

19951081576
350287 GP

N95-14570

NUCLEATION AND CHIRAL SYMMETRY BREAKING UNDER CONTROLLED HYDRODYNAMIC FLOWS

Xiao-lun Wu, Brian Martin and Arnold Tharrington
Department of Physics and Astronomy
University of Pittsburgh
Pittsburgh, PA 15260

ABSTRACT

The effects of hydrodynamic convection on nucleation and broken chiral symmetry have been investigated for a simple inorganic molecule, sodium chlorate (NaClO_3). Our experiment suggests that the symmetry breaking is a result of hydrodynamic amplification of rare nucleation events. The effect is more pronounced when the primary nucleation occurs on the solute-vapor interface, where mixing in the surface sublayer becomes important. The transition from the achiral to the chiral states appears to be smooth as the hydrodynamic parameters, such as flow rate, are varied.

INTRODUCTION

Mirror symmetry is often absent in nature; the universe is asymmetric at all levels, from the subatomic to the macroscopic. Famous examples include the handedness of nucleic acids, DNA and RNA, and the spontaneous broken rotational symmetry of nematic-isotropic phase transitions in liquid crystals. In this paper we present a classical nucleation experiment in which the chiral symmetry breaking is triggered by rarity surface nucleation and promoted by hydrodynamic convection.

It is known that the individual sodium chlorate (NaClO_3) molecule is symmetric (achiral), but its crystal form shows distinctive optical activity [1]. If a solution of NaClO_3 is left undisturbed, a small number of crystals slowly form as the solvent, water in this case, evaporates. If these crystals are examined under crossed polarizers, one finds that about half are left-handed and the other half are right-handed. Equal percentage of the two species indicates that the energy barrier for the nucleation is the same for the different species.

It was found by Kondepudi et al. [2] that under gentle stirring this is no longer true. The crystallization seems to proceed in one direction, favoring either all crystals being left-handed or right-handed for each individual experiment. The optical purity in each sample could be well over 99%. However, if an ensemble of experiments is carried out under identical conditions, one again finds an equal distribution of left-handed and right-handed crystals. This remarkable observation indicates that the system undergoes a transition from a totally symmetric (achiral) state to a totally asymmetric (chiral) state simply by introducing a hydrodynamic flow, without careful control of temperature and other conditions. Kondepudi's experiment touches upon several interesting issues ranging from nucleation, convective diffusion, and autocatalysis, a mechanism believed to be relevant for the symmetry breaking [1,3]. The experiment also raises a number of interesting questions, such as: (1) how do the two vastly different length scales, the size of a primary nucleus ($\sim 10\text{\AA}$) and the hydrodynamic length ($\sim 1\text{ cm}$), couple; (2) what is the mechanism by which the secondary nuclei proliferate; and (3) how does the sharpness of the transition change as the control parameters, such as the flow rate and the nucleation rate, are varied.

To answer some of these questions, systematic measurements were carried out using two different flow geometries, mechanical stirring and electroconvection. In the mechanical-stirring experiments each sample contains approximately one vortex and the flow is rather chaotic even at low stirring rates. The simple mechanical setup allows mass production of crystals under nearly identical conditions, and good counting-statistics can be achieved. On the other hand, in the electroconvection experiments, large numbers of vortices are generated and the flow characteristics can be tuned continuously. Our experiment suggests that primary nucleations occur predominantly on the solute-vapor interface, giving rise to high optical purity even with a moderate stirring rate. This effect has been overlooked in a previous experiment [2]. Our experiment also suggests that flows with random mixing characteristics, are far more effective in producing chiral symmetry breaking than a laminar shear flow with a comparable Reynolds number.

EXPERIMENTAL

The crystallization experiments were performed using a NaClO_3 solution with a weight fraction of 50% [4]. The NaClO_3 was first dissolved in distilled water and constantly stirred at room temperature for 8 hours to ensure complete desolution of the solute. The solutions were then filtered through a $0.2\mu\text{m}$ filter before usage. The crystal growth was initiated by slow evaporation. At the given concentration, the nucleation occurs approximately 4-6 hours after the samples were prepared, and this time interval appears to be independent of the flow rate. In the experiments the crystals were grown to an average size of ~ 1 mm; this takes approximately a couple of hours for quiescent samples and less than an hour for stirred samples, after the first nucleation event is identified.

Different handed crystals can be distinguished by their optical activity. A right-handed (dextro) crystal will rotate polarized light clockwise while a left-handed (levo) crystal will rotate light counterclockwise. A low-power ($12\times$) microscope with a pair of polarizers allows us to determine the handedness of crystals even when they are as small as $100\mu\text{m}$. Under the transmission with a white light source, the two different crystal species appear blue and brown by slightly "uncrossing" the polarizers a few degrees. Since in some cases thousands of crystals are produced in a single sample, only a representative region of a few hundred crystals are analyzed.

Two different flow geometries were employed in the experiments. In the first experiment, NaClO_3 solution (7.5 cc) was placed in a cylindrical dish of 5 cm in diameter. A small Teflon coated magnetic stirring bar (1 cm long and 0.2 cm diameter) was placed in the center of the dish and was driven by a horse-shoe magnet. The stirring bar is light enough to float on the solute-vapor interface, providing effective mixing near the surface sublayer [5]. To improve the statistics, ten such samples were run simultaneously with the horse-shoe magnets connected in tandem, driven by a single DC motor. Flow visualization using a Kallirosopic fluid indicates there is a great deal of mixing even at a very low stirring rate $\sim 1/30$ Hz.

In the second experiment, flow was produced by electroconvection. In this geometry all the mechanical moving parts are eliminated, allowing better control of the flow characteristics. The flow cell has a dimension of $12 \times 20\text{ cm}^2$ with a biased ac current flowing along the long dimension of the cell. The electrodes are made of platinum in order to reduce the contamination of the solution. Directly underneath the cell is an array of 400 cylindrical magnets each having a field ~ 0.4 T. The magnets are arranged in a square lattice with alternating poles pointing vertically. When a current passes through a thin layer of NaClO_3 solution an array of counter rotating vortices is formed. Depending on the strength of the current, both localized and delocalized vortices can be generated. Since the thickness of the fluid is much smaller, ~ 3 mm, compared with the width of the cell, the flow may be considered as two dimensional.

RESULTS

To ascertain that nucleation behaves normally with no bias, a set of quiescent measurements were carried out, and the results were similar to that found by Kipping and Pope [1], and Kondepudi [2]. In a total of 5395 crystals obtained from ~ 100 crystallizations, 2523 were right handed and 2872 were left handed. The bias towards right-handed crystals, though small ($\sim 6\%$), is statistically significant in that the standard deviation predicted from the bimodal distribution is $\sim 1\%$. We noted that similar bias was also observed in Kondepudi's experiment at the level of $\sim 10\%$. If an order parameter is defined as $O = (n_L - n_R)/(n_L + n_R)$, we can plot the distribution function $P(O)$ for the above hundred runs. Figure 1a shows $P(O)$ for the quiescent samples ($f = 0$ hz) together with a Gaussian distribution (solid line) for comparison. As can be seen, the experimental data are in general agreement with the Gaussian distribution except for large O s, where the difference is quite notable.

Constant Stirring of the solution has a dramatic effect on the overall chirality of the crystals. At stirring rates $f \gg 1$ Hz each sample contains either almost all left or right-handed crystals, yielding high optical purity with a great certainty. It is amazing that the ordering process occurs spontaneously in individual cells without much human intervention. Figure 1c shows a typical run with 19 samples at $f = 1$ Hz. Among 19 samples, 7 are right-handed and 12 are left-handed with optical purity in each cells being greater than 95%. As the stirring rate decreases, we found that chiral symmetry is only partially broken in the sense that

a large fraction of samples show no symmetry breaking. Figure 1b shows the distribution for 19 samples at $f = 0.7$ Hz. Among the 19 samples, 2 are right-handed and 1 is left-handed with optical purity again greater than 95%. The other 16 samples show no (or weak) symmetry breaking, and their distribution is clustered near $O = 0$. The general trend seen in the experiment is that as the stirring rate increases from $f = 0$ Hz, the central peak in the distribution decreases in magnitude and its width increases. At the same time two chirally pure states with $O = \pm 1$ gains increasing more weight in the distribution function.

To characterize the order of an assemble of samples by considering $O = +1$ and $O = -1$ to be degenerate, we can define an ensemble averaged order parameter as $\langle |O| \rangle = \sum_{i=1}^N |O_i| N_i / \sum_{i=1}^N N_i$, where $|O_i|$ and N_i are the absolute value of the order parameter and the total number of crystals in sample i , and N is the total number of samples. The average is weighted by the number of crystals in each samples, because samples with more crystals are statistically more significant than those with less crystals. In Fig. 2 we plot $\langle |O| \rangle$ as function of stirring rate for 240 samples spanning f from 0 to 3 Hz. As can be seen, for $f > 2$ Hz the systems are almost completely ordered while for $f < 2$ Hz the systems are only partially ordered. The ordering process as a function of f appears to be smooth. The noise seen in the data is interesting by itself in that it reflects the fact that the distribution function has multiple peaks around $|O| = 0$ and $|O| = 1$ similar to that seen in Fig. 1b. The characteristic frequency $f_c \sim 2$ Hz, separating ordered from partially ordered states, may be interpret as a competition between the rate of nucleation and the rate of convection. In the high stirring rate (convection dominated regime), a single nucleation event apparently suppresses primary nucleation of opposite species and dominates the later evolution of the system. Our experiment may therefore provide an excellent way of measuring the primary nucleation rate.

It should be noted that in the experiments, both with and without stirring, the initial nucleation almost always occurs on the solute-vapor interface. As the crystals grow to a fraction of a millimeter, they fall to the bottom due to gravity. The surface nucleation by itself is not surprising since it is well known that surfaces (and other impurities) can lower the nucleation energy barrier substantially. However, the surface nucleation may explain the efficiency by which the chiral symmetry breaking occurs in the first place. This is because near the surface there is only relatively small volume which needs to be mixed in order to have the transition. This explanation is further enhanced by the observation that if a large crystal, say left handed, is placed in the bottom of the sample and it is not convected by the stirring, the chirality of the system at the later time is not always determined by the crystal we initially put in.

The chiral symmetry breaking experiment has also been carried out in electroconvection cell with different flow characteristics. Shown in Fig. 3 are two pictures that were taken at different driving currents. For low currents, the vortices are localized in space and form a fairly regular lattice. For a high current, however, the vortices become delocalized and the flow is almost turbulent. Our preliminary experiment shows that when the flow is localized (laminar regime), the chiral symmetry is not broken, whereas in the strong flow region the chiral symmetry can be broken with high optical purity. The observation points to the importance of hydrodynamic mixing, rather than local shear, for the broken chiral symmetry. It is apparent that with a comparable Reynolds number, similar to that used in the mechanical stirring experiments, a pure laminar shear flow is not sufficient for bringing about the transition. The nucleation experiment in electroconvection cells is still under way and the results will be reported elsewhere.

INTERPRETATION

To interpret our experimental results, the following mechanisms appear to be relevant: (1) Nucleation is a statistically rare event. Due to a high activation energy for nucleation, $\sim 100k_B T$, a supersaturated solution can persist for hours before a nucleation event is triggered by thermal fluctuations. Because of such a slow nucleation rate, it is possible that only a single primary nucleation event occurs among $\sim 10^{23}$ molecules. This primary nucleus carries a definitive symmetry, or "genetic" code. (2) Secondary nuclei are generated from a primary nucleus due to hydrodynamic convection. For certain unknown reasons, the secondary nuclei have the same symmetry as the primary one and their number proliferates. (3) There is an interaction between distant parts of the fluid, allowing the "genetic" code to pass into other regions of the fluid. The passage of the information needs to be sufficiently fast covering a large fraction of the sample before another primary nucleation event takes place. It is obvious that hydrodynamic convection which cause mixing will allow for such a long-range interaction.

A possible mechanism by which flow can induce the symmetry breaking is the following: The primary and the secondary nuclei are convected by the flow, causing the depletion layers which surround the nuclei to spread out to the regions where the primary nucleations are *most* likely to take place. Because of supersensitivity of the rate of primary nucleation to the solute concentration, spreading of the depletion zone effectively reduces the chance of primary nucleation for the other species. On the other hand, by eliminating the depletion layer near the surface of a nucleus, the growth of such a crystal is further enhanced. Therefore the system has a built-in positive feedback mechanism which propels the nucleation towards one direction. In this sense the spontaneous chiral symmetry breaking is a result of rare statistical fluctuations and non-local hydrodynamic effects. In our experiment, the primary nucleation sites are predominantly on the free surface of the solution. The volume that needs to be mixed in order to produce chiral symmetry breaking, therefore, is rather small. This accounts for the fact that only moderate stirring is sufficient to bring about the symmetry-breaking transition.

What is not known in our experiment is why the secondary nucleation duplicates the symmetry of the primary nucleus. Important as it is, the secondary nucleation is only known empirically [6]. The effect has been phrased as a chirally autocatalytic process [2,3], in which the incipient nucleus undergoes a series of splittings and gives birth to the next generation of crystals. If the effect is hydrodynamic in nature it is not difficult to show that the incipient nucleus must be very weak with the critical shear stress several orders of magnitude smaller than that of a fully grown crystal. To see this we estimate the stress on a nucleus due to shear, $\sigma = \eta\gamma$, where η (=0.1 poise) is the shear viscosity of the solution and γ is the shear rate. In our experiment $\gamma \sim f \sim 1$ hz, we found $\sigma \sim 10^{-1}$ erg/cm³. This is very small compared to the energy density ϵ of a fully grown crystal, $\epsilon = k_B T \rho \sim 10^{10}$ erg/cm³ for $\rho \sim 10^{24}$ cm⁻³. It is clear that an understanding of secondary nucleation requires the investigation of the formation of chiral crystals on microscopic scales, a domain which is beyond the scope of the current experiment.

CONCLUSIONS

Using different flow geometries, we have found that the chiral symmetry breaking correlates strongly with hydrodynamic convections. In particular, random mixing seems to be far more effective in bringing about the transition than a laminar shear flow. The high optical purity obtained with only a gentle stirring is likely to be a result of surface nucleation. Our experiment reveals for the first time the delicate balance between the rate of nucleation and the rate of convection. In the convection dominated regime, the systems self-organize into a chiral state with optical purity > 95%, whereas in the nucleation dominated regime, the system is achiral. The processes studied in the experiment may provide insight into the possible origins of biomolecular chirality and may even lead to the production of chirally pure materials.

REFERENCES

1. F.S. Kipping and W.J. Pope, *J. Chem. Soc. Trans.* **73**, 606 (1898).
2. D. Kondepudi, R. Kaufman, and N. Singh, *Science* **250**, 975 (1990).
3. G. Metcalfe and J.M. Ottino, *Phys. Rev. Lett.* **72**, 2875 (1994)
4. The sodium chlorate, NaClO₃, was purchased from Fisher Scientific. The chemical is 99.9% pure and was used without further purification.
5. It was found that for a heavy magnetic bar which sinks to the bottom, the stirring can crush small crystals, causing chiral symmetry breaking. We learn this the hard way.
6. A. Randolph and M. Larson, *Theory of Particulate Process*, (Academic Press, San Diego, 1988).

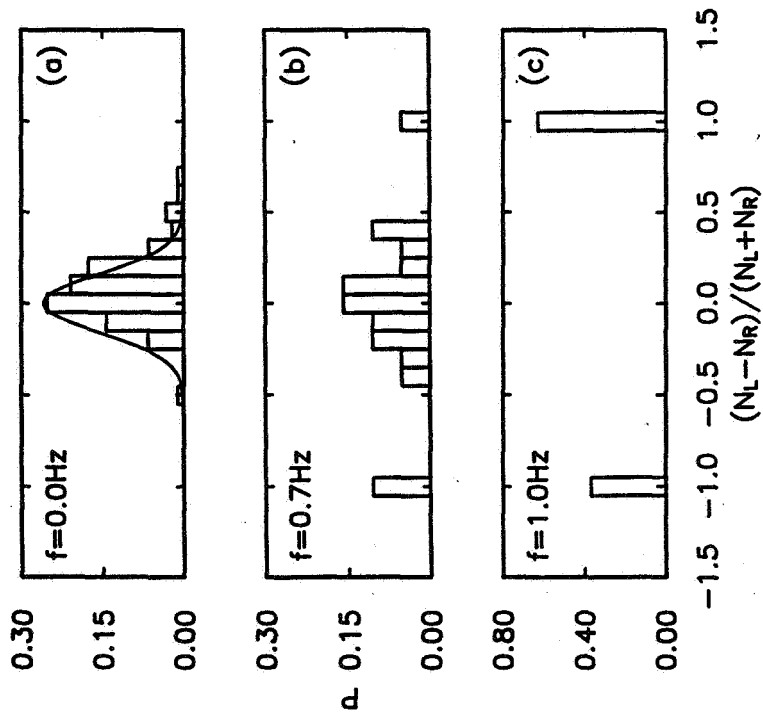


Figure 1. The order-parameter probability function $P(O)$. From top to bottom, the measurements were for samples with stirring rates $f = 0, 0.7$ and 1 Hz , respectively.

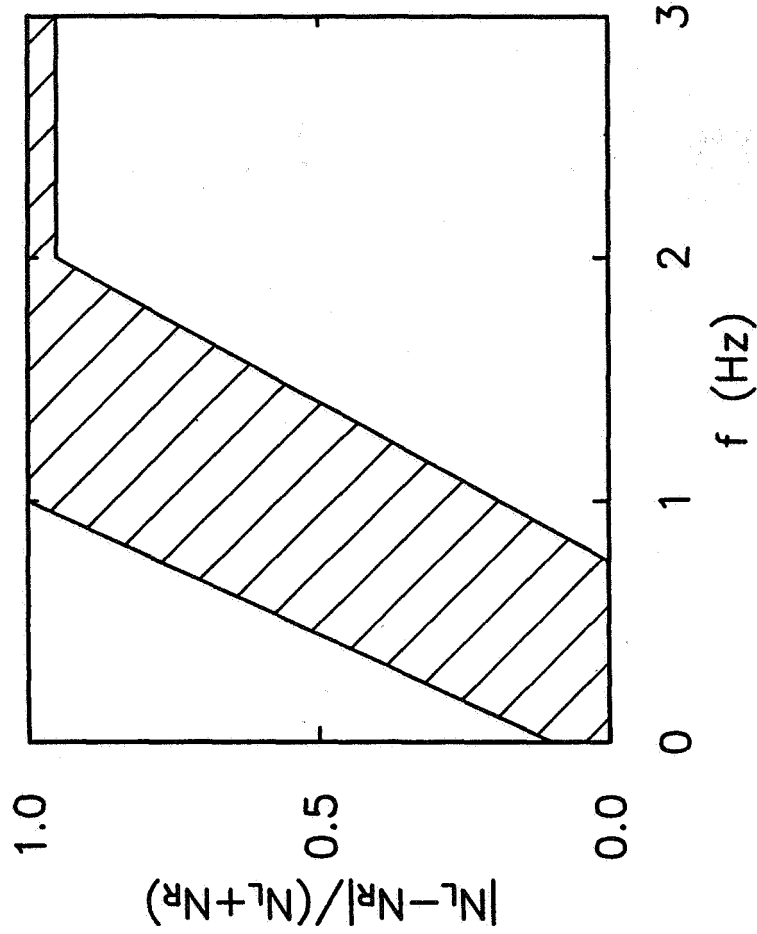


Figure 2. The order parameter vs. stirring rate f . The order parameter increases with f and saturates at high frequencies. Near the transition zone, $\sim 1 \text{ Hz}$, the measurements are noisy with anomalous fluctuations.

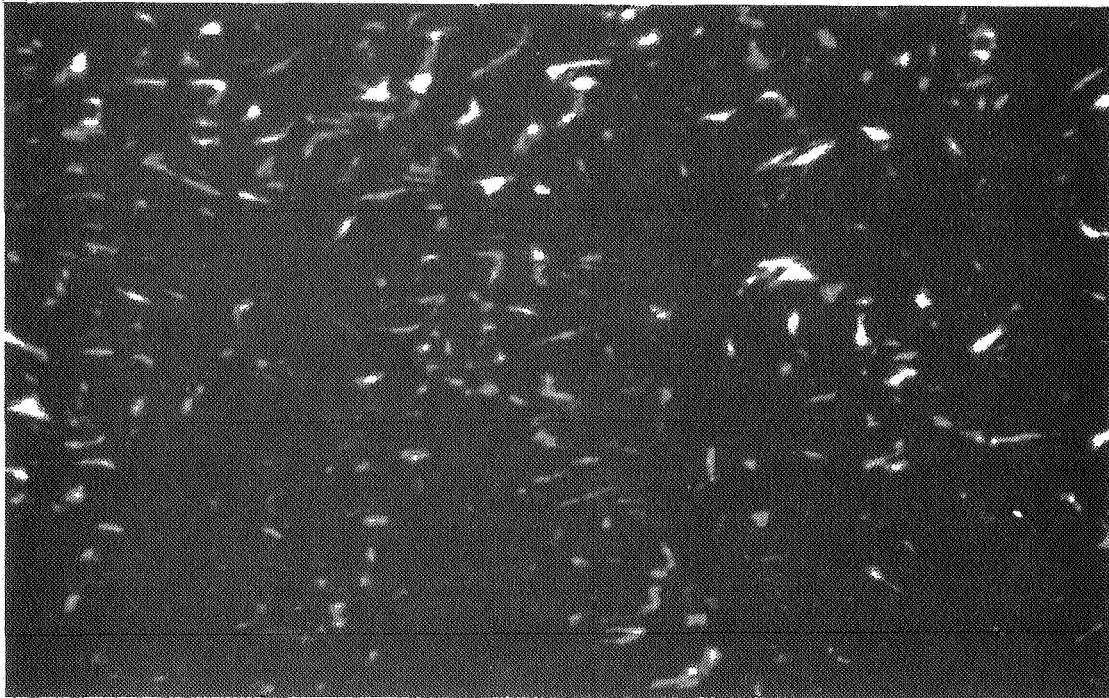
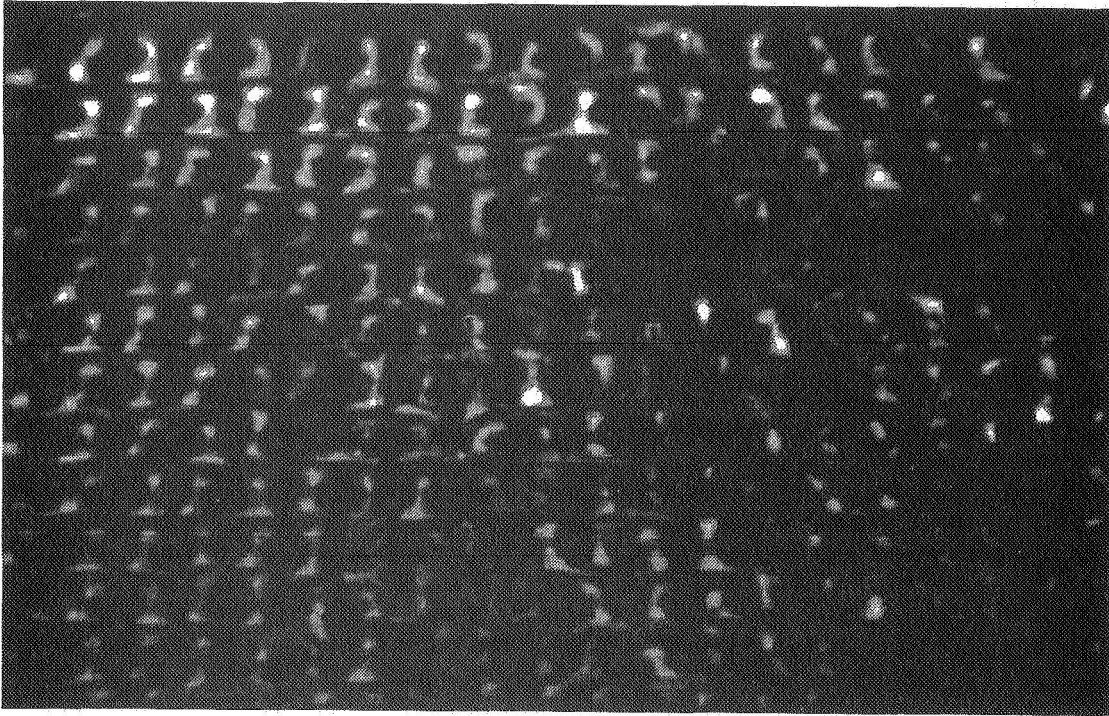


Figure 3. Flow patterns in electroconvection. The vortices are regular and localized with a weak current (top) and become delocalized with a strong current (bottom).