Chiral Symmetry Breaking in Crystal Growth: Is Hydrodynamic Convection Relevant?

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The effects of mechanical stirring on nucleation and chiral symmetry breaking have been investigated for a simple inorganic molecule, sodium chlorate. In contrast to earlier findings, our experiments suggest that hydrodynamic convection may have little to do with the observed symmetry breaking. Rather the effect can be reasonably accounted for by mechanical damage to incipient crystals. The catastrophic events, creating numerous small "secondary" crystals, produce statistical domination of one chiral species over the other. A number of observations using different mixing methods support this conclusion. [S0031-9007(96)01217-3]

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It is fascinating that chirality, when created spontaneously from a random background, can prevail throughout its evolution. The fact that biologically relevant molecules such as amino acids and nucleic acids exist only in one of the two mirror isomers is an intriguing example. What mechanisms are responsible for chiral generation and proliferation? One compelling explanation for this self-organization involves the process of autocatalysis, the enhancement of the rate of growth of a population as that population increases, along with a competition between the two chiral species [1].

In the early 1990s a system having these ingredients for chiral symmetry breaking was reported by Kondepudi *et al.* [1]. Using a supersaturated solution of an inorganic salt, sodium chlorate ($NaClO_3$), it was found that crystals which precipitated from this achiral solution were dominated by a single chiral species when the solution was gently stirred by a magnetic mixer. From 32 individual crystallizations, which yielded 11 829 crystals, he found that the total population was consistent with a 50-50 distribution of left-handed (L) and right-handed (R) crystals. However, each individual crystallization was heavily populated by either the L or the R crystals with chiral purity in excess of 99%. The observation is in drastic contrast with crystal growth in quiescent solutions. In this case, an equal population of L and R crystals was found in individual crystallizations [1–3].

This observation is remarkable in that it suggests that the system undergoes a transition from a totally symmetric state to a totally asymmetric state simply by introducing a hydrodynamic flow without careful control of temperature and other conditions. As pointed out in Ref. [1] such a spontaneous transition has not been previously realized in any laboratory experiment. The authors attribute the observed selectivity to the enhanced autocatalysis caused by the mixing. When the first primary nucleus, which serves as a chiral template, is convected by the flow, secondary nuclei, having the same chirality as their "mother," are quickly generated and dispersed throughout the system. This causes a depletion of the solute, inhibiting the generation of the other chiral species.

Kondepudi's work has stimulated considerable interest in the scientific community. For instance, Metcalfe and Ottino have modeled the experiments by a simple autocatalytic reaction scheme combined with chaotic mixing [4]. Because of repetitive stretching and folding of fluid elements, chirality initially associated with an incipient seed spreads rapidly throughout the entire system. The observed symmetry breaking was considered by Epstein as one of many examples of imperfect mixing in autocatalytic chemical and biological systems [5].

Kondepudi's experiment touches upon a number of issues such as nucleation under flow, convective diffusion, chaotic mixing, and autocatalysis. All of these are of significant fundamental and practical importance. However, the experiment also raises many questions that need to be answered before the effect can rest on firm ground. The most pressing question is the physical origin of the secondary nucleation and its relationship to hydrodynamic convection. For this reason we have designed and carried out a series of experiments aimed at better controlling the flow properties during crystal growth.

Our experiments were performed using a $NaClO_3$ solution with a weight fraction of 50% [6]. The $NaClO_3$ was first dissolved in warm distilled water and then constantly stirred for 8 h to ensure complete dissolution of the solute. Afterwards, the solution was filtered through a 0.2 μm nylon filter. Initiated by slow evaporation, the nucleation occurred approximately 4–6 h after the samples were prepared.

The chirality of the crystals was determined by their optical activity. Under transmission, a R crystal will rotate light counterclockwise while a L crystal will rotate light clockwise. Therefore when a crystal is placed between crossed polarizers it will appear darker or lighter than the other species when one of the polarizers is uncrossed by a few degrees. Viewing the crystals under a $\times 50$ microscope allowed us to determine the handedness of the crystals even when they were only ~ 100 μm in size.

To ascertain that nucleation behaves normally with no substantial bias towards either species, a set of quiescent measurements was carried out. Here our finding was similar to that of previous measurements of this type [2,3]. In a total of 5395 crystals obtained from 94 crystallizations, 2523 were right handed and 2872 were left handed. The difference between the two species was about 6%. We note that a similar bias was also observed in Kondepudi's experiment at the level of ~10%. Defining an order parameter as $\mathcal{O} = (N^L - N^R)/(N^L + N^R)$, we plot in Fig. 1(a) the probability distribution function (PDF), $P(\mathcal{O})$, for all quiescent runs. For comparison a binomial distribution with a width comparable to our measurements is also shown. The 6% bias towards L crystals, as illustrated in the graph, is statistically significant since the standard deviation predicted by the binomial distribution is ~1% for the number of the crystals produced. It may be that the chirality of the crystals is somehow influenced by impurities already existing in the solution or by dust in the air. This conjecture of heterogeneous nucleation is supported by a set of independent measurements where carefully filtered, supersaturated $NaClO_3$ solutions were flame sealed in ampules. These samples were supercooled by as much as 100 °C with no sign of crystallization.

Two different mixing schemes were employed in our experiment. In both cases flow was produced in a petri dish of 5 cm in diameter. In the first experiment, the solution was stirred by a small Teflon-coated magnetic mixer (0.8 cm long and 0.2 cm in diameter). The mixer, driven by a horseshoe magnet, floated on the liquid-vapor interface, and its position was centered by the magnetic field gradient. Though the flow was initiated on the surface, the thin fluid layer was thoroughly mixed in the interior as well. Note that our stirring method is quite different from Kondepudi's in that in their experiments the magnetic stirrers were larger and rotated on the bottom of the sample cells [1]. Our apparatus, designed with counting statistics in mind, ran twenty samples simultaneously with all horseshoe magnets connected in tandem, driven by a single dc motor. The stirring rate f as well as the volume of the solution were the control parameters. As we shall see, the volume, which essentially determines the distance between the mixer and the bottom of the dish, plays an important role for the outcomes of the experiment. In the second experiment, an air jet was used to mix the solution. By blowing nitrogen gas across the liquid-vapor interface, a vortex pair forms in the sample, enabling mixing without mechanical contact. In the following we report our experimental findings for the two mixing schemes.

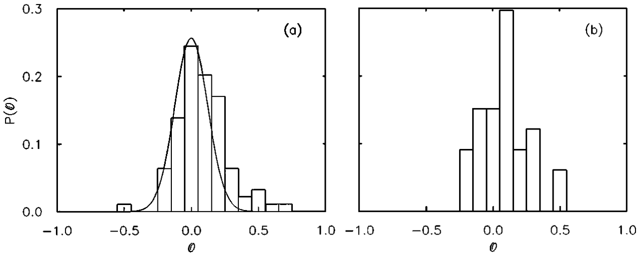

FIG. 1. (a) The order-parameter probability distribution function $P(\mathcal{O})$ for quiescent samples. (b) $P(\mathcal{O})$ obtained in the air-jet experiment.

(a) Nucleation in stirred solutions: Systematic measurements were carried out for samples containing 5 and 7.5 cm^3 of solution. For samples with 5 cm^3, the magnetic mixers touched the bottom of the dishes when the nucleation occurred; whereas for samples with 7.5 cm^3, the magnetic mixers always stayed afloat.

When a small volume of solution (5 cm^3) was used, mechanical stirring had a dramatic effect on the population of the two chiral species. We found that for $f \gg 1$ Hz, each sample was populated almost entirely by either the L or the R crystals, yielding high chiral purity with great certainty. The situation was different at low speeds, $0 < f < 1$ Hz. Here the degree of chiral symmetry breaking depended on the rotation speed of the magnetic mixer. Figure 2(a) shows a series of measurements with different f ranging from 0.02 to 1 Hz. For each stirring frequency, twenty samples were examined. The total number of crystals counted was of the order of 10 000 for the high frequencies and decreased to around 2000 for the lowest frequencies. We note that even at very low frequencies, such as $f \sim 0.02$ Hz, the PDF is already significantly different from that of the quiescent samples shown in Fig. 1(a). The broadening of the central peak indicates that the chiral symmetry in these samples was partially broken. As the stirring rate increased, the PDF began to peak around the two chirally pure states with $\mathcal{O} = \pm 1$. For instance, at $f = 1$ Hz, among the twenty samples, eight of them were left handed with $\mathcal{O} \simeq +0.99$, and twelve samples were right handed with an average order $\mathcal{O} \simeq -0.95$.

The chiral symmetry breaking for an ensemble of samples may be characterized by considering $\mathcal{O} > 0$ and $\mathcal{O} < 0$ to be degenerate. We define an ensemble averaged order parameter: $\mathcal{O}_{\text{avg}} = [\sum_{\mathcal{O}} \mathcal{O}^2 P(\mathcal{O}) / \sum_{\mathcal{O}} P(\mathcal{O})]^{1/2}$. With this definition, $\mathcal{O}_{\text{avg}}$ is nonzero even for quiescent runs, and $\mathcal{O}_{\text{avg}} \simeq 25\%$ as measured by the half width of the PDF shown in Fig. 1(a). In Fig. 3, see solid squares, we show $\mathcal{O}_{\text{avg}}$ as a function of stirring frequency for $0.02 \leq f \leq 3$ Hz. Variations of $\mathcal{O}_{\text{avg}}$ vs f appear to be smooth, and for all runs $\mathcal{O}_{\text{avg}}$ is significantly higher than the background level of 25%, which is delineated by the dashed line. The large noise seen in the data, particularly for the partially ordered samples, is by itself interesting in that it reflects the fact that the PDF is extremely broad in the range $-1 < \mathcal{O} < 1$.

In a surprising observation, the chiral ordering reduced noticeably for samples containing a slightly larger volume though mixed under similar conditions. We pursued the matter systematically by repeating the experiment with a larger volume (7.5 cm^3) over a mixing frequency range of $0 < f \leq 4$ Hz. The PDFs for these samples are shown in Fig. 2(b). The data are in sharp contrast to runs with smaller sample volume, even though a comparable range of mixing frequencies was used. For 5 cm^3 samples, the

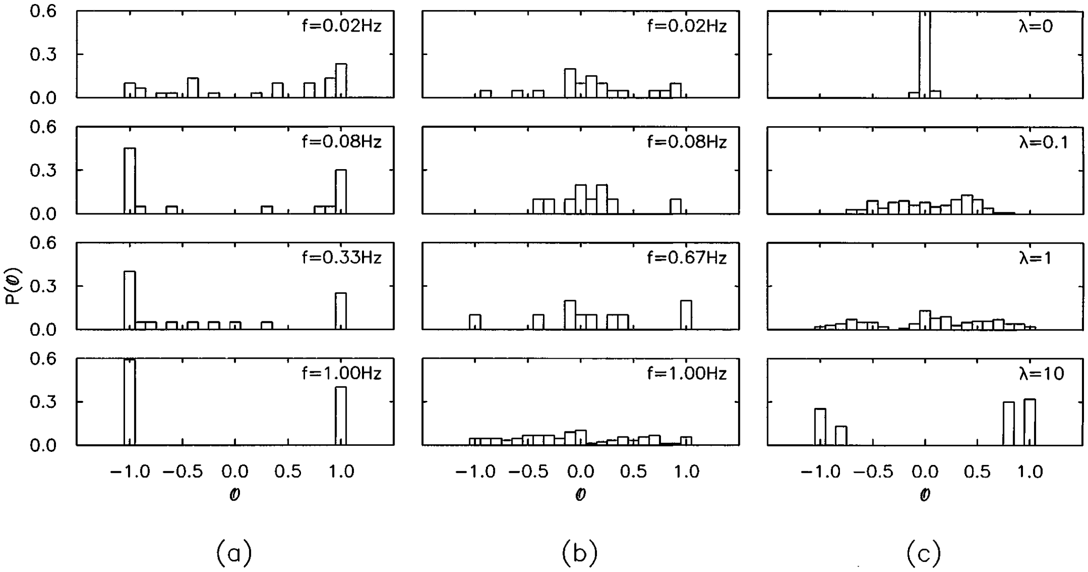

FIG. 2. The order-parameter probability distribution functions for the mechanical stirring experiments (a) and (b), and for the model calculation (c). (a) The volume of the solution is 5.0 cm^3. (b) The volume of the solution is 7.5 cm^3. (c) Model calculations with different crushing rates λ.

PDF peaked at $\mathcal{O} = \pm 1$ at $f = 1$ Hz; whereas for 7.5 cm^3 samples the PDF was essentially flat at the same frequency. For this frequency (1 Hz), instead of 20 samples, 92 separate crystallizations were carried out. It should be noted that increasing the stirring frequency to 4 Hz did not change the character of the PDF. In Fig. 3 we show $\mathcal{O}_{\text{avg}}$ vs f for samples with 7.5 cm^3 of solution. Here the data (open circles) only weakly depend on frequency, and the overall value of the order is not much greater than the background value of 25%. For these samples the chiral symmetry is at best only weakly broken.

(b) Nucleation in air-mixed solutions: In order to eliminate crystal-stirrer contact, the NaClO_3 solution was mixed by a nitrogen gas jet blowing on the liquid-vapor interface. The air jet was aimed along the fluid surface down the center of the cell producing two counter rotating vortices. The rotation rate of the vortices was ~1 Hz, which is comparable to that used in the mechanical stirring experiment. All the samples used here contain ~10 cm^3 of NaClO_3. Experimentally we found the result to be independent of the sample volume used.

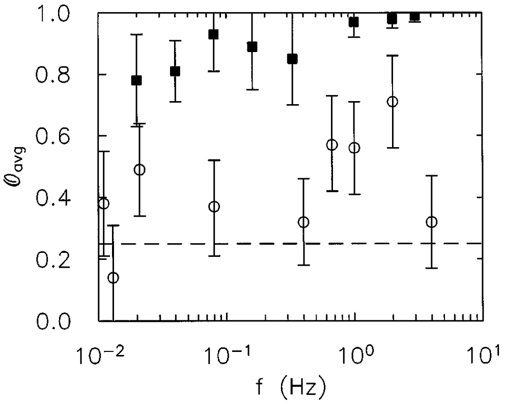

FIG. 3. The ensemble averaged order parameter $\mathcal{O}_{\text{avg}}$ for samples with 5.0 (solid squares) and 7.5 cm^3 (open circles) of solution. The error bars are due to statistical errors and the dashed line represents the background obtained from the quiescent experiments; see Fig. 1(a).

Figure 1(b) shows the PDF of $\mathcal{O}$ for 33 separate crystallizations under air mixing. It is apparent that this PDF shows almost no ordering and closely resembles the data for the quiescent samples, i.e., Fig. 1(a). This result, along with the mechanical stirring experiments with large sample volumes, suggests that hydrodynamic convection plays little or no role in producing high chirally pure states with $|\mathcal{O}| > 0.95$.

Quantitatively it is not difficult to show that hydrodynamic interaction alone is not sufficient to cause a rapid production of secondary nuclei. To see this we estimate the stress on a nucleus due to hydrodynamic shear $\sigma = \eta\gamma$, where η (= 0.01 P) is the shear viscosity of the solution and γ is the shear rate. In our experiment $\gamma \sim f \sim 1$ Hz, we found $\sigma \sim 10^{-2}$ erg/cm^3. This is very small compared to the energy density ϵ of a fully grown crystal $\epsilon = k_B T \rho \sim 10^9$ ergs/cm^3 with $\rho \sim 10^{23}$ cm^{-3}.

However, it is easy to show that stress produced by the weight of the magnetic mixer σ [$\equiv mg/a^2$] $\simeq 10^6$ ergs/cm^3 is not insignificant compared to ϵ. Here $m = 0.1$ g is the weight of the mixer, $g \simeq 1000$ cm/s^2 is the gravitational acceleration, and $a = 0.01$ cm is the size of the crystal. We note that ϵ estimated above is for a bulk crystal material, which may not be applicable to microcrystals, or to the edges and the corners of a fully grown crystals. The mechanical strength of those parts can be significantly lower than ϵ, and they are prone to mechanical damage by either the weight or the impact of the magnetic mixer. Indeed, a close inspection of the crystals in cases where strong symmetry breaking was observed revealed clear signs of mechanical damage. Unlike those crystals grown from a quiescent solution, under mechanical stirring the shape of the crystals is highly irregular, with missing corners and rounded edges. Moreover, precipitated crystals show large size differences, and the broken chiral symmetry is essentially due to the presence of numerous small crystals.

The different degrees of chiral symmetry breaking seen in our experiments can be explained by the following observations: The initial nucleation almost always occurred on the liquid-vapor interface, with the number of L and R crystals being approximately equal. However, as the crystals grew to a fraction of a millimeter, they settled to the bottom of the cell. When a small sample volume was used, the magnetic stirring bar could make contact with the bottom of the dish as sufficient water evaporated. A settled crystal could then be caught between the surfaces of the mixer and the dish, thus being crushed. In the case where larger volumes of solution were used, there still was mechanical contact between the mixer and the crystals on the liquid surface; however, the interaction was much weaker and, correspondingly, a less pronounced chiral symmetry breaking was observed. According to our observation, therefore, the high chiral purity and robustness of Kondepudi's experiment is not surprising since in his experiment the magnetic mixer was larger and always rested on the bottom of the sample cell.

The question then is: "Can mechanical damage alone create the observed symmetry breaking?" A simple growth model which mimics the mixer-crystal interaction may shed light on this question. A difference equation for the growth of each crystal species can be formulated by assuming in each time step one crystal is nucleated from the solution. This crystal can be either left handed or right handed. In addition to this primary nucleation, secondary crystals can be generated by crushing the existing crystals. If we denote the crushing rate by λ, the population of right-handed N^R and left-handed N^L crystals can at any time step i be given by,

$$N^R_{i+1} = N^R_i + k + \lambda N^R_i,$$

$$N^L_{i+1} = N^L_{i+1} + !k + \lambda N^L_i,$$

where $i = 1, \ldots, N_{\max}$. Here k is randomly chosen to be either 0 or 1 per step, and $!k$ is complementary to k. That is, if N^R grows one crystal, N^L does not grow one. The iteration continues until the solution is "depleted," i.e., $i = N_{\max}$. It is obvious that this scheme produces a binomial distribution when $\lambda = 0$. Figure 2(c) shows our simulation result with λ varying from 0 to 10. For each value of λ the PDF is plotted against the order parameter $\mathcal{O}$. All of the distribution functions were calculated using 100 independent runs, and each run evolved for $N_{\max} = 1000$ steps.

Despite its simplicity, with no hydrodynamics or thermodynamics, our model nonetheless captures the basic features seen in the experiment. Namely, in the absence of mechanical damage $\lambda = 0$, the PDF is strongly peaked at $\mathcal{O} = 0$. Introducing a small crushing parameter immediately broadens the PDF. As the crushing parameter increases, the distribution shifts continuously towards the states with $\mathcal{O} = \pm 1$ in a manner similar to that seen in our experiments with small sample volumes. According to our model, in order to have a very high optical purity, the crushing parameter should be more than ten, i.e., within one nucleation time each existing crystal should produce on the average more than ten small crystals. It is interesting to note that one can produce a state of high chiral purity without invoking the competition between different species.

To summarize, we found that chiral symmetry breaking in supersaturated $NaClO_3$ solutions is mainly due to mixer-crystal interactions. The generation of secondary nuclei by breaking off parts of a "mother" crystal was previously considered by Kondepudi and Sabanayagam [7]. However, its severity and extent have not been fully appreciated. We emphasize that by eliminating mechanical contact with the precipitated crystals, even in the presence of strong flow, a high degree of symmetry breaking cannot be realized. A simple growth model captured the behavior of the symmetry breaking remarkably well with only one tunable parameter, the crushing rate of the crystals. It appears that the effects of hydrodynamic convection, as well as other aspects of the experiment, are all but obscured by the proliferation of secondary crystals due to mechanical damage. To this end, it remains to be demonstrated that a totally asymmetric macroscopic state can be spontaneously generated and maintained in a laboratory experiment.

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