

Steady Chirality Conversion by Grinding Crystals —Subcritical and Supercritical Transitions—

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Abstract

With the use of the classical nucleation model, the passage from the initial stage of nucleation to the final stage of Ostwald ripening is surveyed. Direct numerical integration confirms that, under weak initial supersaturation, the drop of supersaturation occurs with a long delay but the relative drop is deep. For various initial supersaturation, the cluster size distribution approaches the single Lifshits-Slyozov-Wagner form. Based on an analysis of current in the cluster size space, a single variable model to describe the time evolution of supersaturation is proposed. The classical nucleation model is generalized and applied to the problem of chirality conversion with grinding crystals.

Keywords: chirality conversion, symmetry breaking, classical nucleation model, sodium chlorate

1. Introduction

Chiral symmetry breaking of crystals originated from molecular chirality was discovered by Pasteur when he observed carefully the shape of tiny tartrate salt crystals. In many organic compounds, right-handed (R) molecules and left-handed (L) molecules form separate crystals of the chiral pair structures which can be detected easily from the shape or from the optical properties¹. Achiral molecules such as SiO₂ may also form crystals of chiral structures as R and L quartz. Without an external bias, R and L crystals are formed with an equal probability and racemic mixture of the chiral crystals are obtained. It has been known that spontaneous chiral symmetry breaking occurs when NaClO₃ crystals are nucleated from a supersaturated solution with vigorous stirring[3]. The obtained crystals are almost homochiral in each trial, and the realization of a homochiral state is attributed to secondary nucleation induced by collision of crystals[4, 5].

Recently, chirality conversion of NaClO₃ crystals by grinding in a solution was discovered by Viedma[1]. Here crystals of both chirality are present at the beginning, and grinding them in a saturated solution converts the minority type of crystals to the majority type via breaking, dissolution and recrystallization. Simple grinding produces a homochiral state of crystals. With regard to the mechanism that realize chirality conversion of NaClO₃, the present author proposed a simple reaction type model with direct crystallization of clusters. The crystallization of clusters acts as an autocatalytic process[10] and accelerates growth of the majority. The grinding method was successfully

applied to an amino acid derivative by Noorduyn et al.[9]. In organic systems, molecules themselves have chirality, and the change of crystal chirality simultaneously implies the change of molecular chirality. Thus chirality of the molecule is converted by simple grinding. Since then, many studies have proved that this method can be applied to various systems, both achiral and chiral molecules(See [11] for a recent review).

To explain the mechanism of chirality conversion with grinding, several theoretical models have been proposed[10, 20, 16, 17, 12, 21, 14, 23, 22, 24]. Although detailed consensus about the mechanism to realize chirality conversion has not been reached, it seems that some kind of autocatalytic process is necessary to reproduce the exponential amplification of the chirality imbalance (enantiomeric excess) observed in many experiments[1, 8, 9, 19, 29]. The Monte Carlo simulation of a cluster model[24] suggests that random fluctuation may bring homochirality of a small system without an autocatalytic process, but the cluster reaction is necessary for a large system[28]. The simple reaction type model[10] assumes a steady size distribution of clusters(crystals) during chirality conversion, and it is confirmed with the use of a generalized classical nucleation model[22].

The grinding method can be used for production of homochiral compounds in chemical engineering. For that purpose, it is desirable to operate the system continuously without interruption by providing ingredients and taking up the chiral products. In this paper we study chirality conversion in an open system, and find conditions for steady state chirality conversion. Since steady removal of chiral products and addition of achiral or racemic molecules are equivalent to circulation in the system, we call a system in this situation a circulating system. In 2 the reaction type models and the generalized CNM are defined. We show results of numerical calculation of the generalized CNM with various circulation rate in ???. The steady state

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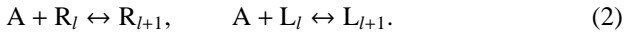
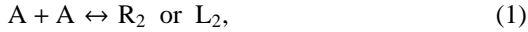
¹The two chiral pairs are called dextrorotatory (D) and levorotatory (L), or rectus (R) and sinister (S) in different contexts. In this paper, we simply use the words, right and left.

under a strong circulation is racemic, and a bifurcation from the racemic state to a chiral state occurs with decreasing the circulation rate. The character of the bifurcation is different for achiral molecules and chiral molecules. The feature is also reproduced in the simple reacton type models in 4.

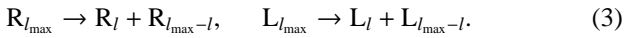
2. Models for chirality conversion

We introduce two types of models[10, 14] which are devised to explain the chirality conversion phenomena for achiral and chiral molecules.

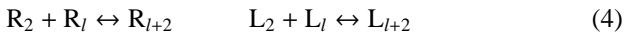
The first model is a generalized classical nucleation model (CMN)[22], which describes time evolution of the system in terms of the size distribution of crystal clusters. We assume that a molecule A is achiral and, for simplicity, all clusters are chiral. The chiral clusters are indicated by R_l or L_l , where l is the number of molecules in a cluster. The following cluster reactions are considered:



Grinding is taken into account by limiting the maximum size of clusters to l_{\max} . Clusters of the maximum size are assumed to decompose into small clusters as

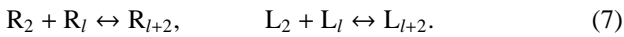
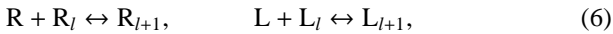


A chirality imbalance in this model is always relaxed to vanish. To realize amplification of an initial chirality imbalance, we need to add crystallization of dimers



for $2 \leq l \leq l_{\max} - 2$. This model reproduces features of the chirality conversion of NaClO_3 .

For the case of organic molecules, the processes 1, 2 and 4 are replaced by



Evolution of the system in these models is described in terms of number of clusters

$$\{n_1(t), n_2^R(t), \dots, n_{l_{\max}}^R(t), n_2^L(t), \dots, n_{l_{\max}}^L(t)\} \quad (8)$$

for the achiral molecules and

$$\{n_1^R(t), n_2^R(t), \dots, n_{l_{\max}}^R(t), n_1^L(t), n_2^L(t), \dots, n_{l_{\max}}^L(t)\}, \quad (9)$$

for the organic system, respectively. The explicit forms of equations are given in [22].

To study an open system, a certain ratio of the largest clusters are taken out from the system and the same mass of the achiral molecules A or racemic mixtures of R and L are added to the

system. Thus the equation the following terms are added to the equations for the change of monomers and the largest clusters:

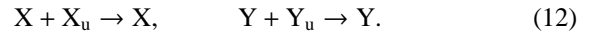
$$\frac{\partial n_1(t)}{\partial t} = \lambda \left(n_{l_{\max}}^R(t) + n_{l_{\max}}^L(t) \right), \quad (10)$$

$$\frac{\partial n_{l_{\max}}^{R(L)}(t)}{\partial t} = -\lambda n_{l_{\max}}^{R(L)}(t), \quad (11)$$

where λ represents the circulation rate.

The second model is the reacton type model, in which only several variables, *i.e.* the masses of chiral crystals, are used to describe the system[10]. The following processes are essential for the amplification of chiral imbalance[13].

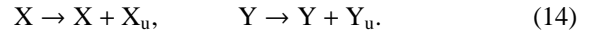
- 1) Growth of crystals by incorporating chiral clusters



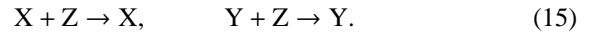
- 2) Decay of chiral clusters



- 3) Dissolution of chiral clusters from crystals

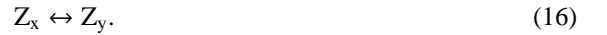


- 4) Growth of crystals by incorporating achiral monomers

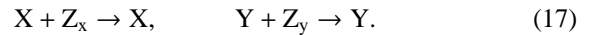


where X, Y, X_u , Y_u , Z represent R crystals, L crystals, R growth units (clusters), L growth units (clusters) and achiral monomers. For the organic systems, molecules are chiral Z_x and Z_y , and (15) is replaced by

- 5) Racemization (change of chirality) of monomers



- 6) Growth of crystals by incorporating chiral monomers



This model neglects the change of size distribution and therefore assuming a steady size distribution of crystals, which is demonstrated in the first model[22].

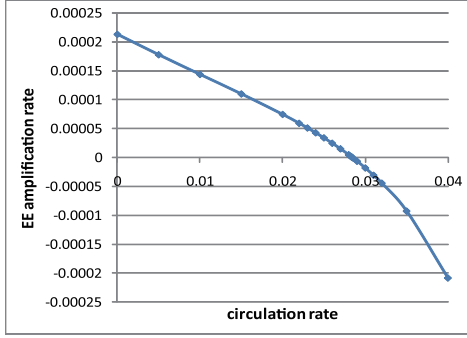
3. Numerical results of the generalized CNM

In the generalized CNM in a closed system (without circulation), if one start with a size distribution of a somewhat arbitrary form with a small chirality imbalance, the distribution soon reaches a seemingly steady but actually an unstable racemic distribution $n_l^R(t_0) \approx n_l^L(t_0) \approx n_l^{\text{unstable}}$ (t_0 : a characteristic time of the initial change). Then after a slow exponential amplification of the chirality imbalance ($n_l^R(t) - n_l^L(t) \propto e^{\omega t}$), the distribution ends up with an almost homochiral stable distribution. In the final steady state, the distribution of the majority (suppose R) is roughly the sum of the two distributions during the slow change:

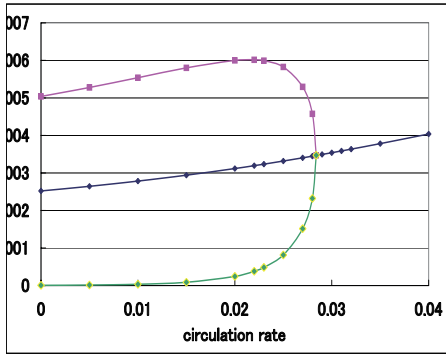
$$n_l^{\text{R,stable}} = n_l^R(t \rightarrow \infty) \approx n_l^R(t) + n_l^L(t) \approx 2n_l^{\text{unstable}}, \quad (18)$$

$$n_l^{\text{L,stable}} = n_l^L(t \rightarrow \infty) \approx 0 \quad (19)$$

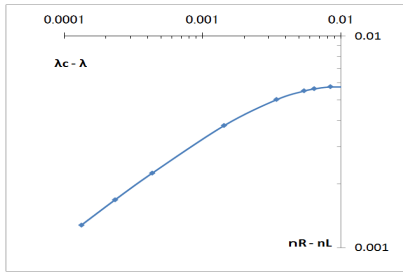
for $t_0 \leq t$ [22].



(a)



(b)



(c)

Figure 1: (a) The amplification rate of EE. (b) Change of the number density of the largest chiral clusters, $n_{l_{\max}}^R$ and $n_{l_{\max}}^L$, as the circulation rate λ . (c) Critical behavior of $n_{l_{\max}}^R - n_{l_{\max}}^L$.

When the circulation of molecules is introduced ($\lambda \neq 0$), the amplification rate ω of the chirality imbalance decreases. In Fig.1(a), we show the amplification rate of the enantiomeric excess (EE) defined by

$$EE = \frac{\sum_{l=2}^{l_{\max}} l n_l^R - \sum_{l=2}^{l_{\max}} l n_l^L}{\sum_{l=2}^{l_{\max}} l (n_l^R + n_l^L)}. \quad (20)$$

The final steady distribution changes as a function of the circulation strength λ [25]. The amplification rate of EE decreases linearly with λ , and above the critical value $\lambda_c = 0.02843$, it becomes negative, which implies relaxation to a racemic state with $EE = 0$ (this is a continuation of the unstable state n_l^{unstable}). The time τ necessary for the chirality conversion diverges as

$$\tau \sim \frac{1}{\lambda_c - \lambda}. \quad (21)$$

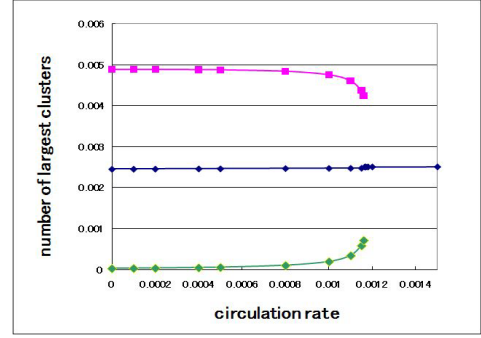


Figure 2: Change of the number density of the largest chiral clusters, $n_{l_{\max}}^R$ and $n_{l_{\max}}^L$, as the circulation rate λ in the case of chiral molecules with $r = 0.1$.

Simultaneously, the steady state distribution changes. In Fig.1(b), we show the steady state value of the number of the largest chiral clusters $n_{l_{\max}}^R$ and $n_{l_{\max}}^L$. For $\lambda \lesssim 0.01$ there are very few minority species and the steady state chirality conversion is perfectly realized. When the circulation rate approaches the critical value, the difference of the steady state numbers of the largest clusters decreases with increasing λ . The transition from the chiral steady state to the racemic steady state is continuous (supercritical bifurcation), and the critical behavior is, as expected from a mean field type model,

$$n_{l_{\max}}^R - n_{l_{\max}}^L \propto (\lambda_c - \lambda)^{1/2} \quad (22)$$

as shown in Fig.1(c).

We may expect similar behavior for the case of organic chiral molecules. In the generalized CNM of chiral molecules, there is an additional parameter, the racemization rate r , which characterizes the rate of molecular chirality conversion (racemization) represented by (5) and appears in the evolution equation as

$$\frac{\partial n_1^{\text{R(L)}}(t)}{\partial t} = -r n_1^{\text{R(L)}}(t) + r n_1^{\text{L(R)}}(t) \quad (23)$$

along with other terms. If the racemization of the molecules is extremely fast ($r \rightarrow \infty$), the system of chiral molecules becomes identical to the system of achiral molecules[14]. We show the change of the largest chiral clusters $n_{l_{\max}}^R$ and $n_{l_{\max}}^L$ with $r = 0.1$ in Fig.2. The amplification rate (not shown here) linearly decreases with increasing the circulation rate λ , similarly to the case of Fig.1(a)[26]. The critical point is $\lambda_c = 0.00117$, which is much smaller than the value in Fig.1(a). Although general trends look similar to the achiral case, the change of the number density of the largest clusters with the circulation strength is not continuous. The transition to the racemic state with high circulation rate shows a large gap: the bifurcation is supercritical. The magnitude of the gap at the transition point decreases when the racemization rate r becomes large.

4. Numerical results of the reaction-type model

We also performed numerical calculation in the simple reaction-type models. Figs.3 and 4 show the masses of chiral crystals X and Y in the steady state. In the system with achiral

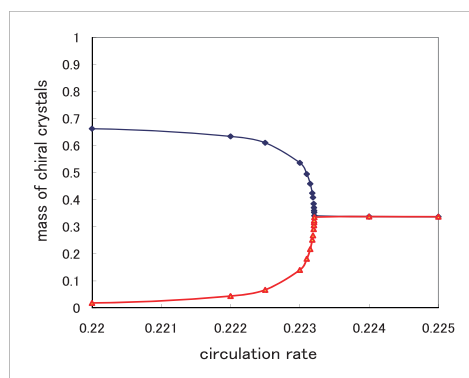


Figure 3: Change of the masses of chiral crystals with the circulation rate λ in the simple reaction-type model for achiral molecules.

molecules (Fig.3), the transition at $\lambda_1 = 0.2232$ is continuous with the critical behavior

$$x - y \propto (\lambda_{1,c} - \lambda_1)^{1/2}, \quad (24)$$

where x and y are the masses of X and Y, and the λ_1 is the rate at which chiral crystals decay into achiral monomers Z in the form $\dot{z} = \lambda_1(x + y)$, $\dot{x} = -\lambda_1 x$ and $\dot{y} = -\lambda_1 y$ [27].

In the system with chiral molecules (Fig.4), the transition from the chiral steady state to the racemic steady state occurs at $\lambda_1 = 0.2195$ with the racemization rate $r = 100.0$ (other parameters are the same as Fig.3), and there is a jump in the mass difference $x - y \approx 0.34$ at the transition point. In contrast to the case of achiral molecules, the transition is discontinuous (a subcritical bifurcation). The gap increases with decreasing the racemization rate r : the transition with $r = 1.0$ occurs at $\lambda_1 = 0.03842$ and the gap is $x - y \approx 0.85$.

5. Summary and discussion

We studied the chirality conversion of crystals by grinding in an open system with circulation. The generalized CNM and the simple reaction-type models both show that perfect chirality conversion is possible if circulation is weak. By increasing the circulation rate λ , the amplification rate ω of a chirality imbalance becomes small and the difference of the amount of the chiral products in the steady state decreases with λ . The chiral steady state disappears above the critical strength of the circulation. The transition between the racemic and the chiral steady states is continuous in the system of achiral molecules and discontinuous in the system of chiral molecules (as in organic systems). The latter feature exhibits strongly with slow molecular racemization.

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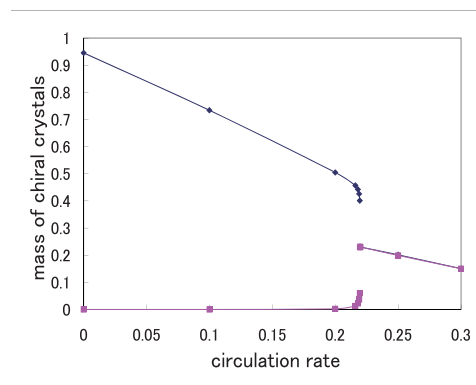


Figure 4: Change of the masses of chiral crystals with the circulation rate λ in the simple reaction-type model for chiral molecules with $r = 100$.

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- [26] The amplification rate is much smaller compared to the case of achiral

molecules since the extra process, the change of molecular chirality, is necessary for the conversion.

- [27] The values of other parameters are: the rate of cluster formation from monomers ($\dot{x}_u = k_0 z^2$, $\dot{y}_u = k_0 z^2$) $k_0 = 0.1$, the rate of monomer growth ($\dot{x} = k_1 xz$, $\dot{y} = k_1 yz$) $k_1 = 1.0$, the rate of cluster growth ($\dot{x} = k_u x_u z$, $\dot{y} = k_u y_u z$) $k_u = 1.0$, the rate of crystal nucleation ($\dot{x} = k_c x_u^2$, $\dot{y} = k_c y_u^2$) $k_c = 0.01$, the rate of cluster decay of crystals ($\dot{x} = -\lambda_u x$, $\dot{y} = -\lambda_u y$) $\lambda_u = 0.05$, the rate of decay of clusters ($\dot{x}_u = -\lambda_0 x_u$) $\lambda_0 = 0.1$. See [10, 14] for complete forms of the equations.
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