

Simple Models for Chirality Conversion of Crystals and Molecules by Grinding

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By grinding crystals in a solution, the chirality conversion of the crystal structure and the resultant conversion of molecular chirality have been realized recently. Reaction-type models that enable the reproduction of these phenomena are studied. In the models, chiral clusters are assumed to be formed by grinding and that these clusters can be integrated into crystals of the same chirality. An initial chirality imbalance is amplified exponentially, and the rate is approximately proportional to the grinding strength and to the molecular racemization rate in a relevant parameter range.

KEYWORDS: chirality, crystallization, enantiomer, dynamical symmetry breaking, chiral cluster, autocatalysis, NaClO_3 , amino acid derivative

The chirality conversion of crystal structure by grinding crystals in a saturated solution has been discovered by Viedma.¹⁾ For NaClO_3 and some other materials, whose molecules are achiral and crystals are chiral, it has been known that spontaneous symmetry breaking occurs during crystallization from a saturated solution with stirring,²⁾ and the cause is attributed to a secondary nucleation.^{3,4)} Viedma put NaClO_3 crystals of both chiralities, dextrorotatory(D) and levorotatory(L), in a solution and ground them continuously. In about a day, all crystals turned into crystals of a single chirality, D or L. The final chirality is that of majority at the beginning. If the initial amounts of D and L are the same, either chirality can be the final one. Recently, this phenomenon has been confirmed for other materials, such as NaBrO_3 ⁵⁾ and ethylenediammonium sulfate.⁶⁾

The present author proposed a simple reaction-type model to explain the spontaneous symmetry breaking and the chirality conversion.⁷⁾ The model reproduces these phenomena qualitatively. The essential assumption of the model is that the grinding produces abundant subcritical chiral clusters that can join crystals of the same chirality. Saito and Hyuga proposed a cluster model, in which a similar process is involved.⁸⁾

Very recently, the same method of grinding crystals has been used for changing the chirality of amino acid derivative molecules.⁹⁾ In this case, a molecule is chiral and its chirality can be changed in a solution. Thus, the chirality conversion of crystals simultaneously implies the chirality conversion of molecules: simple grinding converts the chirality of molecules. The authors of ref.⁹⁾ attributed this phenomenon to Ostwald ripening. However, to date, no convincing explanation has been given in this line. As noted by McBride and Tully,¹⁰⁾ the mechanism that brings about homochirality in this case may be the same as that of NaClO_3 , that is, the crystallization of the

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chiral clusters.

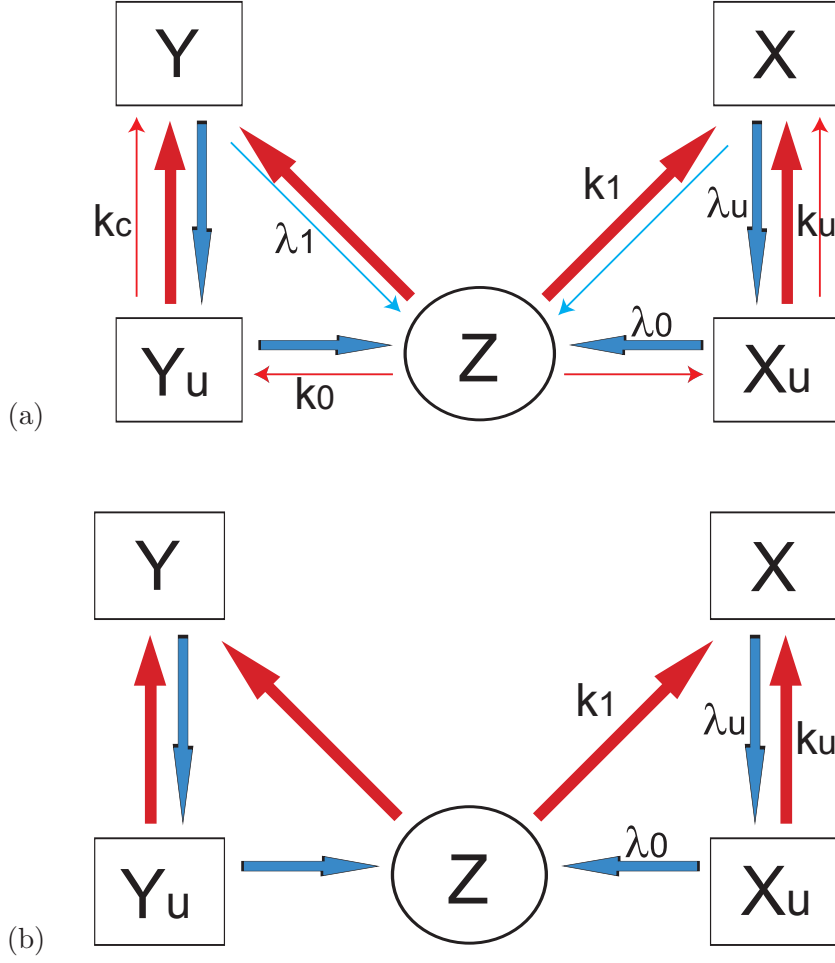


Fig. 1. (Color online) (a) Original reaction-type model.⁷⁾ X and Y: chiral crystals, X_u and Y_u : subcritical chiral clusters, and Z: achiral molecules. (b) Minimal model for chirality conversion.¹⁰⁾

Since the original model⁷⁾ was introduced to explain both chiral crystallization from a supersaturated solution and chirality conversion with grinding crystals, it involves the processes of cluster formation from monomers and crystal nucleation. The reaction scheme is depicted in Fig. 1(a), where X and Y are chiral crystals, X_u and Y_u are subcritical chiral clusters and, Z represents achiral molecules. The model implies the following kinetic equations for describing the change in the mass of each component:

$$\frac{dx}{dt} = k_1zx + k_u x_u x + k_c x_u^2 - \lambda_1 x - \lambda_u x, \quad (1)$$

$$\frac{dy}{dt} = k_1zy + k_u y_u y + k_c y_u^2 - \lambda_1 y - \lambda_u y, \quad (2)$$

$$\frac{dx_u}{dt} = k_0z^2 - k_u x_u x - k_c x_u^2 + \lambda_u x - \lambda_0 x_u, \quad (3)$$

$$\frac{dy_u}{dt} = k_0z^2 - k_u y_u y - k_c y_u^2 + \lambda_u y - \lambda_0 y_u, \quad (4)$$

$$\frac{dz}{dt} = -2k_0z^2 - k_1zx - k_1zy + \lambda_1x + \lambda_1y + \lambda_0x_u + \lambda_0y_u. \quad (5)$$

The parameters indicate the rates of cluster formation (k_0), nucleation of crystals (k_c), growth with monomers (k_1), growth with clusters (k_u), and corresponding decay processes (λ_0 , λ_1 , λ_u). The total mass is conserved and normalized to unity: $x(t) + x_u(t) + y(t) + y_u(t) + z(t) = 1$. As shown in ref.,⁷⁾ starting from almost equal amounts of X and Y with Z, the system shows a rapid relaxation to a saturated racemic state. If a small imbalance between X and Y exists, it is amplified slowly, and a homochiral state is realized at the end. There are three fixed points of the evolution equations (1)-(5): one unstable racemic state and two stable chiral states. The eigenvalues of the linearized evolution equation at the unstable fixed point determine time scales of a fast racemization and a slow chirality conversion.

McBride and Tully¹¹⁾ pointed out that, in the experiment of chirality conversion, the spontaneous formation of chiral clusters and the nucleation of crystal seeds, denoted k_0 and k_c , are not necessary, and the reaction scheme can be reduced to that shown in Fig. 1(b). The dissolution of monomers Z from the crystals X and Y, the terms with λ_1 , certainly exists in the real system, but the elimination of this process does not change the qualitative features described below and makes mathematical analysis easier. The simplified evolution equations now become

$$\frac{dx}{dt} = k_1zx + k_u x_u x - \lambda_u x, \quad (6)$$

$$\frac{dy}{dt} = k_1zy + k_u y_u x - \lambda_u y, \quad (7)$$

$$\frac{dx_u}{dt} = -k_u x_u x + \lambda_u x - \lambda_0 x_u, \quad (8)$$

$$\frac{dy_u}{dt} = -k_u y_u y + \lambda_u y - \lambda_0 y_u, \quad (9)$$

$$\frac{dz}{dt} = -k_1zx - k_1zy + \lambda_0 x_u + \lambda_0 y_u. \quad (10)$$

The numerical solution of eqs. (6)-(10) is similar to that⁷⁾ of eqs. (1)-(5) except at the initial stage, where cluster formation and nucleation are not negligible. It shows a fast relaxation to a saturated racemic mixture and then a slow exponential increase in enantiomeric excess, which is defined by $(x - y)/(x + y)$, to one of the homochiral states, in agreement with experimental results.^{1,6)}

Equations (6)-(10) have two homochiral fixed point solutions¹¹⁾

$$\begin{aligned} \mathbf{x}^R &\equiv (x^R, y^R, x_u^R, y_u^R, z^R) \\ &= \left(x^{**}, 0, \frac{\lambda_u x^{**}}{k_u x^{**} + \lambda_0}, 0, \frac{\lambda_0 \lambda_u}{k_1 (k_u x^{**} + \lambda_0)} \right), \\ \mathbf{x}^L &\equiv (x^L, y^L, x_u^L, y_u^L, z^L) \\ &= \left(0, x^{**}, 0, \frac{\lambda_u x^{**}}{k_u x^{**} + \lambda_0}, \frac{\lambda_0 \lambda_u}{k_1 (k_u x^{**} + \lambda_0)} \right) \end{aligned} \quad (11)$$

with the crystal mass

$$x^{**} = \frac{1}{2} \left(s - \frac{\lambda_0}{k_u} - \frac{\lambda_u}{k_u} \right) + \frac{1}{2} \sqrt{\left(s - \frac{\lambda_0}{k_u} - \frac{\lambda_u}{k_u} \right)^2 + 4 \frac{\lambda_0}{k_u} \left(s - \frac{\lambda_u}{k_1} \right)}, \quad (12)$$

where s is the total mass normalized to unity here. It should be noted that these fixed points are by no means ordinary equilibrium states, since the circulating flux $Z \rightarrow X \rightarrow X_u \rightarrow Z$ exists in the reaction loop (Fig. 1(b)). In addition, an unstable racemic fixed point is observed

$$\begin{aligned} \mathbf{x}^U &= (x^U, y^U, x_u^U, y_u^U, z^U) \\ &= \left(x^*, x^*, \frac{\lambda_u x^*}{k_u x^* + \lambda_0}, \frac{\lambda_u x^*}{k_u x^* + \lambda_0}, \frac{\lambda_0 \lambda_u}{k_1 (k_u x^* + \lambda_0)} \right), \end{aligned}$$

with

$$x^* = \frac{1}{2} \left(\frac{1}{2} - \frac{\lambda_0}{k_u} - \frac{\lambda_u}{k_u} \right) + \frac{1}{2} \sqrt{\left(\frac{1}{2} - \frac{\lambda_0}{k_u} - \frac{\lambda_u}{k_u} \right)^2 + 2 \frac{\lambda_0}{k_u} \left(1 - \frac{\lambda_u}{k_1} \right)}. \quad (13)$$

The antisymmetric deviation from this fixed point $\delta \mathbf{x} = \mathbf{x} - \mathbf{x}^U = (\delta x, -\delta x, \delta x_u, -\delta x_u, 0)$ has a positive eigenvalue, which characterizes the exponential amplification of the enantiomeric excess.

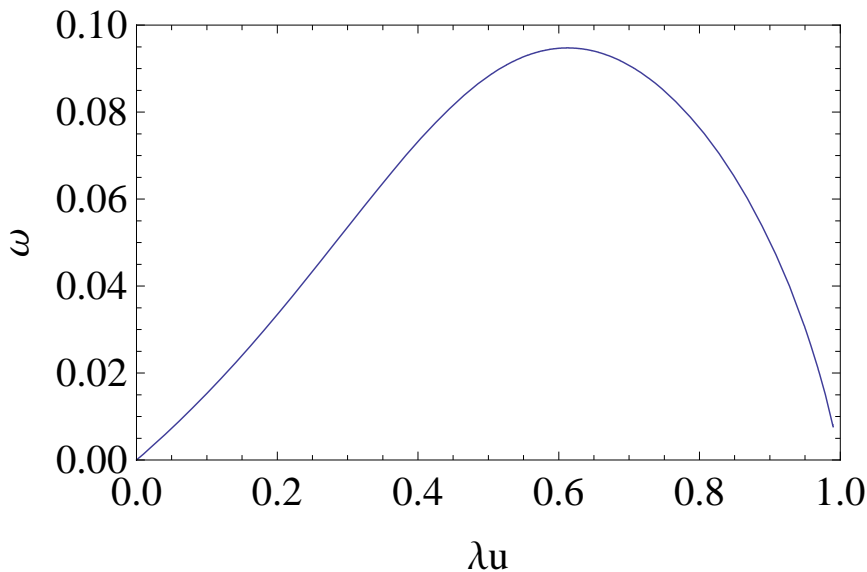


Fig. 2. (Color online) Positive eigenvalue ω of the unstable racemic fixed point. The values of other parameters are $k_1 = 1.0$, $k_u = 1.0$, and $\lambda_0 = 0.1$.

With these formulae and the numerical example, several important features of this system are noted. Firstly, the eigenvalue ω , which can be calculated analytically for this simple case, increases roughly linearly with λ_u , as shown in Fig. 2, unless λ_u is very large. Since the increase in λ_u implies a fast crystal decay, the result agrees with the experimental results^{1,6)} indicating that the time necessary to attain the homochiral state is inversely proportional to the strength of grinding (rotation frequency of the mixer or the number of glass beads). Secondly, the monomer

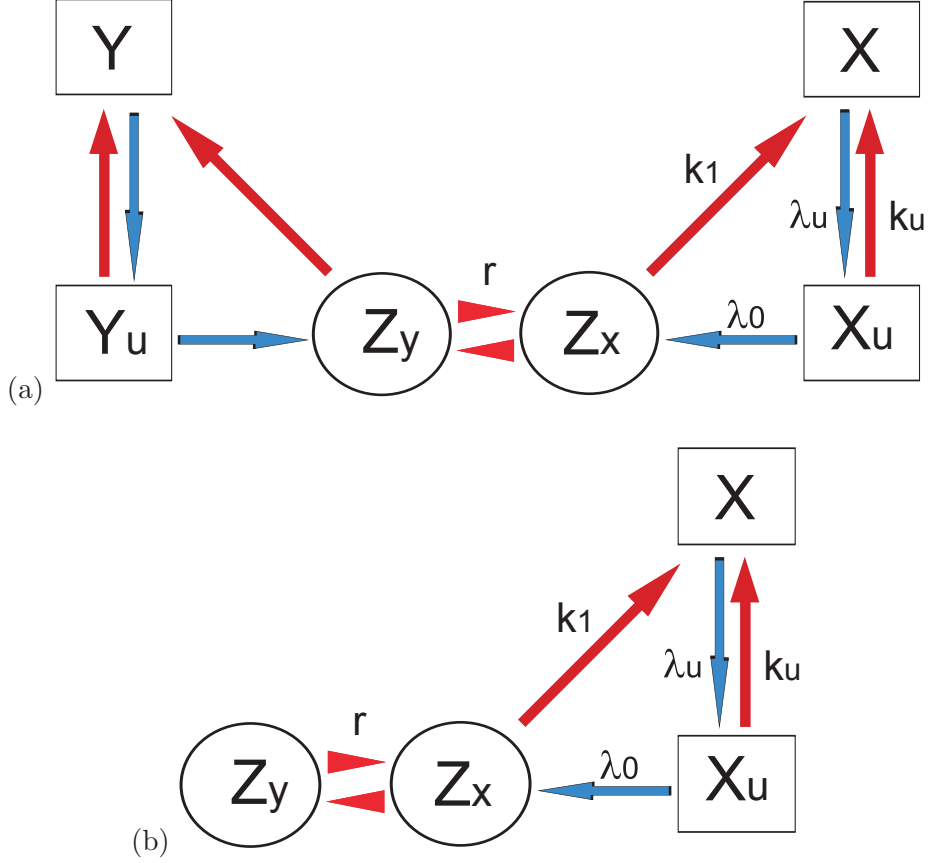


Fig. 3. (Color online) (a) Reaction scheme for chirality conversion of molecules via grinding crystals in a solution .
 (b) Reaction scheme of the homochiral state .

concentration in the racemic state (13) is higher than that in the final chiral state (11). This is not the Gibbs-Thomson effect since the size distribution of crystals must be steady in the experiment with grinding and must be the same in these two states (the change in size distribution is not considered in our model from the beginning). The second feature can be confirmed experimentally to test our simple model.

It is easy to extend the model to the conversion of molecular chirality. In place of achiral molecules Z , there are chiral molecules, Z_x and Z_y , which are converted to each other with a racemization rate constant r in a solution (Fig. 3(a)). The time evolution equations are

$$\frac{dx}{dt} = k_1 z_x x + k_u x_u x - \lambda_u x, \quad (14)$$

$$\frac{dy}{dt} = k_1 z_y y + k_u y_u y - \lambda_u y, \quad (15)$$

$$\frac{dx_u}{dt} = -k_u x_u x + \lambda_u x - \lambda_0 x_u, \quad (16)$$

$$\frac{dy_u}{dt} = -k_u y_u y + \lambda_u y - \lambda_0 y_u, \quad (17)$$

$$\frac{dz_x}{dt} = -k_1 z_x x + \lambda_0 x_u - r z_x + r z_y, \quad (18)$$

$$\frac{dz_y}{dt} = -k_1 z_y y + \lambda_0 y_u - r z_y + r z_x. \quad (19)$$

The total mass is conserved: $x + y + x_u + y_u + z_x + z_y = 1$. In the limit of infinitely fast racemization, $r \rightarrow \infty$, the model reduces to the previous one with $k_1 \rightarrow k_1/2$ and $Z_x + Z_y \rightarrow Z$.

The evolution equations (14)-(19) have an unstable racemic fixed point \mathbf{x}^U , which is only a superposition of the two homochiral fixed points (11):

$$\begin{aligned} \mathbf{x}^U &= (x^U, y^U, x_u^U, y_u^U, z_x^U, z_y^U) \\ &= \left(\bar{x}^*, \bar{x}^*, \frac{\lambda_u \bar{x}^*}{k_u \bar{x}^* + \lambda_0}, \frac{\lambda_u \bar{x}^*}{k_u \bar{x}^* + \lambda_0}, \frac{\lambda_0 \lambda_u}{k_1 (k_u \bar{x}^* + \lambda_0)}, \frac{\lambda_0 \lambda_u}{k_1 (k_u \bar{x}^* + \lambda_0)} \right), \end{aligned}$$

where \bar{x}^* is equal to x^{**} in eq. (12) with $s = 1/2$. There are also two stable homochiral fixed points, in which the two chiral monomers have the same concentration. Its reaction scheme is shown in Fig. 3(b). The right-handed chiral state is

$$\begin{aligned} \mathbf{x}^R &= (x^R, y^R, x_u^R, y_u^R, z_x^R, z_y^R) \\ &= \left(\bar{x}^{**}, 0, \frac{\lambda_u \bar{x}^{**}}{k_u \bar{x}^{**} + \lambda_0}, 0, \frac{\lambda_0 \lambda_u}{k_1 (k_u \bar{x}^{**} + \lambda_0)}, \frac{\lambda_0 \lambda_u}{k_1 (k_u \bar{x}^{**} + \lambda_0)} \right), \end{aligned} \quad (20)$$

where \bar{x}^{**} is given by (12) with $s = 1$ and $k_1 \rightarrow k_1/2$. The corresponding left-handed state \mathbf{x}^L has a similar expression.

The time evolution with $r = 0.1$ is shown in Fig. 4. The overall behavior is similar to that of the previous model, although the initial fast relaxation takes twice as much time and the conversion to the homochiral state takes three times as much time. A temporal increase in the concentration of minority monomers Z_y at the end of conversion due to the decay of minority clusters Y_u is observed (Fig. 4(c)).

As shown in Fig. 5, the change in crystal enantiomeric excess is exponential, in agreement with the experimental result.⁹⁾ The time necessary for the completion of chirality conversion (neglecting a small slow deceleration at the end) is plotted as a function of the racemization rate r in Fig. 6. If the racemization rate r is very high compared with the monomer crystallization rate $k_1 = 1$ ($r \gtrsim 10$), the completion time does not depend on r since a fast racemization in a solution can follow other slow processes. On the other hand, if the rate is very low ($r \lesssim 0.1$), it slows down the whole process, and the completion time becomes inversely proportional to r .

We have analyzed the simple models showing the complete chirality conversion of crystals and, in the case of racemizing molecules, the resultant chirality conversion of the molecules. The most important ingredients of the model are chiral clusters in a solution. The chiral clusters are produced by the perpetual grinding of crystals, and they are integrated into the crystals of the same chirality with the rates proportional $x_u x$ or $y_u y$. Because of the forced decay of crystals, there are no (quasi-)equilibrium states, but only (quasi-)steady states with a circulating flux in the reaction loop. The chirality conversion proceeds exponentially. Its rate is determined by the unstable racemic fixed point and is approximately proportional to the strength of grinding λ_u . Our model predicts a slight

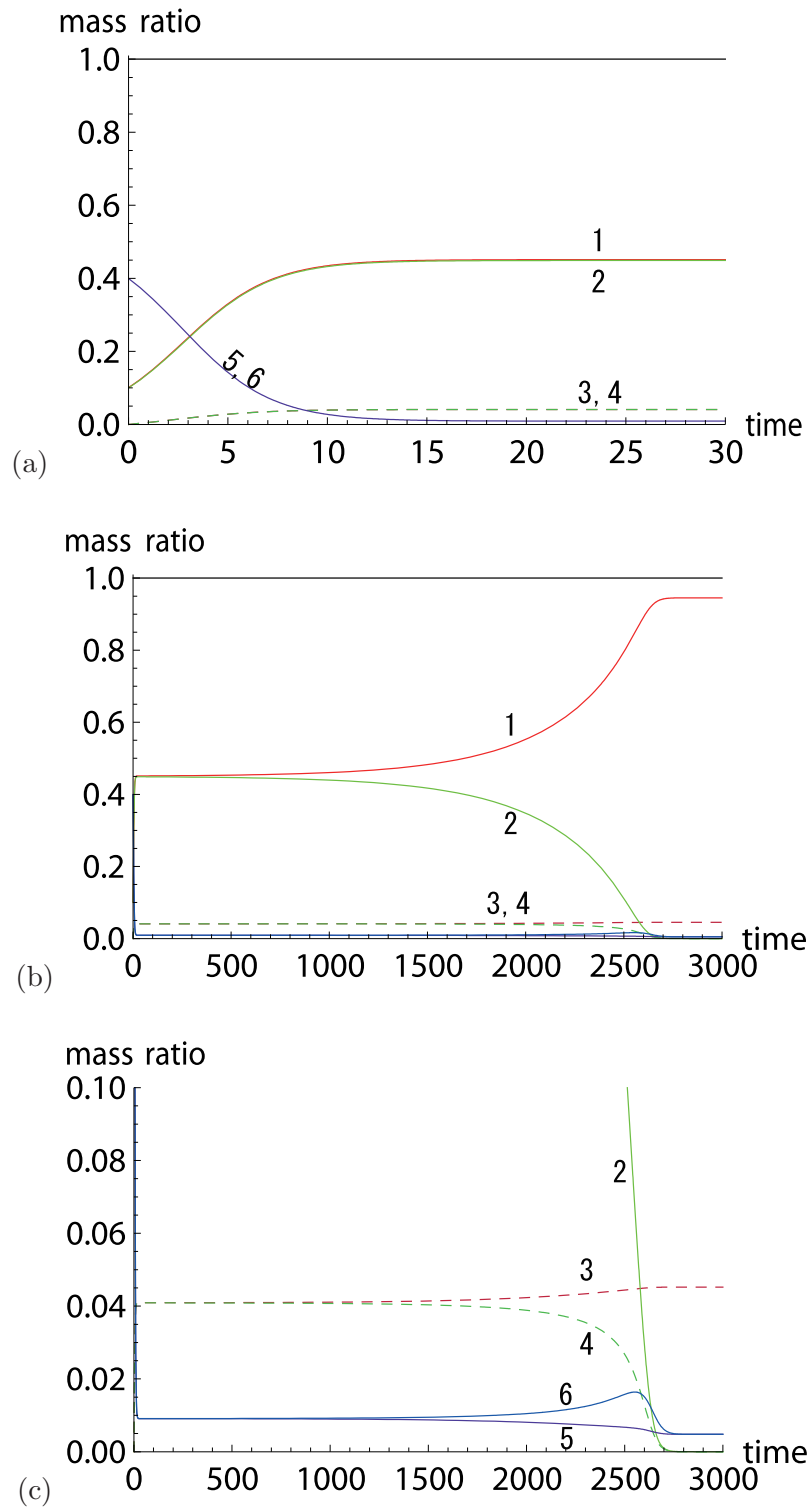


Fig. 4. (Color online) Time evolution of a solution of eqs. (14)-(19) with the parameter values $r = 0.1$, $k_1 = 1.0$, $k_u = 1.0$, $\lambda_u = 0.05$, and $\lambda_0 = 0.1$, and the initial conditions $x(0) = 0.101$ (1: red line), $y(0) = 0.100$ (2: green line), $x_u(0) = 0.0$ (3: broken redish purple line), $y_u(0) = 0.0$ (4: broken bluish green line), $z_x(0) = 0.3995$ (5: purple line), and $z_y(0) = 0.3995$ (6: greenish blue line). (a) Short-time behavior, (b) long time behavior, and (c) enlargement of (b).

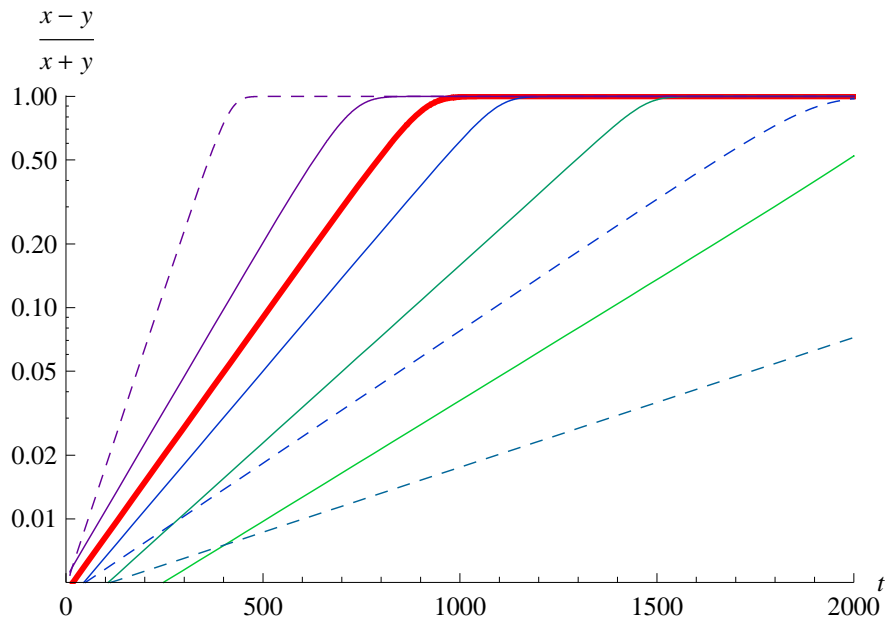


Fig. 5. (Color online) Exponential time evolution of the crystal enantiomeric excess with the parameter values $r = 1.0$, $k_1 = 1.0$, $k_u = 1.0$, $\lambda_u = 0.05$, and $\lambda_0 = 0.1$, and the initial conditions are the same as those in Fig. 4 (thick line). Thin solid lines indicate the results obtained with $r = 100, 0.5, 0.25$, and 0.125 , and broken lines, with $\lambda_u = 0.1, 0.025$, and 0.0125 from left to right. Other parameters take the same values.

decrease in monomer concentration from the racemic steady state to the final homochiral state. The model for molecular chirality conversion is similar to that for crystal chirality conversion. The difference is only appreciable when the racemization rate r in a solution is low. In this case, a temporal increase in the concentration of minority monomers in the solution may be observed, and the completion time of chirality conversion is inversely proportional to r .

Since our models contain the autocatalytic mechanism, they predict the exponential amplification of the initial chiral imbalance, as observed in the experiments.^{1,6,9)} Some authors attribute the chirality conversion phenomena to stochastic selection and Ostwald ripening.^{9,12,13)} As pointed out by McBride,¹¹⁾ stochastic selection¹⁴⁾ may realize the homochiral state but the increase in chirality imbalance in the stochastic model is fast in the beginning and gradually slows down, in contradiction to that observed in the experiments.

Noorduyn et al.¹³⁾ proposed a stochastic model to reproduce the relevant features of a molecular conversion experiment.⁹⁾ They introduced direct mass exchange between two solid clusters from the smaller cluster to the larger cluster. With exchange rates biased between clusters of the same kind and of a different kind, which supposedly corresponds to slow racemization in a solution, an exponential amplification is reproduced. The authors call the direct mass exchange ‘‘Ostwald ripening,’’ but Ostwald ripening is a mean field effect mediated by monomer concentration. Thus, the physical justification of this model is not clear. Also, for the case of fast racemization (without the bias), $r \rightarrow \infty$, corresponding to the case of NaClO_3 , the time dependence obtained¹³⁾ indicates

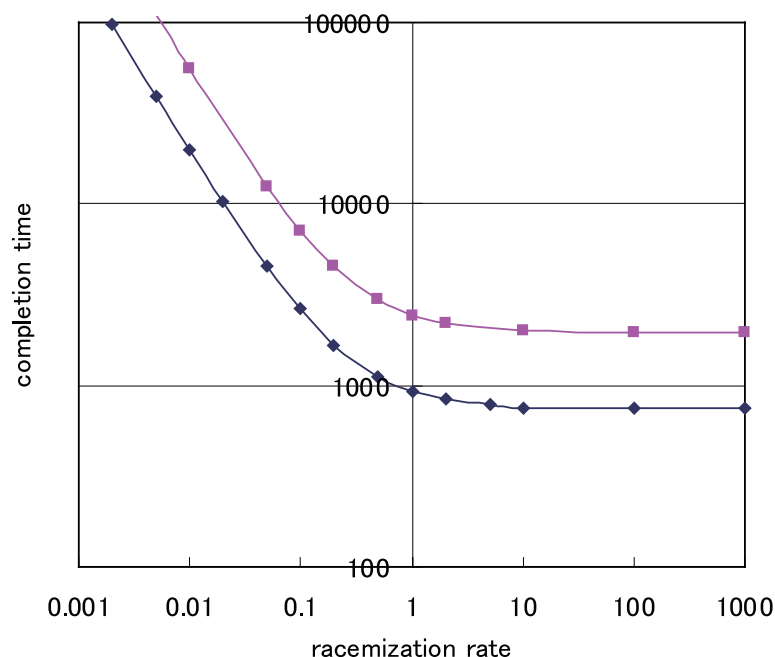


Fig. 6. (Color online) Completion time for deracemization as a function of the deracemization rate in a solution. Upper curve with $\lambda_u = 0.02$ and the lower curve with $\lambda_u = 0.05$.

the following characteristics of a simple stochastic selection: random final chirality, no amplification of averaged enantiomeric excess, and completion time being proportional to system size. In contrast, in our model, a fast racemization results in a fast chirality conversion. This effect of racemization rate r can be tested experimentally. The other stochastic model¹²⁾ does not show the exponential amplification either. This is a crucial point that distinguishes between the model with the nonlinear amplification of chiral imbalance and that without.

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