Stirring Rate as a Critical Parameter in Chiral Symmetry Breaking Crystallization

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Abstract: Symmetry breaking processes in both equilibrium and nonequilibrium systems are associated with critical parameters. In the general theory of symmetry breaking transitions, critical parameters have an important role. In this article, we present our study of rpm as a critical parameter in chiral symmetry breaking crystallization. The random distribution of crystal enantiomeric excess is obtained for various rpm. The results show how the probability distribution initially spreads and then develops two peaks in a way similar to that observed in a second-order symmetry breaking phase transition. It is also shown that the stochastic kinetic equations that we had proposed for this process could reproduce the experimentally observed relation between crystal enantiomeric excess and rpm.

Introduction

Processes that can produce states of broken chiral symmetry are of particular interest to physics, chemistry, and biology.[1,2] Spontaneous symmetry breaking is a general phenomenon known to occur in systems in thermodynamic equilibrium as well as systems far from thermodynamic equilibrium.[3-5] One speaks of "symmetry breaking" in the following sense: though the basic interactions, such as spin—spin interaction, and processes, such as chemical reactions and diffusion, may be symmetric with respect to symmetry operations such as mirror reflection, the states generated by these interactions and processes need not possess the same symmetries; they may be states with "broken symmetries". For example, in a reaction that produces chiral products from achiral reactants, the rates of reactions for the production of the two enantiomers must be identical; nevertheless, if there is chiral autocatalysis, it is possible to produce a large enantiomeric excess (ee) in the product. In any particular run, the ee could be due to an excess of either *l*- or *d*-enantiomer. In fact, in the absence of any chiral influences, an excess of *l*- or *d*-enantiomer will be produced with equal probability. The process is stochastic, not deterministic. Another example is the well-known ferromagnetic second-order phase transition that occurs in material such as iron. In this case, though the spin—spin interaction is isotropic, the cooperative interaction between spins may produce an anisotropic state in which the spins point in a particular direction. The direction in which the spins will point is random and, in the absence of any external magnetic field, each direction occurs with equal probability. Depending on the conditions, the degree to which symmetry is broken varies. The ultimate goal of theories that describe such symmetry breaking transitions is to obtain the probability distribution for the states with varying degrees of broken symmetry. The probability distributions associated with second-order phase transitions are described to a good approximation by the Ginsburg—Landau theory (which was improved upon by the modern theory of critical phenomenon which utilizes the idea of a renormalization group[4]).

Theories of symmetry breaking transitions are usually formulated in terms of an "order parameter" μ which is a measure of the asymmetry. The order parameter in turn is a function of a parameter called the "critical parameter" λ. The transition from a symmetric to an asymmetric state occurs when the critical parameter crosses a threshold value λ_c. In the case of second-order phase transitions, the Ginsburg—Landau theory gives the probability distribution $P(\mu)$ of the order parameter at various values of the critical parameter λ. In the case of breaking of a 2-fold symmetry, such as mirror reflection symmetry, the probability distribution $P(\mu)$ changes form a one-peak distribution to a two-peak distribution when λ crosses the critical value λ_c. Our investigation was partly motivated by our interest in looking for similarities between second-order phase transitions and symmetry breaking in stirred crystallization that is described below. The advantage in looking for such similarities is that many of the features of the Ginzburg—Landau theory are derived from the symmetry properties of the system and are independent of the detailed form of the kinetic rates. Thus a Ginzburg—Landau type theory for stirred crystallization will be a theory of general applicability to all crystallization processes that break chiral symmetry, regardless of the particularities of the kinetics.

For the formulation of a general theory of chiral symmetry breaking, the identification and study of an order parameter and a critical parameters is necessary. For chiral asymmetry, enantiomeric excess is clearly a natural choice for the order parameter. In this article, we present our study of stirring rate (rpm) as a critical parameter in the breaking of chiral symmetry in stirred crystallization of $NaClO_3$. We show that the qualitative feature of the experimentally obtained distribution of the crystal enantiomeric excess as a function of stirring rpm is similar to that seen in second-order symmetry breaking phase transitions.

Regardless of its theoretical implications, our study shows how the enantiomeric excess produced in stirred crystallization depends on the stirring rpm. We also show that the stochastic kinetics that we proposed in an earlier article[6] are able to reproduce many of the observed qualitative features.

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Chiral Symmetry Breaking in Stirred Crystallization

The achiral compound $NaClO_3$ crystallizes in enantiomeric forms. The optical activity of the enantiomeric crystals enables us to easily separate and count the number of l- and d-crystals. In analogy with the usual enantiomeric excess, a crystal enantiomeric excess (cee) can be defined as:

$$cee = \frac{|N_l - N_d|}{N_l + N_d} \qquad (1)$$

in which N_l and N_d are the number of l- and d-crystals respectively. In recent articles, we have reported the phenomenon of chiral symmetry breaking in which a large crystal enantiomeric excess is produced in stirred crystallization.[6-8] When the stirring rate is zero, the probability distribution for $(N_l - N_d)/(N_l + N_d)$ has a single peak at zero, but when the stirring rate is nearly 1000 rpm, the probability distribution has two peaks, one near $(N_l - N_d)/(N_l + N_d) = +1$ and the other near $(N_l - N_d)/(N_l + N_d) = -1$.[6]

In this article we present the probability distribution of cee for a range of intermediate rpm. The data show that, as the rpm is varied, the one-peak probability distribution spreads and then develops two peaks just as it does in a second-order symmetry breaking phase transition. This result supports the notion that rpm can be taken as a critical parameter in the theory of symmetry breaking crystallization and that such a theory may be similar to the Ginzburg—Landau theory of second-order phase transitions. It has been shown that there is a similarity between the theory of symmetry breaking nonequilibrium transitions and the Ginzburg—Landau theory of second-order phase transitions,[9,10] but neither of these theories is directly applicable to the system under study.

In our previous study, we proposed a set of stochastic kinetic equations with the aim of describing both the variation of concentration and stochastic production of l- and d-crystals in stirred crystallization of $NaClO_3$. Numerical solutions obtained through a computer code (written in Mathematica) showed that this model could reproduce the observed time-variation in concentration and the large cee observed in a single run. In the present study, we use these stochastic kinetic equations to obtain the distribution of cee for different stirring rates by simply repeating the computer runs with randomly varying initial conditions. The results are then compared with the experimental data. For the convenience of the reader, we shall present the main aspects of these kinetic equations here while a more detailed discussion can be found in ref 6.

On our model, the kinetics of stirred crystallization consist of three main processes: evaporation of the solvent, nucleation, and crystal growth. The nucleation and crystal growth changes the concentration, which in turn affects the rates of crystallization and crystal growth. The nonlinearity of this feedback creates interesting situations. In stirred crystallization, the nucleation proceeds via two major mechanisms: (i) *primary nucleation*, which may be homogeneous or heterogeneous, and (ii) *secondary nucleation*, a process by which new crystals are generated from an existing crystal due to the fluid motion. For the rate of primary nucleation, we use two stochastic processes,

one for nucleation at the air/solution interface and the other for nucleation in the bulk, the average rate in either case being a concentration-dependent function.

Secondary nucleation is the chiral autocatalytic process that is responsible for the production of the observed large cee. The rate of secondary nucleation, which is the most important aspect of the process, is assumed to depend on the surface area of the existing crystals and the stirring rate, in addition to supersaturation. Though the exact nature of secondary nucleation is not well understood, it has been well established that the rate depends on the rate of stirring and supersaturation.[11-15] Because of the lack of fundamental understanding of the processes of secondary nucleation, we could only use the following empirical expressions for the rate of secondary nucleation (which is used mostly in chemical engineering literature[14,16]):

$$S_l = s\sigma_l K_s (C - C_s)^\alpha \qquad (2)$$

Here S_l is the rate of production of secondary nuclei from an l-crystal; s is a parameter which is assumed to be proportional to the rpm, σ_l is the total surface area of the l-crystals that can generate secondary nuclei, K_s is a constant that depends on temperature, C is the concentration, C_s is the concentration at saturation, and α is an empirical parameter. In our previous numerical simulation[6] of the process we used the values $\alpha = 2.75$, $s = 2$, and $K_s = 5.0 \times 10^8$ to obtain a good fit for the observed experimental data. It is noteworthy that a non-integer value of the exponent α has been commonly used[14]—perhaps an indication that secondary nucleation is a complex process. Since the rate of production of secondary nuclei depends on the stirring rate s, the cee produced in any particular crystallization depends on rpm. In our experiments, the generation of secondary nuclei could be the result of stirrer crystal contact[17] but not necessarily so.[11] Indeed it was recently reported that chiral symmetry breaking in $NaClO_3$ crystallization could be accomplished through electroconvection[18] in which convection occurs without a stirrer. Also, we found that a large cee also could be produced sometimes by the use of a sonicator (21 kHz) in the place of a stirrer. In a total of seven runs only once did we find 100% cee. The cee produced by a sonicator were 0.07 (NL = 84, ND = 98), 0.18 (NL = 83, ND = 58), 0.13 (NL = 53, ND = 41), 0.27 (NL = 43, ND = 75), 1.00 (NL = 201, ND = 0), 0.21 (NL = 42, ND = 65), 0.17 (NL = 43, ND = 60), in which NL is the number of l-crystals and ND is the number of d-crystals. We have not yet found conditions under which large cee could be produced consistently using a sonicator.

The Empirical Relation between Crystal Enantiomeric Excess and rpm

Figure 1a summarizes the result of 17 unstirred and 63 stirred crystallizations done at various rpm. The rpm of the 1 cm stirrer

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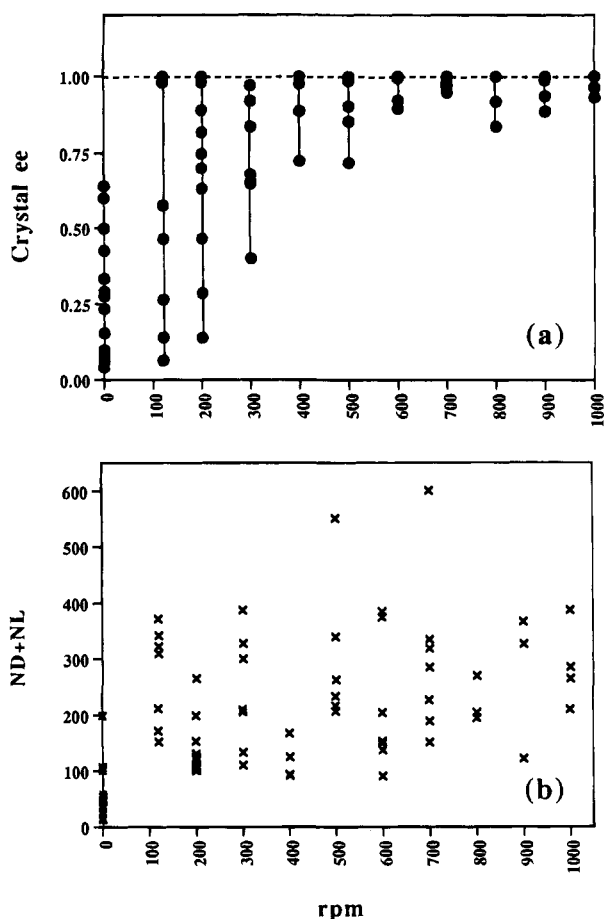
Figure 1. 1. (a) The experimentally obtained random distribution of crystal enantiomeric excess (cee) (see eq 1) obtained from 63 stirred and 17 unstirred crystallizations at various rpm is shown. The data show the range over which the cee randomly varies from sample to sample for a given rpm. For rpm greater than 600, the cee is always nearly one. (b) The total number of crystals counted to sample the cee in each crystallization is shown. As can be seen, most of the sample sizes were between 100 and 400.

was stable within ±10. All the crystallizations were done as described in ref 6, the only difference being the careful control of the rpm of the stirrer. In each stirred crystallization, we tried to count at least 100 crystals, though in a few cases we could clearly identify only about 90. For the case of unstirred crystallization the total number of crystals in the systems was often less than 100 and almost all were counted. As shown in Figure 1b, in all the stirred crystallizations, the total crystal count (NL + ND) in each crystallization ranged from 90 to more than 600. Figure 1b also shows the number of independent stirred crystallizations performed at each rpm.

Crystallization processes in general and symmetry breaking crystallization in particular exhibit randomness: for a given set of conditions such as rpm, the resulting cee may fluctuate randomly over a wide range. It is therefore more appropriate to associate a probability distribution, not a specific value, for the cee at a given rpm. Since the probability distribution of $(N_l - N_d)/(N_l + N_d)$ is symmetric under the interchange of N_l and N_d, its qualitative aspects may be seen with half the data points if we look at the distribution of cee = $|N_l - N_d|/(N_l + N_d)$. For this reason we chose to present the data in terms of cee. The probability distribution of $(N_l - N_d)/(N_l + N_d)$ is obtained by simply considering a mirror-reflection of the probability distribution of cee about zero.

The probability distribution of cee may be broad for certain rpm and narrow for others. When the crystallization is per-

formed in the absence of stirring, there is the expected statistical fluctuations in the cee,[19] but in general the standard deviation is found to be much larger than what is expected on the basis of a binomial distribution. When the solution is stirred, the data shown in Figure 1a indicate that the probability distribution of the cee initially spreads with increasing rpm and subsequently accumulates near the value of cee = 1. Viewed in terms of the probability distribution of $(N_l - N_d)/(N_l + N_d)$, a single-peak probability distribution spreads and gradually becomes a distribution with two peaks. A similar study in which the stirrer was placed at the liquid surface has recently been reported;[18] in this case the rpm was very low, ranging from 0 to 1.

The observed initial spreading of the probability distribution and subsequent development of two sharp peaks is similar to the expected qualitative relationship between the probability distribution and a critical parameter in a second-order phase transition. Such features are general to many symmetry breaking transitions, regardless of the details of the dynamics. We note, however, that there is not yet a theory that enables us to obtain the probability distribution for the cee as a function of the rpm. A Ginzburg−Landau type theory for the symmetry breaking process is yet to be developed.

The experimental relationship between the rpm and the crystal cee shown in Figure 1a could be used to test the validity of the stochastic kinetic equations that we had proposed for this process in an earlier publication.[6] With these equations, the stochastic crystallization processes can be simulated on the computer using appropriate random number generators. Though our kinetic model was able to reproduce the observed variation of the concentration during stirred crystallization,[6] because of the complex nature of the kinetics, it is difficult to predict if it will indeed reproduce the experimentally observed random distribution of cee for various stirring rates.

The results of computer simulation are shown in Figure 2a. In the simulation, rpm is assumed to be proportional to a parameter s which appears in the rate of secondary nucleation as shown in eq 2. (An identical rate equation is used for the secondary nucleation of *l*- and *d*-crystals.) The random distribution of cee produced by the stochastic kinetic equations for various values of *s* is shown in Figure 2a. All other parameter values are the same as in ref 6. In accordance with experimental observation, in the simulation it is assumed that due to nucleation at the air/solution interface, crystals of varying sizes enter the system randomly. The computer simulation data shown in Figure 2a was obtained by varying the size of "seed" crystals from the air/solution interface from 0.03 to 0.07 cm. At each rpm 5 or 10 simulations were performed with crystal sizes of 0.030, 0.035, 0.040, ..., 0.07 cm. All the crystals were introduced into the system when the concentration C of the solution reached the value $0.998C_s$, where C_s is the concentration at saturation; in the simulation the concentration reached this value at $t = 55$ min. As can be seen, there is good qualitative similarity between the experimentally obtained cee Vs rpm data shown in Figure 1a and the simulation data for cee Vs *s* shown in Figure 2a. For low values of *s*, the variation in the size of the "seed" crystals from the air/solution interface results in a large variation of cee, but at higher values of *s*, the variation in "seed" size has almost no effect on the cee. Figure 2b shows the total number of crystals generated in each of the simulations. For the same range of variation of size of the crystals from the air/solution interface (0.03−0.07 cm), it is interesting to note that the total number of crystals produced in the simulation varies over a wider range when *s* is small. Whether this was also true experimentally was difficult to ascertain. We intend to investigate this aspect in our future studies.

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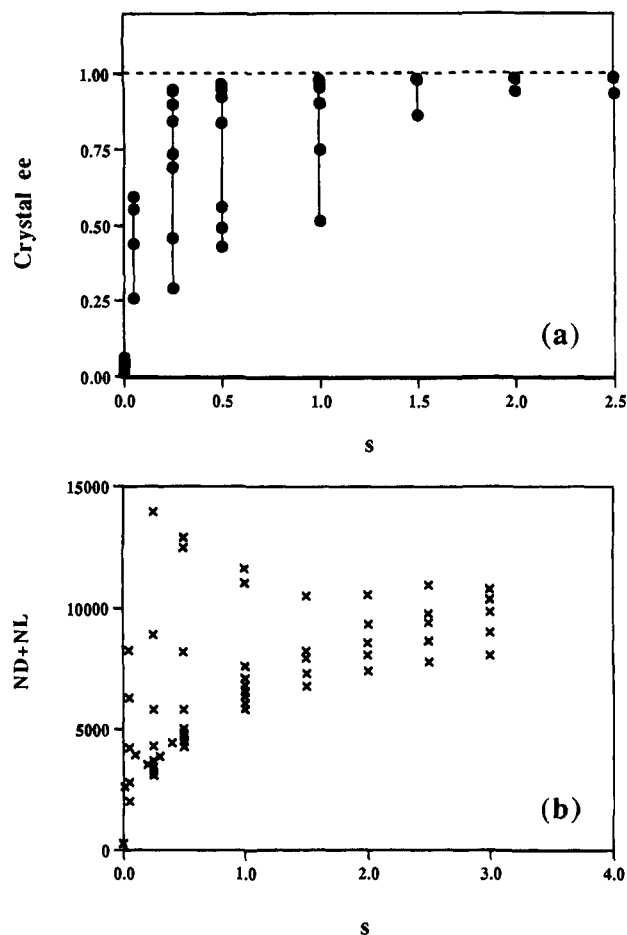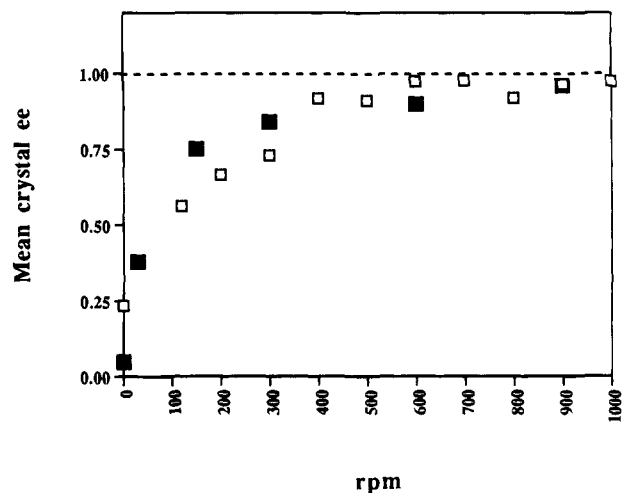
(a)

rpm

Figure 3. 3. A quantitative comparison between the data shown in Figure 1a and Figure 2a can be made by relating the parameter *s* to the rpm by setting rpm = *s* × 600. The open squares show the average cee of the data shown in Figure 1a at various rpm while the filled squares are the average cee of the data shown in Figure 2a at various values of *s*.

through a multiplicative factor. With this assumption, a quantitative comparison of the simulation and experimental data for the average cee Vs rpm can be made. The comparison shown in Figure 3 is obtained by using the following relation: rpm = *s* × 600. Considering the statistical fluctuations in the data, the agreement between the simulation and experiment is fairly good. This comparison enables us to relate the parameter *s* to the rpm for the particular stirring conditions.

Concluding Remarks

Our study establishes that the stirring rate has the qualitative properties of a critical parameter in a second-order phase transition. More detailed studies are necessary to reveal the differences, if any, between the observed symmetry breaking in crystallization and similar symmetry breaking transitions in equilibrium and nonequilibrium systems. Whether the existing theories of symmetry breaking transitions are adequate to describe the chiral symmetry breaking in crystallization remains an open question.

(b)

Figure 2. 2. (a) The random distribution of crystal enantiomeric excess (cee) (see eq 1) obtained from 60 computer runs for various values of the parameter *s* is shown. The rate of secondary nucleation depends on the parameter *s* as shown in eq 2. The values of all the parameters are the same as in ref 6. (For *s* = 1.5, 2.0, and 2.5, most of the runs produced a cee of nearly 0.98 and hence they overlapped and appear as one point.) As can be seen, the random distribution is qualitatively similar to that shown in Figure 1a. One significant difference is the range over which the cee fluctuates in the absence of stirring; the experimentally observed range is generally larger. (b) The distribution of the total number of crystals (NL + ND) obtained in each computer simulation is shown for various values of the parameter s (see eq 2). The random variation in (NL + ND) is over a wider range for smaller values of *s*.

Since the parameter *s* is related to the stirring rate, as a first approximation, we may assume that it is related to stirrer rpm