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I. INTRODUCTION

It has long been known that natural biomolecules choose one type of enantiomer among the two possible stereoregularities, and the chiral symmetry is broken in life: Amino acids in proteins are all L-type, while sugars in nucleic acids are all D-type [1, 2, 3]. There are many studies on the origin of this homochirality, but the asymmetry caused by various proposed mechanisms turned out to be very minute [4, 5, 6]. Frank found more than fifty years ago that a linear autocatalysis accompanied by mutual inhibition are necessary in an open system for the amplification of enantiomeric excess (ee) of one type [1]. The model with enantiomeric cross-inhibition is extended to polymerization models [8, 9]. Experimental realization of the ee amplification is found recently in pyrimidyl alkanol [10], and explained by a nonlinear autocatalytic process in a closed system [11, 12]. Addition of a recycling process to this nonlinear system is shown to realize an asymptotic selection of a unique chiral state [13]. The importance of recycling process is also shown in nonautocatalytic but a polymerization-epimerization model [14].

All the above arguments assume that the reaction takes place homogeneously. For spatially extended systems, however, the inhomogeneity affects symmetry breaking in general. In condensed matter systems, for instance, elements are located densely in contact with each other, and interactions propagate through neighboring elements so as to cause coherent phase transitions. In contrast to the equilibrium symmetry breaking in the condensed matter, organic molecules in the primordial era might have been distributed dilutely in a solution. If this were the case, molecular transport is necessary in order to bring molecules come into contact to activate autocatalysis.

In a previous letter [12], we briefly reported the diffusion effect on the chiral symmetry breaking. Here we give a more detailed work of the diffusion effect on the chirality proliferation in an extended system. After introducing the model and Monte Carlo simulation algorithm in §2, we consider first the chirality selection in a diffusionless system, and point out some similarity of the present chemical reaction system to the Ising ferromagnet in §3. There, the effect of site dilution is also discussed. In §4, the diffusion effect is studied systematically and the chiral symmetry breaking is found to be enhanced by the diffusion. It is qualitatively interpreted that the diffusion effectively increases the concentrations of chemically active molecules, and consequently promotes autocatalysis. The idea is summarized in a simple interpolation formula as for the diffusion coefficient dependence of the order parameter and the concentration relation. The study is summarized in §5.

II. MODEL AND SIMULATION ALGORITHMS

The model we study is essentially the same with the one proposed in a previous letter [12]. There are four types of molecules: an achiral reactant A, two types of product enantiomers R and S, and a solvent molecule in a diluted system, which we call a vacancy V. Molecules are treated as entities which occupy square lattice sites and can move randomly thereon. Double occupancy of a lattice site is forbidden.

Various processes in the system are summarized in Fig.1. An isolated achiral reactant A turns into a chiral R or S molecule with a rate k_0, as in Fig.1(a). When there is one R(S) molecule in the nearest neighbor of a reactant A, the production rate of R(S) increases by an additional linear autocatalytic rate k_1, as in Fig.1(b). When there are two or more R’s(S’s) in the nearest neighborhood, the production rate of R(S) is further enhanced by an additional nonlinear autocatalytic rate k_2, as in Fig.1(c).
S vary, but the total number density of active molecules in the enantiomeric excess (ee) order parameter. The degree of chiral symmetry breaking is represented by a closed system corresponding to the Soai reaction \[10\].

When in a closed system, the number densities of chemically active species, A, R and S, are neighboring to V, they exchange their sites with V randomly with a rate \(\lambda\). Therefore, even by starting from an achiral initial configuration with only achiral reactants A, domains of R and S are formed in the early stage, whereas the initial reactant A quickly reduces to chirality in space without the material transport. The rate of back reaction \(\lambda\) is assumed constant, independent of the environment around chiral molecules, R or S.

The simulation runs as follows: All the positions which can undertake a process \(i\) are tabulated in a list; every site in the list has the same transition probability \(P_i\) to perform the reaction or diffusion process \(i\), shown in Fig.1. Assume that there are \(n_i\) lattice sites in the corresponding list of the process \(i\). Then, the total probability of events in a unit time is obtained as \(P_{\text{tot}} = \sum_i P_i n_i\). In other words, in a time interval \(dt = 1/P_{\text{tot}}\), one of the processes takes place on average. By generating a quasi-random number \(x\) which is uniformly distributed between 0 and \(P_{\text{tot}}\), the process \(j\) which satisfies the condition

\[
\sum_{i=1}^{j-1} P_i n_i < x \leq \sum_{i=1}^{j} P_i n_i
\]

is to be performed. The lattice site which performs the process \(j\) is listed at the \(k\)-th position in the list of \(n_j\) sites, where \(y = x - \sum_{i=1}^{j-1} P_i n_i\) and \(k\) is the integer part of \(y/P_j + 1\) as

\[
k = \left\lfloor \frac{y}{P_j} + 1 \right\rfloor.
\]

After performing the process \(j\) on the site in the \(k\)-th position in the list, the time is advanced by \(dt\) and the lists are updated. We simulate systems with sizes 50\(^2\) and 100\(^2\), but in the following we show results obtained for the larger system with a size 100\(^2\).

### III. WITHOUT DIFFUSION

From our previous works on a homogeneous system \[13\], the nonlinear autocatalysis with a finite \(k_2\) is found essential for the chiral symmetry breaking, whereas the linear autocatalysis \(k_1\) is inefficient. Therefore, \(k_1\) is set absent hereafter: \(k_1 = 0\). In order to find out the effect of diffusion, we consider in this section the development of chirality in space without the material transport. The effect of diffusion is studied in the next section. Here, the order of chiral symmetry breaking is studied as a function of the strength of the nonlinear autocatalysis or of the concentration of active molecular species.

### A. Chiral Symmetry Breaking as a function of Nonlinear Autocatalysis

First, we consider the \(k_2\)-dependence of the chiral symmetry breaking, when the whole lattice sites are occupied by chemically active species; \(c = 1\). When the nonlinear autocatalytic effect is strong enough such as \(k_2 = 100k_0\) with \(\lambda = k_0\), achiral reactant A quickly reduces to chiral species R or S. Therefore, even by starting from an achiral initial configuration with only achiral reactants A, domains of R and S are formed in the early stage, as shown at a time \(k_0 t = 50\) in Fig.1. Then, the domain competition sets in, and those domains surrounded by another type shrink as shown in the middle column in Fig.2. Eventually, competition ends up by the dominance of...
FIG. 2: Configuration evolution of (a) R and (b) S molecules in a diffusionless system. Times are \( k_0 t = 50, 250, 1750 \) from left to right. Parameters are \( k_0 = \lambda, k_1 = 0, k_2 = 100k_0 \) with \( c = 1 \), and the system size is \( 100 \times 100 \).

FIG. 3: Enantiomeric excess \( |\phi| \) versus \( k_2/k_0 \) at the full occupation \( c = 1 \) in a semi-logarithmic plot. A curve represents the temperature dependence of the magnetization [20] of a square Ising model, where a temperature is related to the chemical reaction rates as \( k_2/k_0 = \exp(4J/k_BT) - 1 \).

FIG. 4: Analogies of state transition in the reaction model (above) and the Ising ferromagnet (below). (a) \( n = 2 \), and (b) \( n = 3 \).

of one enantiomeric type, S in the case shown in the right column of Fig.2. In some cases the system decouples into two inter-penetrating domains of R and S, both of which in effect extend to infinity due to the periodic boundary conditions in the \( x \) and \( y \) directions: Then, it takes an enormous time until the minor domain extinguishes and the system accomplishes the final equilibrium state.

In order to obtain the equilibrium value of the order parameter \( \phi \) in a reasonable simulation time, therefore, we start simulations from an initial configuration such that the whole lattice sites are occupied by R species. Equilibrium states are readily realized from this initial configuration, and the equilibrium value of the order parameter \( \phi \) thus obtained is shown in Fig.4 at various strength of nonlinear autocatalysis \( k_2/k_0 \). Since the non-autocatalytic reaction \( k_0 \) drives the system to the racemic state, the value of the order parameter \( \phi \) decreases as \( k_2 \) decreases, and vanishes at a critical value of \( k_2/k_0 \) around 10: The system recovers the chiral symmetry, getting into the racemic state.

The qualitative features of domain competition shown in Fig.2 and the emergence of symmetry breaking at large \( k_2 \) as shown in Fig.3 suggest us some resemblance with the phase transition in an Ising ferromagnet. In fact, one may find some analogy of our reaction system to an Ising ferromagnet: In the latter, each lattice site is occupied by an Ising spin, which can be in one of the two states; up or down. When a nearest neighboring spin pair have the same orientation, the energy is low as given by \( -J < 0 \), whereas when a pair is in opposite orientations, the energy is high as \( J > 0 \): The energy difference is set to be \( 2J > 0 \). At a temperature \( T \), a spin flips its orientation with a transition probability which depends on the associated energy change. Let the spin to flip have \( n \) nearest neighboring spins with the same orientation. Then, it will have \( 4 - n \) spins of the same orientation after the flip, and we denote the transition probability as \( W(n \to 4 - n) \). In order to ensure thermal equilibrium asymptotically, it is known to be sufficient if the detailed balance condition between the transition probabilities of
one process and its reverse
\[
W(n \rightarrow 4 - n) / W(4 - n \rightarrow n) = \exp(-\Delta E/k_B T) \tag{4}
\]
is satisfied, where \(\Delta E = 4(n - 2)J\) represents an energy change. For example, when a site is surrounded by two up spins and two down spins, \(n = 2\) and the transition probability of an up spin to flip downward is equal to its reverse process, as shown in the lower column of Fig.4(a). Then, in equilibrium the probability \(P_+(2, 2)\) of an up spin surrounded by two up spins and two down spins is equal to that of a down spin in the same environment \(P_-(2, 2)\): \(P_+(2, 2) = P_-(2, 2)\). We associate, for instance, R and S molecules to the up and down Ising spins, respectively. Then, the transitions for \(n = 2\) in the Ising model correspond to transitions between an R and S molecule surrounded in the neighborhood by two R’s and two S’s (upper column of Fig.4(a)). Since the alternation of R and S is mediated by an achiral reactant A, the equilibrium probabilities of R and S in the configuration Fig.4(a) are related as \(\lambda P_R(2, 2) = (k_0 + k_2) P_A(2, 2) = \lambda P_S(2, 2)\), and thus \(P_A(2, 2) = P_S(2, 2)\), consistent with our assignment of R and S molecules to up and down spins. When a site is surrounded by three R’s and one S molecule as in the upper column of Fig.4(a), the equilibrium probability that the site is occupied by an R molecule \(P_R(3, 1)\) is higher than the one by an S molecule \(P_S(3, 1)\). They are related as \(\lambda P_R(3, 1) = (k_0 + k_2) P_A(3, 1)\) and \(k_0 P_A(3, 1) = \lambda P_S(3, 1)\), and thus \(P_R(3, 1) = (1 + k_2/k_0) P_S(3, 1)\). At a lattice site surrounded by three R’s and an S, the probability of finding an R molecule is higher than that of finding an S molecule by a factor \((1 + k_2/k_0)\). For the Ising system, the corresponding situation is the spin on the site surrounded by three up’s and one down; \(n = 3\). The relation between probabilities that a site is occupied by an up spin and by a down is \(e^{-4J/k_B T} P_+(3, 1) = P_-(3, 1)\). Thus, we may assume that the ratio \((1 + k_2/k_0)\) corresponds in the Ising model to the ratio of the transition probabilities \(\exp(4J/k_B T)\). (See the lower column of Fig.4(b)). In other word, the nonlinear autocatalytic rate \(k_2\) in our chiral model might correspond to the coupling constant of the two-dimensional Ising model as
\[
k_2/k_0 = e^{4J/k_B T} - 1. \tag{5}
\]
Since the numbers of R and S molecules correspond to those of up and down spins in the Ising ferromagnet, the chiral order parameter \(\phi\) corresponds to the spontaneous magnetization \(M\) of the Ising model. The latter is exactly known to behave as \(M = 1 - \sinh(2J/k_B T)^{-4}]^{1/8}\). By using the relation \(M\), the magnetization \(M\) is plotted in Fig.3 by a continuous curve.

The transition temperature \(T_c\) of the Ising model on the square lattice is exactly known to be at \(k_B T_c/2J = 1/\ln(1 + \sqrt{2}) \approx 1.135\). Thus in the present reaction model the chiral symmetry breaking is expected to take place at \(k_2 \geq k_2c = 2(\sqrt{2} + 1)k_0 \approx 4.83k_0\). However, the order parameter \(\phi\) obtained by simulations decreases faster than the Ising magnetization as \(k_2\) decreases: For the chiral symmetry breaking a larger value of the nonlinear autocatalysis \(k_2 \approx 10k_0\) is required, as shown in Fig.5. This is because of the approximate character of the relation between the Ising coupling constant \(J\) and the nonlinear autocatalytic rate \(k_2\). The production rate in our model is independent of the number of neighboring R(S) species as far as it is more than 2, whereas transition rate to the up spin state in an Ising model increases as the neighboring number of up spins increases: This means that our coupling constant \(k_2\) is effectively weaker than the Ising coupling parameter. Also the existence of an achiral species is not included in the Ising model. The decomposition process from a chiral species R or S back to an achiral reactant A induces fluctuation which breaks ordering, and a chirally ordered state in our reaction model is less stable than the ferromagnetic state in the Ising ferromagnet: The strong nonlinearity is necessary for the symmetry breaking. In fact, the critical value for the chiral symmetry breaking \(k_{2c}\) depends on the decomposition rate \(\lambda\), though the \(k_2\) versus \(J\) relation in eq.(5) is independent of \(\lambda\). From simulations with a large \(\lambda = 10k_0\), the order is found to be easily broken at \(k_{2c} \approx 23k_0\), whereas for small \(\lambda = 0.1k_0\) the order holds until \(k_{2c} \approx 9k_0\).

**B. Dilution Effect on Chiral Symmetry Breaking**

We now keep the nonlinear autocatalytic effect as strong as \(k_2/k_0 = 100\), and consider the dilution effect \(\phi < 1\) on the chiral symmetry breaking. If there is no material transport, the behavior of the system depends strongly on the arrangement of vacant sites. Therefore, in order to obtain the order parameter \(\phi\) we average 9 samples at concentrations lower than \(c = 0.7\), whereas 3 samples seem sufficient at higher concentrations. As the system is diluted, the probability that active chemical species are contiguous to each other decreases. In the present reaction model, however, a reactant A should be surrounded by chiral products R or S to sustain the autocatalysis. Therefore, the chiral symmetry breaking is possible only at concentrations at least larger than the site percolation threshold of the square lattice \(c_p = 0.592746^{10}^{17}\). Below \(c_p\), the information of one site is unable to propagate through the whole system, and thus the system cannot be in one single state. The order parameter \(\phi\) actually decreases as the system is diluted, as shown in Fig.5a, and the system becomes racemic at concentrations lower than the critical value \(c_c(D = 0) \approx 0.639\), the order parameter \(\phi\) shows a power-law dependence \(\phi \propto (\sqrt{c} - c_c(D = 0))\), as shown in Fig.5(b). The critical concentration \(c_c(D = 0)\) without diffusion is close to but larger than \(c_p\).

A rather large discrepancy between \(c_c(D = 0)\) and \(c_p\) might be understood by using the similarity of the present diluted reaction model to a site-diluted Ising fer-
romagnet, where lattice sites are diluted substitutionally by nonmagnetic impurities [10]. In a site-diluted Ising model, the transition temperature is known to decrease as the concentration of nonmagnetic impurity increases, and the phase transition vanishes at the critical concentration close to the percolation threshold \( c_p \) [10]: The transition temperature is zero at the critical concentration. If the relation (5) holds, however, our reaction model with \( k_2 = 100 k_0 \) corresponds to an Ising ferromagnet at a finite temperature \( k_B T/2J = 0.433 \) or \( T/T_c = 0.38 \). A thermal fluctuation favors the recovery of the symmetry even if a percolating cluster exists, and this may be the reason that the critical concentration \( c_c(D = 0) \) is larger than the percolation threshold \( c_p \).

\[ \phi = \frac{c - c_0}{c - c_0} = \frac{3.3\sqrt{0.639}}{0.001} \]

(a) Enantiomeric excess \( |\phi| \) versus \( c \) in a diffusionless system with a strong nonlinear autocatalysis \( k_2/k_0 = 100 \).

(b) Enantiomeric excess \( |\phi| \) versus \( c \) in a diffusionless system with a strong nonlinear autocatalysis \( k_2/k_0 = 100 \).

IV. DIFFUSION ENHANCEMENT OF THE CHIRALITY SELECTION

We now study the diffusion effect on the chirality selection in a diluted system. The transport of material in general increases the chance for an achiral reactant \( A \) to meet chiral products \( R \) and \( S \) in their lifetimes, and may enhance the autocatalytic effect. When the diffusion is extremely fast, the system becomes homogeneous: This case will be studied in the following subsection analytically. With a finite diffusion coefficient, numerical simulation is the only possible method to study, and the results so obtained will be analyzed by the interpolation formula in the second subsection.

A. Homogeneous Case with \( D = \infty \)

When the diffusion is extremely fast, the system becomes homogeneous. Then, the simple mean field approximation leads to the rate equations for the homogeneous concentrations:

\[ \dot{r} = k(r)a - \lambda r \]
\[ \dot{s} = k(s)a - \lambda s, \]  
with the rate constant \( k(r) = k_0 + 4k_1 r + 6k_2 r^2 \). Here in this subsection we restore the rate \( k_1 \) of the linear autocatalytic reaction, in order to be general. The factors \( 4r \) and \( 6r^2 \) represent the probabilities that at least one or two of the four neighboring sites are occupied by \( R \) species, respectively, in the sense of mean field approximation. Since the system is assumed to be closed, the total concentration of chemically active species satisfies the conservation law; \( a + r + s = c = \text{const.} \). Then, the total concentration of chiral products \( u = r + s \) is shown to varies as

\[ \dot{u} = [2k_0 + 4k_1 u + 3k_2 u^2(1 + \phi^2)](c - u) - \lambda u, \]

whereas the order parameter \( \phi \) evolves as

\[ \dot{\phi} = \frac{c - u}{u} \phi[-2k_0 + 3k_2 u^2(1 - \phi^2)]. \]

Since \( 0 \leq u \leq c \), eq.(8) is similar to the time-dependent Landau equation with nontrivial fixed points if \( u^2 > 2k_0/(3k_2) \). The other point to remark is that eq.(8) does not depend explicitly on the linear autocatalytic rate \( k_1 \); \( \phi \) depends on \( k_1 \) only implicitly through \( u \). Thus the linear autocatalysis alone cannot break the chiral symmetry.

The equilibrium values of \( u \) and \( \phi \) are calculated from the algebraic equations given by \( \dot{\phi} = \dot{u} = 0 \). The spontaneous chiral symmetry breaking takes place at a critical concentration \( c_c(D = \infty) \) when the diffusion is infinitely fast: The order parameter \( \phi \) of a homogeneous system takes a finite value for \( c_c(D = \infty) < c \leq 1 \). For \( k_1 = 0 \) the order parameter \( \phi \) is explicitly written as a function of the concentration \( c \) as

\[ \phi^2 = 1 - \frac{6k_0 k_2}{\lambda^2} \left( c - \sqrt{c^2 - \frac{2\lambda}{3k_2}} \right)^2, \]

and the critical concentration is calculated to be \( c_c(D = \infty) = (4 + \lambda/k_0)/\sqrt{k_0/24 k_2} \). It takes the value \( c_c(D = \infty) = 0.1020 \) for the parameter values \( k_1 = 0, k_2 = 100 k_0, \lambda = k_0 \).

B. Finite Diffusion Constant

The emergence of chiral order at a finite vacancy diffusion is studied by the Monte Carlo simulation. It is found that the symmetry breaking takes place rather rapidly
even if we start from a completely achiral initial con-
figuration with all the chemically active molecules be-
ing achiral reactant A as \( a = c \). The order parameter
approaches quickly the asymptotic value, though which
enantiomer dominates over the other is determined ran-
domly in each simulation run. Therefore, we initiated
the simulation from the complete achiral state with only
A and V species.

The steady-state value of \( \epsilon c \) or \( |\phi| \) at various values of
diffusion coefficient \( D/k_0 \). The reaction parameters are
\( k_2/k_0 = 100, \ k_1 = 0 \) and \( \lambda = k_0 \). A continuous curve represents
the relation (9) for a homogeneous system. Dashed
curves represent the interpolation (10) at various diffusion coef-

\[
c(\phi; D) = \frac{c(\phi; 0) + c(\phi; \infty)(AD/\lambda)}{1 + (AD/\lambda)},
\]

\[
c(\phi; \infty) = \frac{1}{\sqrt{42k_0k_2}}(\lambda\sqrt{1 - \phi^2} + \frac{4k_0}{\sqrt{1 - \phi^2}}).
\]

To determine the constant \( A \), we fit the formula (10) with
simulation data at \( \phi = 0.6 \). The reason for the choice of a
non-zero value of \( \phi \) is that the value of \( c(\phi; D) \) is expected
to be more accurate away from the transition point, \( \phi = 0 \).
The fit gives the value \( A \approx 0.235 \), and agrees well at
small \( D \) but deviates systematically at large \( D \), as shown in
Fig. 6(b).

With this value of \( A \), we interpolate the whole \( \phi - c \)
curve for arbitrary \( D \) by eq. (10), as is drawn by broken
curves in Fig. 6(a). The trend of the down shifting in the
concentration as the diffusion increases is well repro-
duced, even though the fitting is not perfect, especially
at a large diffusion coefficient \( D \). There, we have so far
no plausible theory on the \( D \)-dependence of \( c(\phi; D) \).

V. SUMMARY AND DISCUSSIONS

We study diffusion effect on the chirality selection dur-
ing a chemical production of chiral molecules, R or S,
from an achiral substrate A in a solution by means of a
square lattice model. In addition to the usual reactions of
the production and the decomposition of chiral species,
autocatalytic processes are incorporated such that an
achiral substrate surrounded by many enantiomers of one
type increases the turn-over rate to that type. Specifi-
cally, the nonlinear autocatalysis which takes place when
the substrate is surrounded by two or more enantiomers of
one type is found to be essential in the chiral symmetry
breaking.

When all the lattice sites are occupied by chemically
active species, A, R or S, the spontaneous symmetry
breaking has some similarity to the phase transition of
an Ising ferromagnet. The strength of the nonlinear au-
tocatalysis \( k_2 \) in our chemical model is approximately
related to the Ising coupling constant. The chemical model
at very large $k_2$ evolves through the domain competition, similar to the dynamics of the Ising model at low temperatures. As $k_2$ decreases, the chiral order extinguishes, but earlier than the expectation from the Ising model. The discrepancy may be due to the larger degrees of freedom; three in the chemical model whereas two in the Ising model.

Inclusion of vacancies or dilution suppresses the degree of the chiral symmetry breaking or the enantiomeric excess $\phi$, and below the critical concentration of chemically active species, the system is in a racemic state with a chiral symmetry. In a diffusionless system ($D = 0$) with a strong nonautocatalysis, the system is similar to the site-diluted Ising model, and the critical concentration is close to but larger than the percolation threshold $c_p$.

Diffusion enhances the chiral order $\phi$, since the migration of chiral products enhances the chance of molecular collision and the autocatalytic process as well. In the limit of an infinitely fast diffusion ($D = \infty$), the system behaves as if it is homogeneous and the rate equation in the mean field approximation describes the chiral symmetry breaking: The steady state solution is obtained analytically in this limit. At a finite diffusion coefficient $D$, the concentration dependence of $\phi$ is shifted from the diffusionless limit ($D = 0$) to the homogeneous limit ($D = \infty$). The behavior is interpreted as the diffusive enhancement of concentrations of chiral species, and is summarized in an interpolation formula of $c$-dependence of $\phi$ or $c(\phi; D)$ between the two limits.

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