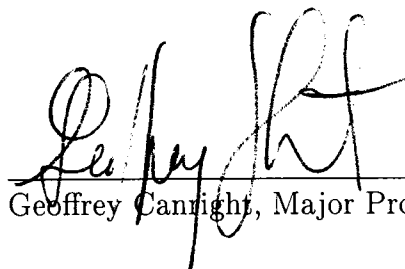
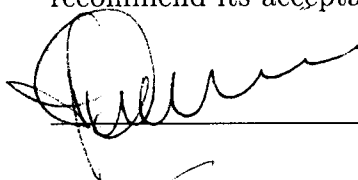
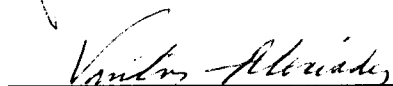
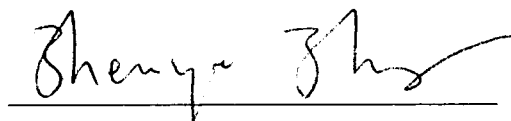
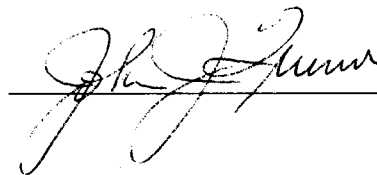


To the Graduate Council:

I am submitting herewith a dissertation written by Ilya Moiseevich Sandler entitled "Spontaneous Chiral Symmetry Breaking in 2D Aggregation." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy with a major in Physics.


Geoffrey Canright, Major Professor

We have read this dissertation and
recommend its acceptance:


_____
_____
_____

Accepted for the Council:


Associate Vice Chancellor and
Dean of The Graduate School

SPONTANEOUS CHIRAL SYMMETRY BREAKING IN 2D
AGGREGATION

A Dissertation
Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Ilya Moiseevich Sandler

May 1998

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Abstract

Recently, unusual and strikingly beautiful seahorse-like growth patterns have been discovered. These patterns possess a spontaneously broken chiral (left/right) symmetry. To explain this spontaneous chiral symmetry breaking, we develop a model for the growth of the aggregate, assuming that the latter is charged, and that the incoming particles are polarizable, and hence drawn preferentially to regions of strong electric field. This model is used both for numerical simulation and theoretical analysis of the aggregation process. We find that the broken symmetry (typically, an 'S' shape) appears in our simulations for some parameter values. Its origin is the long-range interaction (competition and repulsion) among growing branches of the aggregate, such that a right or left side consistently dominates the growth process. We show that the electrostatic interaction may account for the other geometrical properties of the aggregates, such as the existence of only 2 main arms, and the "finned" external edge of the main arms. The results of our simulations of growth in the presence of the external electric field are also in a good agreement with the results of new experiments, motivated by our ideas. Thus, we believe that our growth model provides a plausible explanation of the origin of the broken symmetry in the experimental patterns.

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1 Introduction

Growth phenomena are known for the complexity and beauty of the patterns they can lead to [1]. Most of this complexity results from different kinds of instabilities associated with growth, such as the Mullins-Sekerka instability of growth fronts [2], or fingering instability [3, 4, 5]. The presence of instabilities implies that a tiny microscopic noise can result in macroscopic changes of shape and hence lead to variety of shapes. (For instance, the formation of snowflakes, a growth phenomenon familiar to everyone, produces hundreds of different shapes [6]). However, despite all the variety of shapes, the vast majority of growth patterns preserve left-right symmetry; in other words, essentially all of the known growth patterns are *achiral*. In those few rare cases, where chiral growth patterns do appear [7, 8], it is believed that the left-right symmetry is already broken at the microscopic level – that is, the observed macroscopic chirality results from the microscopic chirality. (Individual particles in these growth phenomena possess a 3D chirality, which, when coupled with a 2D substrate, gives rise to a 2D chirality of the aggregates. From now on, when discussing chirality, we will always mean 2D chirality).

However, recently a novel and very beautiful type of growth pattern has been reported [9, 10]. A typical pattern strikingly resembles a seahorse and has a strongly broken left-right symmetry (Fig. 1). The patterns were discovered during the growth studies of fullerene-tetracyanoquinodimethane (TCNQ) thin films. Later very similar patterns were obtained using TCNQ

only [11]; and in contrast with other chiral growth phenomena, in these experiments there is no microscopic symmetry breaking: both TCNQ molecules and TCNQ crystals are achiral [12]. We will describe these experiments in more detail in section 3.1.

It is however necessary to emphasize that during the growth both left- and right-handed patterns appear in approximately equal numbers (Fig. 2). Thus, on average, the experiment does not break the left/right symmetry, but apparently, the symmetry breaks spontaneously for each island during the growth. We are not aware of any theoretical (or computational) growth model which could account for such symmetry breaking. In this thesis we will consider a novel growth model (more exactly, a set of models) which spontaneously break the left-right symmetry of the growing aggregate.

All the growth models which we will consider share several important properties. These properties are simple and can be formulated independently of the nature of the underlying physical processes. The model needs to possess (i) branching, that is, every growing branch should eventually give rise to new branches; (ii) strong branch competition – in fact, the competition has to be so strong, that only 2 main branches “survive”; (iii) long range branch repulsion: the branches need to “feel” one another and curve away from each other.

Branching is a very common property in growth phenomena [1]. Branch competition is also very common. It is usually caused by screening – that is, by the competition between growing branches for incoming particles. But competition due to screening is not strong enough to lead to 2-arm shapes.

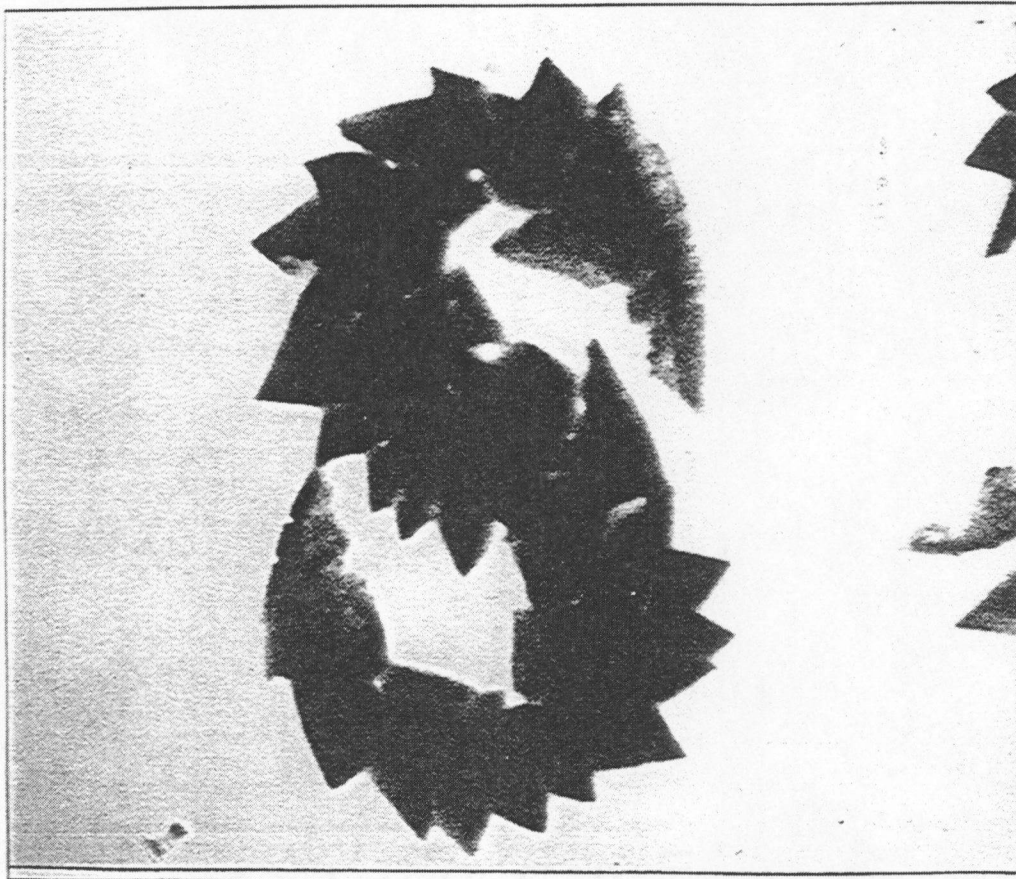


Figure 1: A typical seahorse-like pattern (courtesy of Hongjun Gao, Oak Ridge National Laboratory).

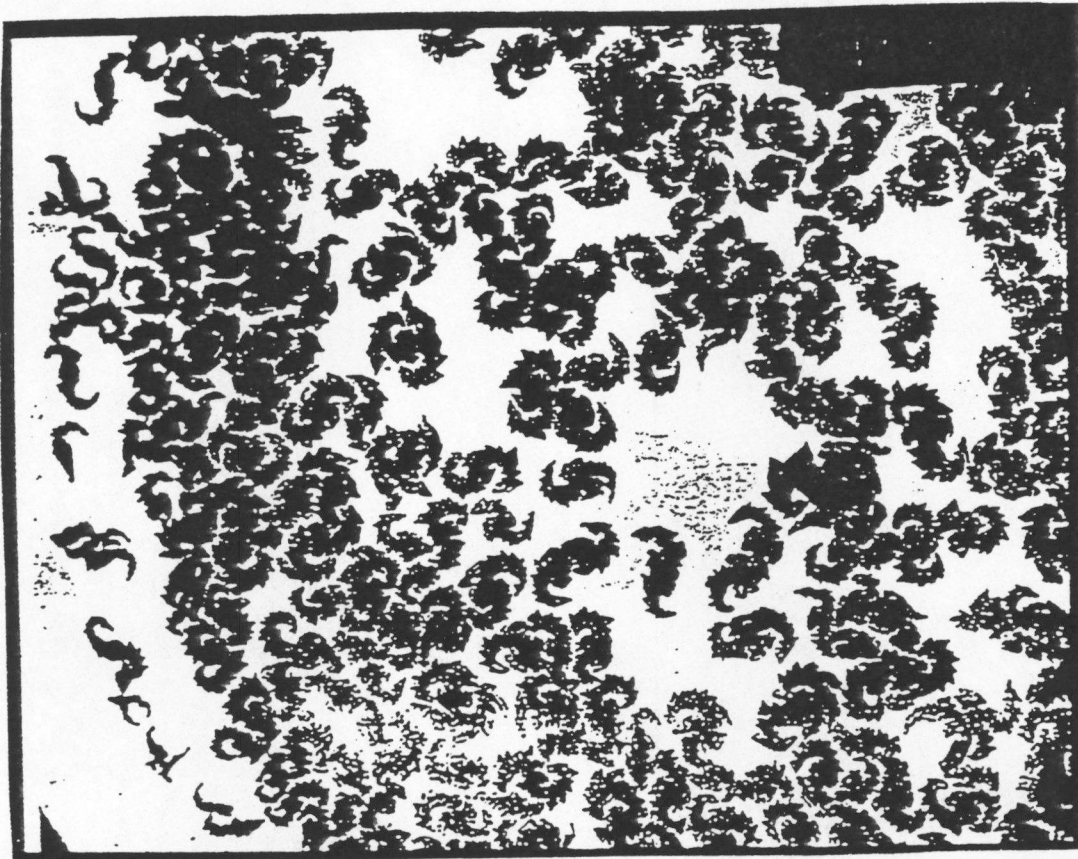


Figure 2: A seahorse "zoo". Both right- and left- handed seahorses occur in roughly equal numbers (courtesy of Hongjun Gao, Oak Ridge National Laboratory).

For instance, the diffusion limited aggregation (DLA) model leads to clusters having 4 or more branches [13, 14, 15]. Competition for incoming particles may also cause some branch repulsion. But this effect is obviously very short-ranged (a branch “feels” only its neighbors). Thus in order to achieve (i)-(iii), one needs to introduce a long range interaction into the system. As will be discussed later in section 3.1, electrostatic forces are believed to play an important role in formation of seahorse patterns. Hence, in our models, the long range interaction between branches is also of electrostatic origin.

We will start with a very simple “tree” growth model which has all the properties (i)-(iii) “built-in” and will show that this model “prefers” chiral rather than symmetric shapes. Then we will consider a quasi-equilibrium continuum model, where properties (ii)-(iii) arise naturally due to electrostatic interactions. Finally, we will consider a microscopic kinetic Monte-Carlo approach.

2 Charged Tree Models

The purpose of this chapter is to demonstrate how branch repulsion and competition may cause chiral symmetry breaking. We will construct a model where branch repulsion and competition are “built-in” and will show that chiral shapes are preferred energetically over symmetric shapes.

A charged tree model is constructed as follows (Fig. 3). A tree starts as a single charged rod. The ends of this rod are considered to be “alive”. Then each alive branch emits two branches: one branch of length l_0 and the other of length l_1 ; both new branches grow at a predefined angle α . All three quantities: l_0 , l_1 , and α are the same for opposite ends and do not change during the growth. When $l_0 \neq l_1$, there are 4 possible combinations of growth on every step, among these the model chooses the tree with the lowest electrostatic energy. Then the longer of the newly added branches become new “alive” branches, the shorter ones “die”, and the process is repeated again. If two (or more) configurations have the same energy then the selection is done randomly. The first 2 steps of growth are shown in Fig. 3.

To complete this model we need to specify how we will compute the electrostatic energy, as the energy of a 1D charged rod diverges. The most obvious way to deal with this problem is to assign some small (but finite) width w to the branches, with this width satisfying $w \ll l_0, l_1$. This allows us to work with 2D, rather than with 1D, charge density. To compute the electrostatic energy of the system, we further break the branches into smaller

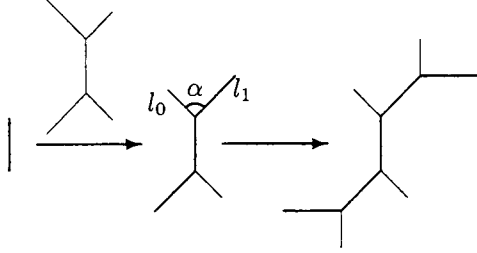


Figure 3: First 2 steps of charged tree's growth. On every step the tree selects a configuration with lowest electrostatic energy. For the first step one of the rejected configurations is shown.

(linear) pieces. The i -th piece has the length l_i , and the linear charge density λ_i , which is in an obvious way related to 2D charge density $\sigma_i = \lambda_i/w$.

We will consider 2 possible charge distributions: 1) a conducting charge distribution $U_i = \text{const}$, where U_i is the potential at the center of the i -th piece; 2) a uniform charge distribution $\sigma_i = \text{const}$. In both cases the total charge of the system will be normalized by the requirement that the average linear charge density be equal to unity (in Gaussian units), that is

$$\bar{\lambda} = \sum_i \lambda_i l_i / L = 1 \quad (1)$$

where $L = \sum_i l_i$ is the total length of the structure.

For the conducting charge distribution the electrostatic energy of the system is given by $W_c = VQ$, where V is the electrostatic potential of the system and $Q = \sum_i \lambda_i l_i$ is the total charge of the system.

To find the charge densities of pieces we construct a set of linear algebraic equations

$$\sum_{j=0}^{N-1} U_{ij} \lambda_j = 1 \quad (2)$$

where $i = 0, \dots, N-1$ and U_{ij} is the electrostatic potential which would be induced at the center of the i -th piece by the j -th piece if the latter had a *unit* charge density. Obviously, the solution $\{\lambda_i\}$ of Eq. (2) would meet the requirement $U_i = \text{const}$ (the constant was set to 1) and can be then easily rescaled to meet the normalization condition (1).

The constants U_{ij} are given by (see Appendices A.2 and A.3 for derivations)

$$U_{ii} = 2 \ln(5.44 d_b / l_i) \quad (3)$$

and for $i \neq j$

$$U_{ij} = \ln \frac{\sqrt{(l_j/2 - x_i)^2 + y_i^2} + (l_j/2 - x_i)}{\sqrt{(l_j/2 + x_i)^2 + y_i^2} - (l_j/2 + x_i)} \quad (4)$$

where l_j is the length of j -th piece, x_i, y_i are the coordinates of the center of the i -th piece (origin is assumed to be at the center of j -th piece, and the x -axis directed along the j -th piece).

The growth of such trees was studied numerically, and all “clusters” grown according to these rules demonstrate some chirality. One of the typical S-like shapes is shown in Fig. 4.

Why does the tree “prefer” to break the left/right symmetry? To answer this question, we note that by introducing the repulsive electrostatic interaction we effectively made the tree to keep its branches as far away from each other as possible. This observation alone accounts for the fact that the tree “chose” the S-shape on the first split. However, during subsequent splits

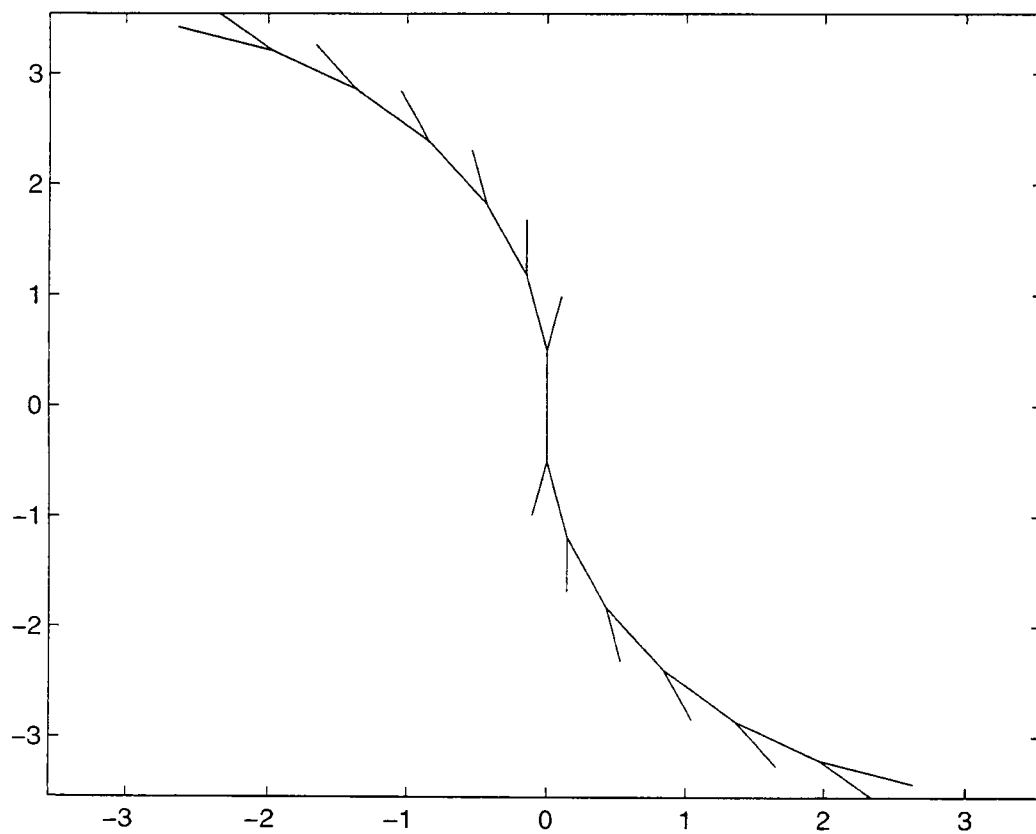


Figure 4: The growth of a conducting tree. $l_1 = 0.7, l_0 = 0.5, \alpha = 12^\circ$ (arbitrary length units).

the result is determined by the interaction between *all* branches, and the outcome depends crucially on how the charge is distributed over the tree: the more charge is concentrated on the small “dead” branches, the stronger is the symmetry breaking (i.e. the higher is the achievable curvature of the main arms). We can illustrate this point by considering the uniform charge distribution $\lambda_i = \text{const}$. In this case the potential energy of a tree is given by

$$U_u = \frac{1}{2} \sum_{i,j} U_{ij} \lambda_j \lambda_i l_i = \frac{\lambda^2}{2} \sum_{i,j} U_{ij} l_i$$

We performed a simulation of growth of a uniformly charged tree (other parameters of the tree were the same as before: $l_1 = 0.7, l_0 = 0.5, \alpha = 12^\circ$), and the final tree is shown in Fig. 5.

We see that, while the left/right symmetry is broken for this case as well, the chirality of the tree stopped improving after the 2nd split. This result is in the agreement with our observation that the higher charge density on the external “dead” branches (which results for instance from the conducting charge distribution) enhances the overall chirality of the cluster. We will return to the question of how the charge redistribution influences which branches survive and which die in the next chapter.

We also note that one can construct a non-deterministic charged tree growth model, where the growth rates themselves are determined by the electrostatic interaction between branches. This non-deterministic growth model also leads to a spontaneous chiral symmetry breaking [16].

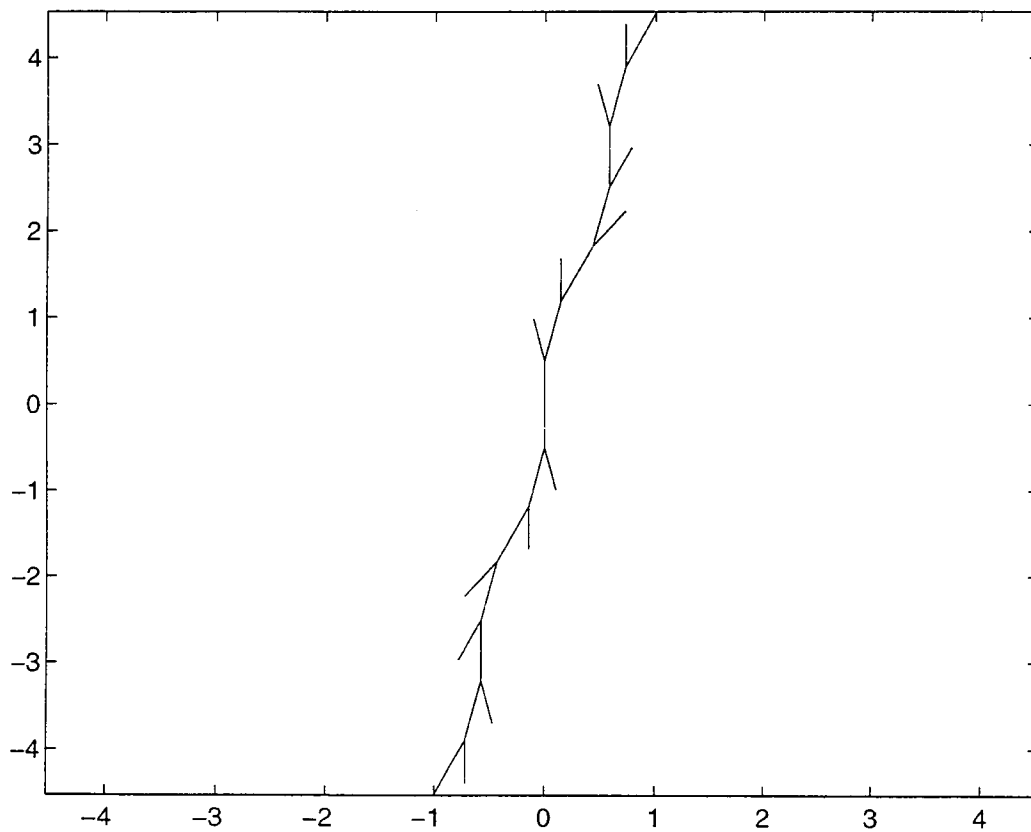


Figure 5: The growth of a uniformly charged tree. $l_1 = 0.7, l_0 = 0.5, \alpha = 12^\circ$ (arbitrary length units).

3 The Continuum Model

3.1 Construction of the Model

In this chapter we will consider an entirely different growth model in which strong branch competition and survival of only 2 main arms occur naturally due to the presence of a long range electrostatic interaction.

First, we will consider in more detail what actually happens in the “seahorse” experiments [9, 10]. In these experiments layers of TCNQ are deposited using the ionized cluster beam (ICB) deposition [17, 18] method, that is, the clusters of TCNQ molecules are ionized and then accelerated towards the substrate, where they disintegrate into single molecules which have high energy (and thus high mobility) and therefore can diffuse along the substrate and form growing clusters. A small fraction the α of diffusing particles (estimated to be typically $\sim 10\%$) are charged (all of the same sign). Thus the growing islands will also carry some charge. (Apart from acquiring charge from the particles diffusing on the substrate, islands will also acquire charge from the particles being deposited directly on them. Because of this direct deposition, islands can possibly retain sufficiently large charge, even if the substrate is not a good insulator (and therefore “leaks” some of the charge). We note, however, that no direct measurements of islands’ charges have been done in the seahorse experiments).

The field of the island, in contrast with the field of walkers, is not random, and therefore will play the dominant role in how the particles (walkers) diffuse (we assume that neutral walkers have a non-zero polarizability and thus also

“feel” the electric field). Hence in our work we neglect the random field of the walkers. Also we will neglect any possible cluster-cluster interactions and consider only the growth of an isolated island.

An obvious approach to this problem would be a Monte Carlo simulation. However, a simple estimate of the number of particles in seahorse clusters in the experiments gives $10^6 - 10^7$ particles. Obviously, a direct microscopic Monte-Carlo simulation for the problem of such a size is very hard if not impossible. Possible approaches, optimization techniques and some of the results of Monte-Carlo simulations will be discussed in the last chapter of this thesis. In this section we will consider an alternative approach in which instead of tracing individual particles we will compute local average growth rates for the cluster boundary, which we treat as a continuous 1D curve.

First, let us consider a growing island surrounded by the freely moving walkers. If a walker hits the island, then with some probability p_s (“sticking” probability) it (the walker) becomes a part of the island. Then the local growth rate (local advancement speed) is obviously

$$\vec{G}(x, y, t) = \frac{d\vec{h}(x, y)}{dt} = \hat{n}(x, y) \delta_i^2 \frac{d^2 N_{hits}(x, y)}{dt dl} p_s \quad (5)$$

where $d\vec{h}(x, y)$ is the displacement of the given boundary point (x, y) during the time dt , $\hat{n}(x, y)$ is the unit vector normal to the boundary, δ_i is a typical intermolecular distance in the growing cluster (thus, δ_i^2 is the area occupied by a single molecule), and $d^2 N_{hits}(x, y)/(dt dl)$ is the number of hits per unit boundary length per unit time. Obviously,

$$\frac{d^2 N_{hits}(x, y)}{dt dl} = \alpha_{hits} N(x, y) v_T$$

$N(x, y)$ is the walker concentration near the point of interest, v_T is an average thermal velocity of walkers, and α_{hits} is a numerical factor of order of unity. Thus, we can rewrite the equation for local growth rates as

$$\vec{G}(x, y, t) = \frac{d\vec{h}(x, y)}{dt} = \hat{n}(x, y) G_T p_s N(x, y) \quad (6)$$

where $G_T = \alpha_{hits} v_T \delta_i^2$ is a constant which depends only on the temperature.

Here we will assume that the growth is slow enough to be considered as a quasi-equilibrium process (which is the case when $p_s \ll 1$). In this case the concentration of walkers is given by a quasi-equilibrium Boltzmann distribution: $N(x, y, t) = N^{(0)} \exp[-U(x, y, t)/kT]$ where $U(x, y)$ is the potential energy of a walker at the point (x, y) , $N^{(0)}$ is the concentration far away from the cluster and k is the Boltzmann constant.

In our case there are 2 different kinds of particles present in the system: charged and neutral walkers, each kind having a different concentration and a different potential energy function. The overall growth rate is given by

$$dh(x, y, t)/dt = dh_n/dt + dh_c/dt \quad (7)$$

where subscript n denotes neutral and subscript c charged walkers, and the concentrations of walkers are given by

$$N_i(x, y, t) = N_i^{(0)} \exp[-U_i(x, y, t)/kT]$$

with $i = n$ or c and $N_c^{(0)} \ll N_n^{(0)}$. The potential energy $U(x, y)$ is equal to $-\chi E^2/2$ for neutral walkers (of polarizability χ) in a field $E = |\vec{E}(x, y, t)|$, and $V(x, y, t)e$ for charged walkers (we assume that the charged particles

carry a single positive charge e , hence the electrostatic potential of the cluster is also positive).

We will assume that the cluster is conducting; therefore U_c (and dh_c/dt) is independent of position on the growing cluster.

The electric field is determined by the charge distribution $\sigma(x, y, t)$ on the island. However, $\vec{E}(x, y)$ diverges near the edge of any 2D charge distribution, so instead of using the field at the edge, we will use the field at some distance from the edge. (That is, instead of $\vec{E}(x, y, t) = \vec{E}(\vec{r}, t)$ we will use $\vec{E}(\vec{r} + \delta \hat{n}(x, y), t)$, where δ is the ‘sticking distance’ —the distance at which a diffusing particle sticks to the cluster; we will assume $\delta \sim \delta_i$). The electric field is determined by the shape of the island, to within an overall scale factor given by Q , the net charge on the island.

We can now introduce a simpler charge non-conserving model. The majority of particles are neutral and hence one can expect that most of the growth will result from aggregation of neutral particles; then one can just neglect the term due to charged particles in Eq. (7). The charge effects are taken into account by rescaling $Q(t)$. We will use the simplest possible rescaling rule, namely, we will assume that $Q(t) = A(t)\bar{\sigma}$ where $A(t)$ the overall area of the cluster and the average charge density $\bar{\sigma}$ is assumed to be constant. The problem of charge aggregation during quasi-equilibrium growth is considered in more detail in Appendix B.

Thus we have a complete growth model in place: initial shape $\implies$ charge distribution $\implies$ field $\implies$ growth $\implies$ new shape $\implies \dots$.

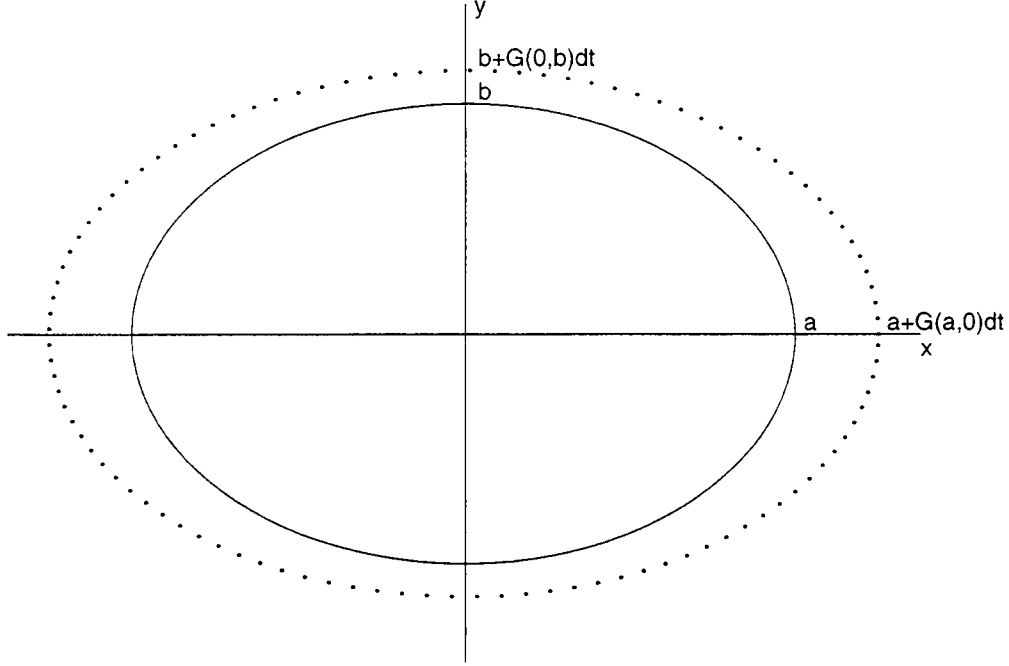


Figure 6: Development of elongation instability.

3.2 Analysis and Simulation

Now we will show that, within this model, a growing island will eventually transform from a compact to an elongated shape. Let us consider a cluster of elliptical shape with radii a , b (Fig. 6).

If we compute the new boundary, using Eq. (7), the new shape will not be exactly elliptical; however, the ellipse's field may still be used as an approximation. It is then obvious that this new ellipse will have greater eccentricity than the original one if

$$\frac{a + G(a, 0)dt}{b + G(0, b)dt} > \frac{a}{b} , \quad (8)$$

which is equivalent to

$$\frac{G(a, 0)}{G(0, b)} = \exp\left(\frac{\chi}{2}(E^2(0) - E^2(\pi/2))/kT\right) > a/b . \quad (9)$$

In the last equation we used a charge non-conserving approximation. The electrostatic field $E(\phi)$ at the distance δ from the point $(a \cos \phi, b \sin \phi)$ is given by

$$E^2(\phi) = \frac{Q^2}{2\delta ab}(b^2 \cos^2 \phi + a^2 \sin^2 \phi)^{-1/2}$$

(see Appendix A.1 for derivation). After introducing the average charge density $\bar{\sigma} = Q/A$, where $A = \pi ab$ is the total area of the cluster, Eq. (9) becomes

$$\exp\left[\frac{\chi \bar{\sigma}^2 \pi^2}{2kT\delta}(a - b)\right] > \frac{a}{b} \quad (10)$$

It is obvious from this equation that, if at some time during the growth the relationship (10) becomes valid, it will remain valid afterwards. Initially, the shape is compact (circular), i.e. $a = b = R$. However, due to randomness of the growth there are always small variations in the radius. One can expect that the magnitude of these variations is at least $\sim \delta$, that is $|a - b| \sim \delta$. The transition from the compact to elongated shape occurs when the compact shape becomes unstable with respect to such variations. This happens when R reaches some critical value R_0 , determined by

$$1 + \delta/R_0 = \exp\left(\frac{\chi \bar{\sigma}^2 \pi^2}{2kT}\right)$$

or

$$R_0 \approx 2\delta kT / \chi \bar{\sigma}^2 \pi^2 .$$

Now estimating $\bar{\sigma} \sim \alpha e / \delta_i^2$, $\chi \sim 2 \times 10^{-24} \text{cm}^3$, $\delta_i \approx \delta \sim 10^{-7} \text{cm}$, $\alpha = 10\%$, and $T \approx 300K$, we get the estimate $R_0 \sim 0.2 \mu\text{m}$. We see that R_0 is smaller (by a factor of 10–20) than the size of seahorses observed in the experiment. Thus this result is consistent with the experiment.

The charge density and the resulting electric field can be computed exactly only for a few highly symmetric shapes. In other cases we will study the growth numerically.

The growth can be simulated numerically in an obvious manner: the current boundary of the cluster is represented as a set of vertices $\{\vec{r}_i : i = 0 \dots N_b - 1\}$, connected by line segments. For each vertex we compute the potential energy of a walker near this point $U(\vec{r}_i)$; then a unit normal vector $\hat{n}_i$, and the displacement vector $\vec{\Delta}_i = \hat{n}_i G(r_i) \Delta_t$ are computed (where Δ_t is a time-scaling constant). After all displacements are computed, all vertices are moved to their new positions. The only remaining problem is to compute the field distribution near the boundary.

One can try to deal with this problem by solving straightforwardly Laplace's equation for the electrostatic potential. However, despite the fact that our problem is 2-dimensional, Laplace's equation for the electrostatic potential is still 3-dimensional. Hence, to find the local electrostatic field, one would need to solve this 3D problem for the full space. To take advantage of the lower dimension of the problem, we will use a surface charge method [19, 20, 21, 22], which we will outline below.

Given the cluster C , we first compute the 2D charge density $\sigma(x, y)$, and then find the electrostatic field. To find $\sigma(x, y)$, we introduce a grid $\{\vec{D}_i, i =$

$1..N_g, \vec{D}_i \in C\}$, forming a square lattice inside the cluster. Each square of this lattice is assigned a charge density σ_i (we will refer to these squares as elements). Now we replace the continuous equation for the electrostatic potential $V(x, y) = \text{constant}$ for all $(x, y) \in C$ by the discrete equation $V(\vec{D}_i) = \text{constant}$, which gives rise to the following set of linear algebraic equations:

$$\sum_{j=0}^{N-1} U_{ij} \sigma_j = 1 \quad (11)$$

where $i = 0, \dots, N-1$, and the scaling constant in the right-hand side (here set to 1) can be chosen arbitrarily (after the system is solved we can rescale the σ_i). U_{ij} is the electrostatic potential which would be induced at the point $\vec{D}_i$ by the square element j , if the latter had a *unit* charge density. Therefore, one can approximate U_{ij} as follows

$$U_{ij} = \frac{A_j}{r_{ij}}, \text{ for } i \neq j \quad (12)$$

where A_j is the area of j -th element, and $r_{ij} = |\vec{D}_j - \vec{D}_i|$. For most uses the accuracy of this point-charge equation is sufficient, but one can also use more accurate expression for U_{ij} which takes into account a quadrupole correction

$$U_{ij} = \frac{A_j}{r_{ij}} \left(1 + \frac{A_j}{24r_{ij}^2} \right)$$

The expression for the self-induced potential is derived in Appendix A.2 and is as follows

$$U_{ii} = 3.525 d \quad (13)$$

where d is the element size (i.e. grid step).

Eq. (11) can be solved numerically and then the electric field can be computed. However at this point we face another difficulty. As we have seen earlier, the field intensity E diverges near the edge of the cluster. In addition, the charge density itself diverges near the cluster's boundary. Thus we are trying to find small variations in a diverging quantity, which itself depends on another diverging quantity. We can alleviate the problem by introducing line charges along the boundary. That is, in addition to charged square elements, we will assume that the boundary segments are also charged. This modification can be easily incorporated into Eq. (11); one needs only to distinguish between the self-potential U_{ii} for square elements, which is given by Eq. (13), and the self-potential U_{ii} for line elements at the cluster's boundary, which is derived in Appendix A.3 and is given by

$$U_{ii} = 2d_b \ln(5.44d_b/l_i)$$

where d_b is the segment's width (i.e. border width) and l_i is the length of the segment. The accuracy can be further improved by using the exact field of a uniformly charged rod (which is given by Eq. (29) derived in Appendix A.3) rather than point charge field given by Eq. (12).

As an even further simplification of the problem, we may use the linear (boundary) elements *only*. The basis for neglecting the interior elements is the fact that the charge density is the largest near the boundary, so that charges located close to the boundary give the main contribution to the electric field. This simplification not only reduces the number of elements to consider (and thus speeds the computation), but also makes it easy to

compute the electric field intensity: to compute a field at distance δ from element i , one can just use

$$\vec{E}_i = 2\hat{n}_i\sigma_i d_b/\delta$$

The Boltzmann factor for a neutral particle in this field is, then, given by $\exp(\chi E_i^2/(kT)) = \exp(\gamma \sigma_i'^2)$ where $\gamma = 4\chi d_b^2 \bar{\sigma}^2/(\delta^2 kT)$ is the dimensionless interaction constant, and σ_i' is the dimensionless charge density determined by Eq. (11) and rescaling condition $\sum(\sigma_i' l_i)/\sum l_i = 1$.

We find this simplification to be very important, because, when the charge density is modeled by a square grid (even if the grid is very fine), the nonuniformity in the charge density (arising from the finite grid step) causes noticeable (artifactual) fluctuations in electric field, which are then *amplified* by the growth of the island. Of course, this simplification results in a less realistic field, but we believe that the main physical features of the system—the charge redistribution within the cluster, and the resulting branch repulsion and competition—are preserved.

Obviously, the model described above lacks any “built-in” noise (apart from some tiny numerical “noise”, which is always inevitably present), which means that all symmetries present in the initial shape of the cluster will be preserved during the growth. To explore the possibility of chiral symmetry breaking we need to introduce noise into the system.

First, we will explore how small perturbations in the starting shape of the cluster will influence the growth. Of course, the most fascinating question is: what happens if this perturbation slightly breaks left/right symmetry?

Figure 7 represents a partial answer to this question. The cluster starts as an ellipse with 2 tiny defects, which are small dents placed near (but not at) ellipse tips. The left dent is placed above the x axis, and the right dent below the x-axis. These defects are so tiny that they are almost invisible in Fig 7. However, 10 growth steps later these defects cause a noticeable macroscopic breaking of the chiral symmetry.

Of course, one should ask whether this effect is physical (i.e. follows from the assumptions made above) or artifactual (i.e. results from some defects in the implementation of the model). In fact, it is easy to “discover” a chiral symmetry breaking in the model where a certain ordering of points along the boundary is present in the numerical algorithm (as is the case in our model). Obviously such an ordering can break the left/right symmetry of the model unless the necessary care is exercised. To test whether our own numerical model preserves the existing symmetries, we performed a numerical simulation when the starting shape was an ellipse with 2 defects which *do not* break the symmetry (i.e. the defects are located exactly at the tips of the ellipse). The result is presented in Fig. 8. As we can see, the symmetry is preserved. Thus, we conclude with the high degree of confidence that our model is free of *artificial* chiral symmetry breaking.

Now we add another ingredient to our model, namely, when a branch reaches a certain size (or after a certain number of growth steps), we force it to split exactly at the point of the fastest growth (as determined by the charge distribution) into 2 branches. This branch splitting is just the simplest implementation of the fingering instability which is present in many growth

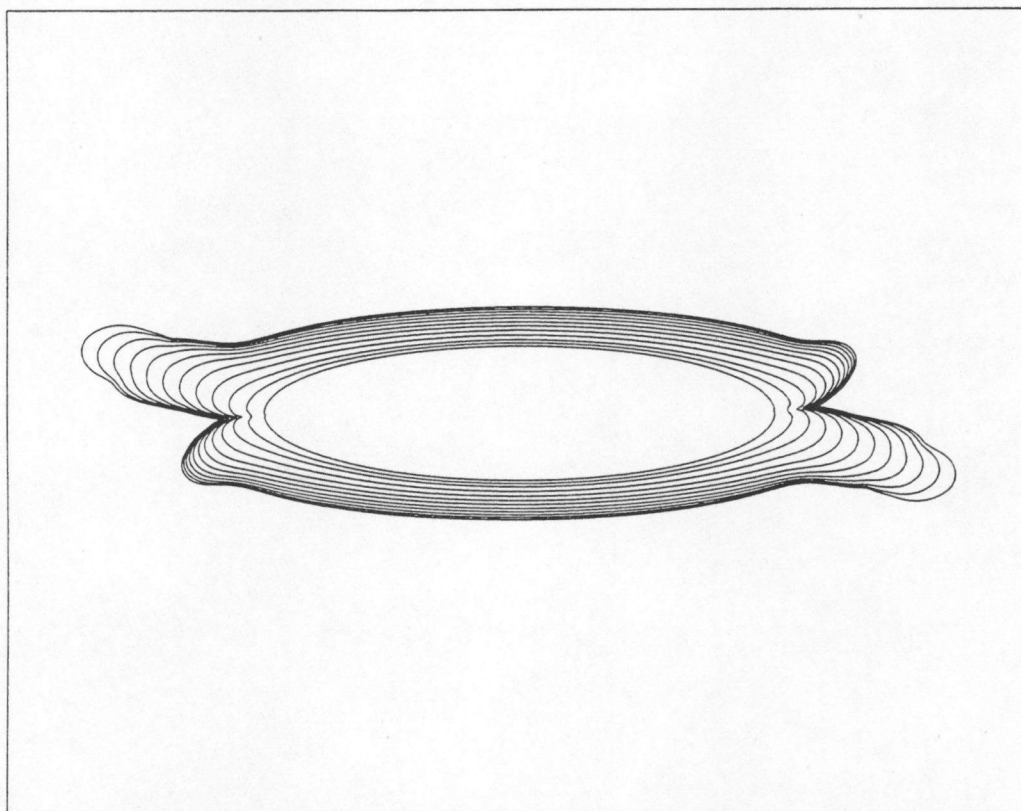


Figure 7: 12 steps of growth of an ellipse with 2 tiny chiral symmetry-breaking defects. Chirality of the aggregate has been greatly increased during the growth.

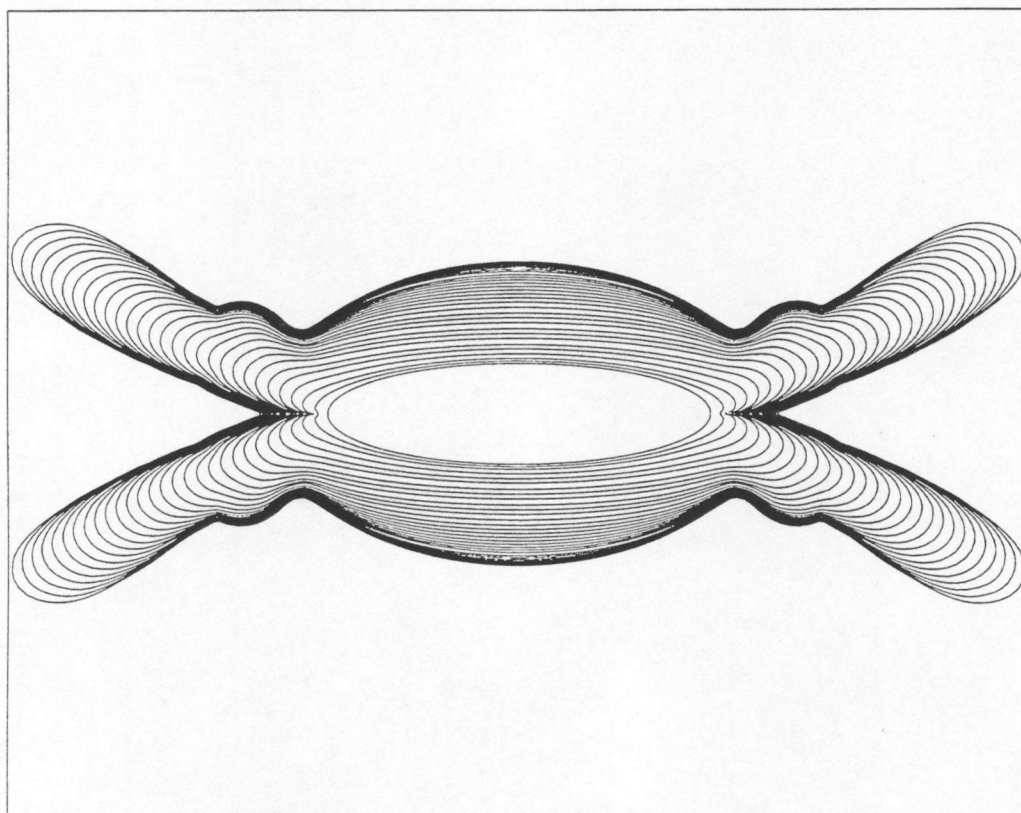


Figure 8: Growth of an ellipse with 2 tiny *symmetrically* located defects. Such a shape preserves its symmetry during the growth.

phenomena [3]. This instability arises near the tips of fast advancing branches and the faster the growth the more likely the split to occur [3].

We used this branching rule for simulating further stages of growth for the cluster shown in Fig. 7. The branches were split after every 12 growth steps. The resulting cluster after 60 growth steps is presented in Fig. 9.

We see that the original tiny chirality has been increased dramatically by repeating branching. We also see Fig. 9 bears an obvious resemblance the experimentally observed “seahorses”. In fact, it has essentially the same geometric properties as a typical experimental “seahorse”: 1) only 2 main arms; 2) these main arms are curved; 3) the curvature is correlated (that is the branches curve in the opposite directions); 4) the outer edge of the main arms is covered by “fins” (small dead branches).

Now let us consider in more detail how the observed curvature arises. Fig. 10 gives a more detailed picture of the growth and branching processes. After the first split (Fig. 10a), the new branches compete for the further growth (as determined by the electric field), and one of the new branches “dies” (i.e. stops growing (Fig. 10b)). The winning branch eventually reaches the critical length and then again splits (Fig. 10c). Let us consider what happens when the branch splits in more detail. First, we note that the new branches “feel” one another. The repulsion between charges will cause charges to redistribute, so that the points of fastest growth will no longer coincide with tips of the new branches. Instead, the fastest growth will occur at points of maximal local charge density (hence maximal $|\vec{E}|^2$), which are farther away from each other than tips of the branches. This will force the

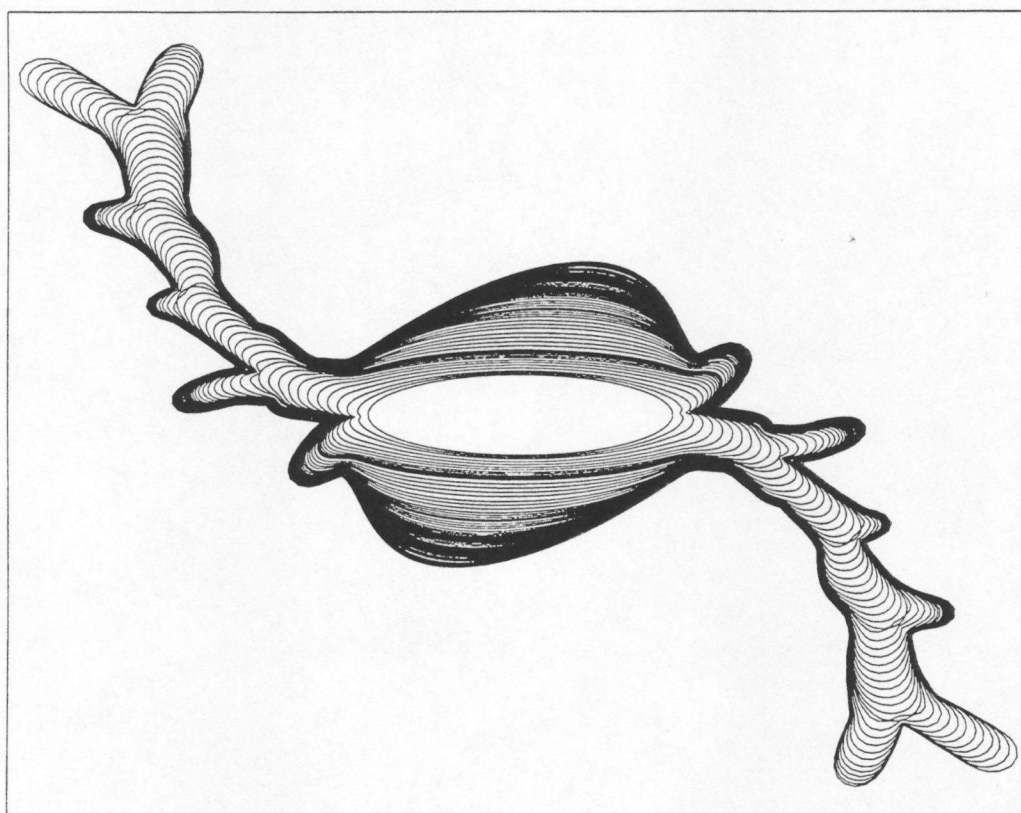


Figure 9: 60 steps of growth of an ellipse with 2 tiny chiral symmetry-breaking defects. Chirality of the aggregate has been dramatically enhanced during the growth.

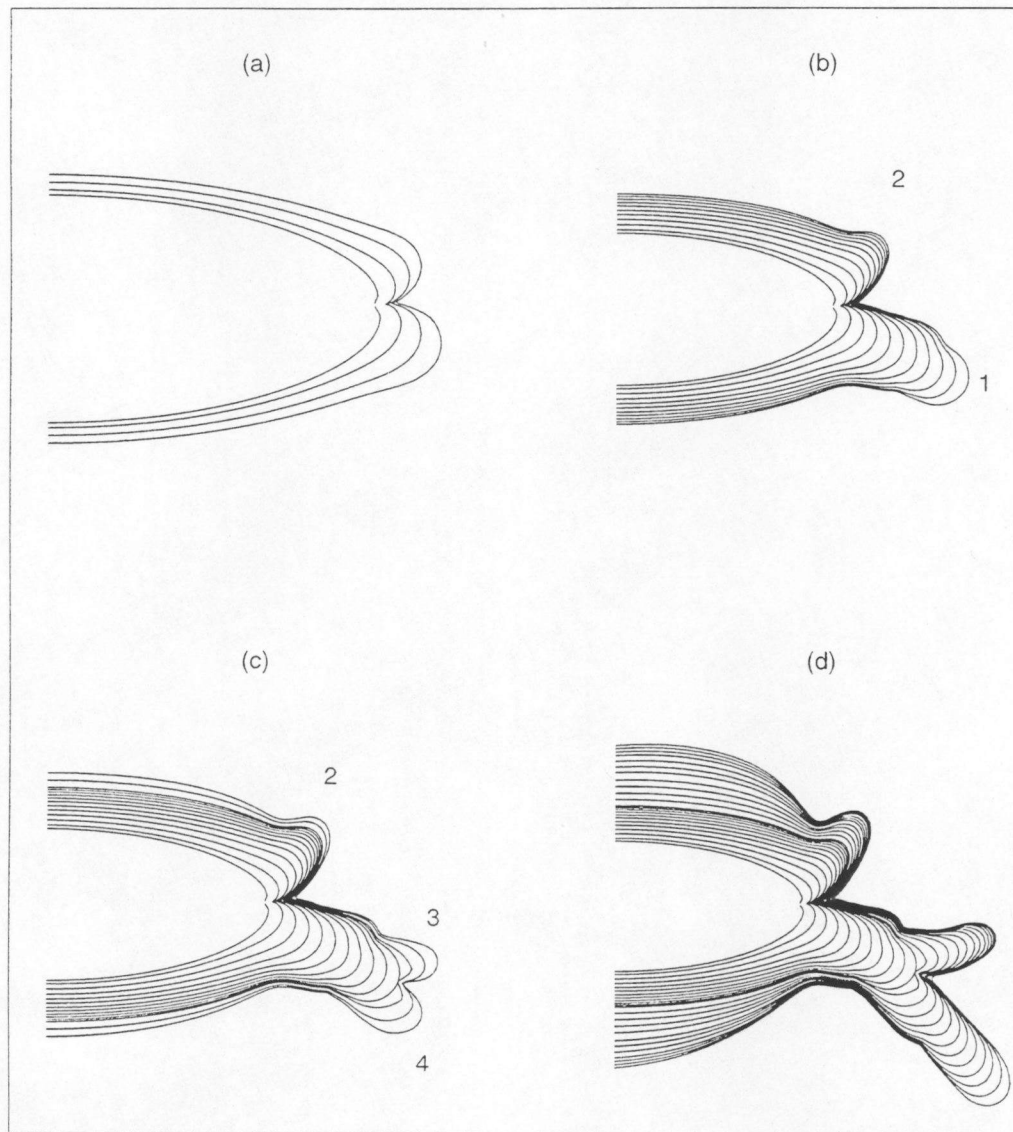


Figure 10: Improving the curvature via branch repulsion and competition.

branches to curve away from one another. If the split is symmetric, then the result of competition between the new branches will be determined by the influence of all the other (already dead) branches. In particular, the main body (being closer to the lower branch) favors the upper new branch (branch 3), and while the previous branch (branch 2) favors the lower new branch (branch 4)]. Branch 2 is smaller than the main body, but the main body is further away. If the parameter values are “right” (in particular, the distance between splitting points should be small enough and dead branches should be large enough), then branch 4 will win the competition. Then, due to the exponential difference in the growth rate, branch 2 will stop growing, i.e. the main arm of the cluster curves even further. A similar process happens on the opposite end of the cluster. We note that the weak long range repulsion between the main arms favors an “S”-like overall shape, rather than a “C”-like shape (as an “S”-shape corresponds to the main arms being further away from each other than is the case for a “C”-shape).

Now we should ask whether the observed chirality is robust. What happens if we vary the parameters of the system?

We have performed simulations for different values of parameters L_0 , (the branching length), and the interaction constant γ . The results are presented in Fig. 11.

We see that, for a large enough interaction constant, all the clusters possess some chirality. We also see that branching is crucial for enhancing chirality; if branches do not split (the bottom row of figures), then the chirality of the aggregates is very weak.

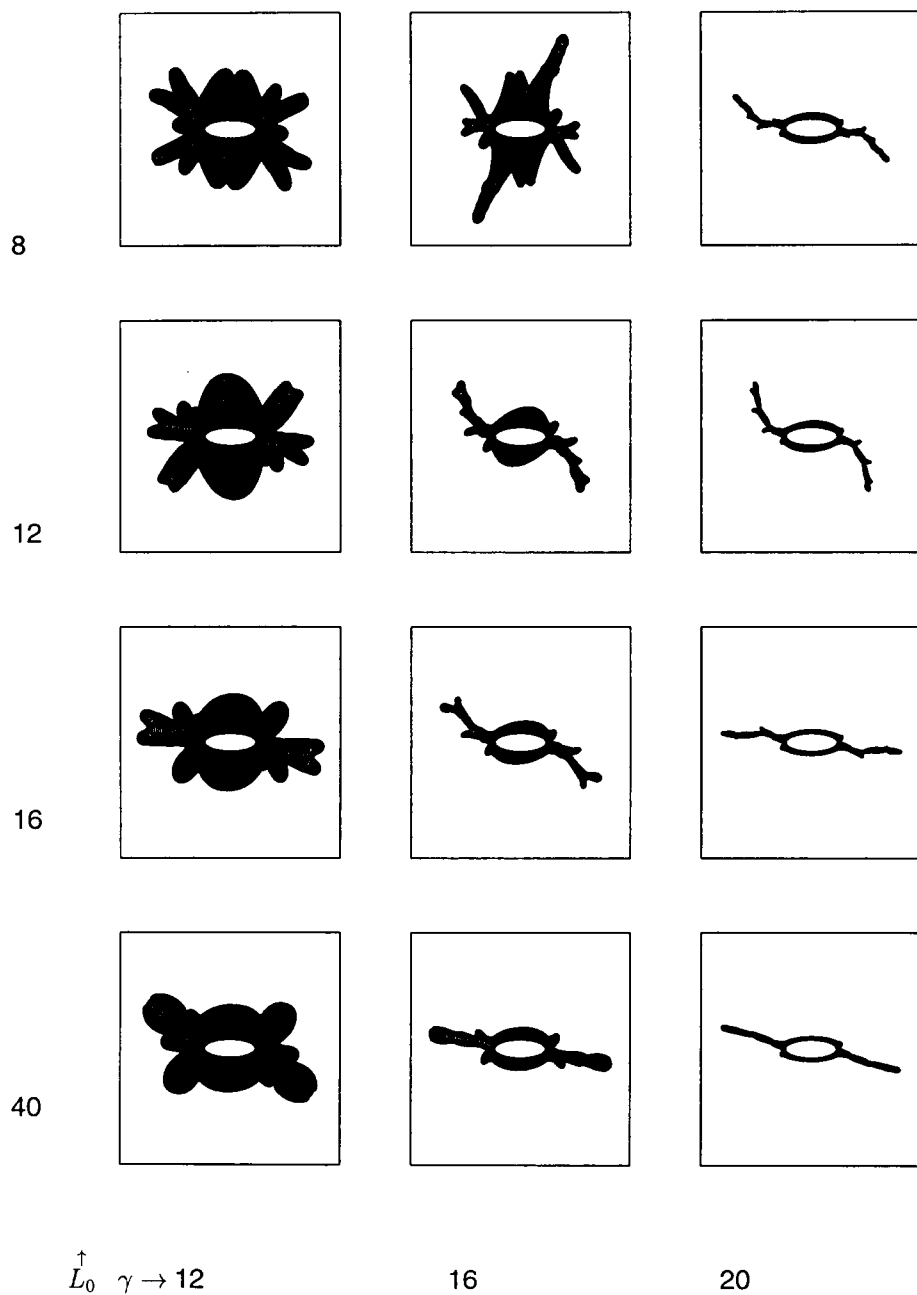


Figure 11: The growth for different values of branching length L_0 and interaction constant γ .

What happens if we reduce the amount of original symmetry breaking? In particular, what happens if one of the original dents is located off axis and the other one is put symmetrically on axis? The result of a simulation with this initial condition is shown in Fig. 12.

We see that the branch repulsion not only causes the right arm of the cluster to curve downwards, but also *causes* the opposite (upper left) branch to dominate – even though the noise on the left side is symmetric. Thus we find that dominance and curvature are *correlated* between the two main arms, leading to strong chirality of the cluster.

All the presented results allow us to assert that our model possesses a *chiral* growth instability, that is, that it amplifies drastically any tiny perturbation that breaks the left/right symmetry. Thus the left/right symmetry inevitably breaks spontaneously during the growth.

How can one test whether this model is directly related to the experiments? Later experiments (prompted by our ideas) showed that if an external in-plane electrostatic field is present during the growth then the shape of the clusters changes considerably: most of the curvature disappears, and the orientation of clusters with respect to the direction of electric field is irregular [23] (there seems to exist a weak tendency among clusters to align along the electric field, but we do not have enough data to judge whether this tendency is statistically significant). This result not only proves the importance of electrostatic effects in the original seahorse experiments, but also provides an important test for our model. The result of the simulation of growth in an external electrostatic field is presented in Fig. 13. We see that the cluster

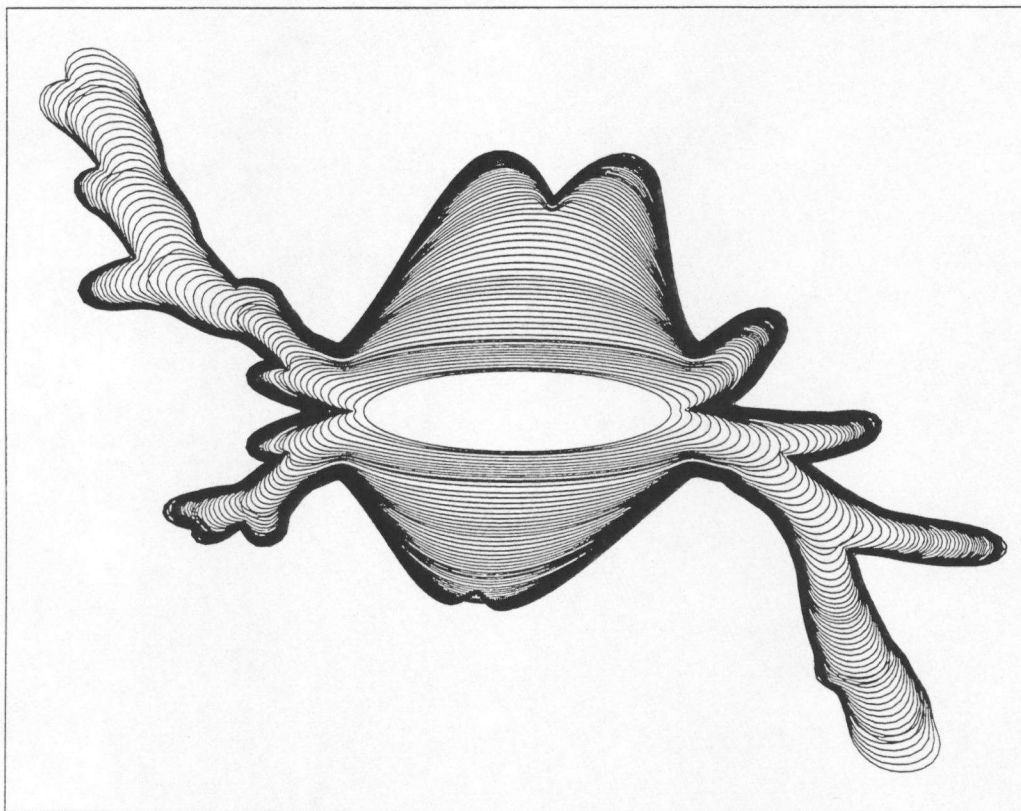


Figure 12: Growth from an initial shape which is an ellipse with two dents. One of the dents is located symmetrically, the other one is off-axis.

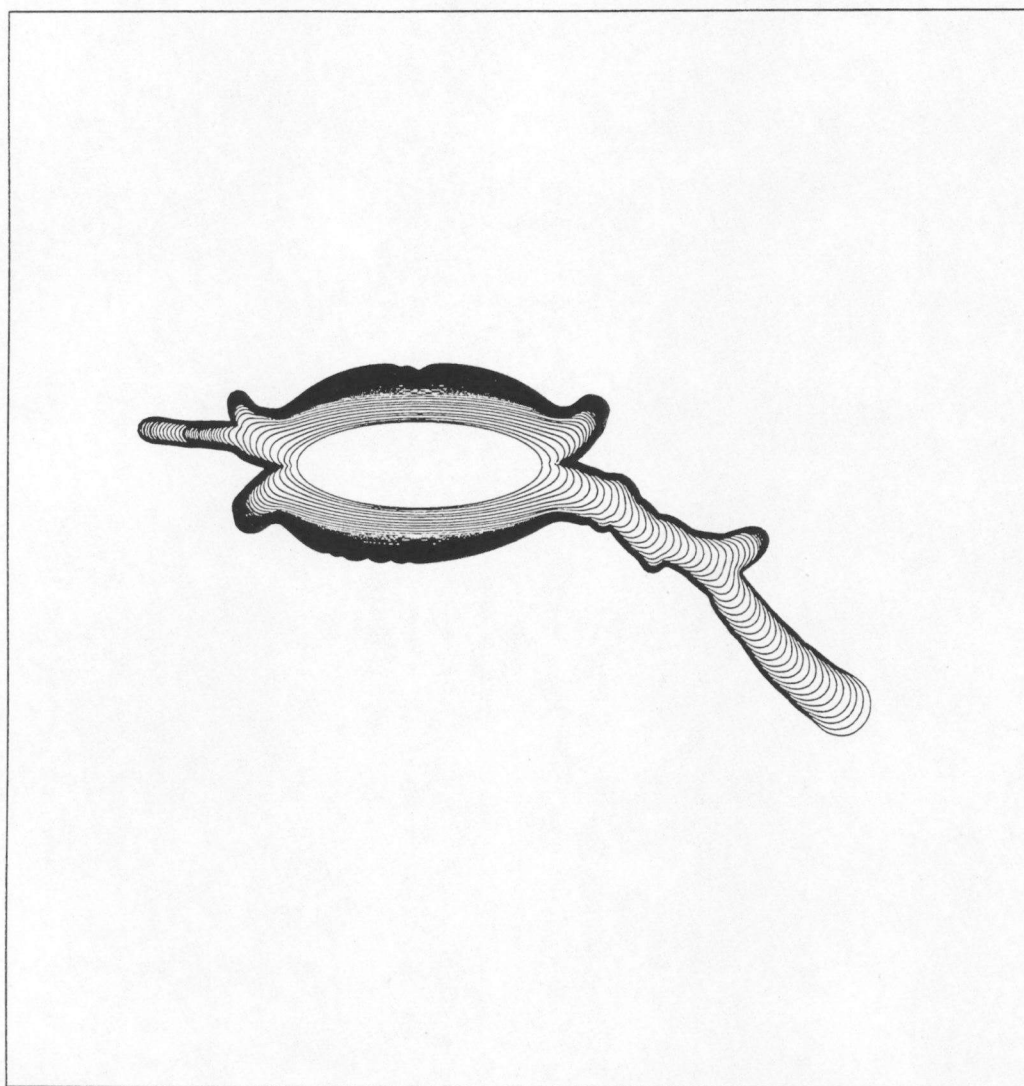


Figure 13: The growth in the presence of an external electrostatic field, oriented to the right.

also lost most of its curvature. Apparently, there is a competition between curving and the external field (which tends to align the growth along the field direction), leading to straight branch growing at the angle to the field. These results show a good qualitative agreement with the experiments: in each case the curvature of the main arms is suppressed, only one arm grows, and there is (possibly) some weak tendency for growth to follow the direction of external field.

Despite the obvious resemblance between the experimental results and our simulations, many questions need to be answered before one can claim that our model is directly related to the experiment. First, TCNQ crystals are not conducting [24, 25]. However they are believed to have a large (about 8) dielectric constant [26]. Obviously, the polarization charge distribution on the surface of a dielectric will be different from the charge distribution on the surface of a conductor; but the larger the dielectric constant, the smaller this difference is (usually the electric field within a dielectric $E \sim 1/\epsilon$). Second, our model relies crucially on the assumption of a slow growth (this assumption leads to exponential differences in growth rates). It is not clear how close this assumption is to what really happens in the experiments. Third, as shown in Appendix B, the near-equilibrium growth can not account for maintaining the constant average charge density, as was assumed in our simulations. However, it is not at all clear how important this assumption is for our model. In any case a realistic treatment of charge accumulation is probably not possible with the charged wire model. In addition, in the seahorse experiments during the growth there is a “rain” of charged particles being de-

posited directly on the cluster. This fact alone may account for maintaining large enough charge on the growing island. Finally, some additional work is needed to achieve the better understanding of noise effects and their relation to branching in the continuum model.

We wish to emphasize that our mechanism for spontaneous chiral symmetry breaking – whether or not it ultimately proves to explain the seahorse experiments – is, to the best of our knowledge, entirely novel, relying only on the existence of a strong long-ranged interaction between branches in the system. Thus our model has the potential to describe a variety of phenomena in which such a long-ranged interaction is present.

4 Monte-Carlo Simulations

The most challenging task is to try to simulate the growth of sea-horses at the microscopic level. The most obvious obstacle to overcome is the size of clusters; as we mentioned earlier, there are $10^6 - 10^7$ particles in a typical cluster. Thus we will try to find a regime where the desired behavior (formation of S-like clusters) is achieved with smaller numbers of particles. In particular, we will use much stronger interaction constants than those in the real experiment. Another serious problem is recomputation of the field, which depends on the shape of the cluster, and changes with any change in the cluster. This field recomputation adds a serious overhead to simulations, and this overhead increases with increasing size of the aggregate. In this chapter we will consider possible optimization techniques which help to alleviate this problem. These techniques can be applied not only to simulations of seahorse experiments, but also to any other lattice growth simulation which involves fields which depend on the shape of the growing aggregate.

4.1 Description of the Model

In all our Monte-Carlo simulations we used a hexagonal underlying lattice, that is, a particle can only occupy positions given by $n\hat{a}_1 + m\hat{a}_2$, where n, m are integer numbers, and $\hat{a}_1, \hat{a}_2$ are unit basis vectors (that is all lengths in the system will be measured in units of lattice distance a); for a hexagonal lattice $\hat{a}_1 \cdot \hat{a}_2 = \sqrt{3}/2$. The choice of a hexagonal lattice instead of rectangular one was dictated by the hexagonal lattice's higher symmetry. (A hexagonal

lattice has 6-fold rotational symmetry, while a square lattice has only a 4-fold symmetry; thus a hexagonal lattice is less likely to cause artifacts in growth). Advantages of a hexagonal lattice over a square lattice are discussed in [27].

We have explored several approaches. In all of them the growing cluster carries some charge, and the resulting electric field biases the growth. All of the models can be classified by several criteria which are discussed below.

Charge Conserving vs Charge Non-Conserving Models

The most realistic simulation requires independent tracking of both neutral and charged particles. We will refer to such models as “charge conserving” models. However, as was noted earlier, it is much easier to keep track of only neutral particles and account for presence of charged particles by rescaling the overall charge of the cluster. The simplest rescaling law is $Q = \alpha N_c e$, where Q is the total charge of the cluster, e is an elementary positive charge, and N_c is the total number of particles in the cluster. Also, one can use a charge conserving model to obtain a more realistic scaling dependence $\alpha(N_c) = Q/N_c$ and then use the obtained dependence for charge non-conserving simulations. One can expect (and our simulations confirm this) that in any diffusion based model, the growth of the total charge would deviate from the linear law (being much slower). However, in the seahorse experiments there is a “rain” of particles being deposited directly on the cluster. This factor alone can account for a much faster charge accumulation than could be the case in a diffusion based charge accumulation. Hence, we believe that a charge non-conserving model with a linear law of charge accumulation is worth considering.

Non-local and Semilocal Models

We have considered 2 kinds of growth rules: non-local lattice gas [28] growth, where we keep track of walker movements from the moment they are injected into the lattice until the moment they join the cluster; and semilocal growth rules, when the probability for an empty lattice site near the cluster to become filled is determined by local parameters of this site. However at least one of these parameters – the electrostatic field – is inherently non-local, i.e. depends on the overall shape of the cluster (hence we call this model *semilocal*).

In the lattice gas model the growth starts with a one-particle growth center in the center of the lattice. There is also a “gas” of free particles. Gas particles can hop between nodes of the lattice. With the constraint that 2 particles cannot occupy the same site, relative (unnormalized) hopping probabilities for neutral particles are determined by

$$P_i^n = \exp(\chi E_i^2 / (2kT))$$

where χ is the polarizability, subscript i numbers the neighbor sites (in the hexagonal lattice, there are 6 nearest neighbors), and $\vec{E}$ is the electric field intensity at the i -th neighbor site. The absolute (normalized) probabilities of jumps are given by

$$p_i^n = P_i^n / \sum_j P_j^n$$

For charged particles the non-normalized probabilities are given by

$$P_i^c = \exp(-e U_i / kT)$$

where e is a unit (positive) charge, and U_i is the electrostatic potential at the i -th neighbor site.

Particles belonging to the cluster cannot move, except for particles located at the edge of the cluster. The latter particles can move if they have less than some predefined number of neighbors (in our simulations we set this threshold number of neighbors to be 3). Such particles can hop along the cluster's boundary until they find a site with 3 or more neighbors. The edge hop rate is measured in units of the surface hop rate; obviously, the higher the edge hop rate is, the smoother the edges of the cluster become [29, 30, 31]. At sufficiently high edge hop rate the young cluster will have a hexagonal shape; however eventually, when the length of the boundary reaches some critical size, the edge diffusion can no longer keep the cluster smooth, and the hexagonal shape will be replaced by a less compact dendritic shape.

When only one walker at a time is present on the lattice and the edge diffusion rate is zero (and no electrostatic field is present) this model degenerates into the diffusion limited aggregation (DLA) model [32].

In our semilocal model, the growth rule is as follows: given a shape of the cluster, we first find all non-occupied lattice sites near the cluster. Then, for all sites simultaneously, we compute the non-normalized probability of a new particle joining the cluster at this site according to

$$P_i = A \exp((\chi E_i^2/2 + K_i E_b)/kT) \quad (14)$$

where subscript i numbers sites along the cluster boundary, A is the normalization constant (choice of A will be discussed below), K_i is the number of

neighbor sites which are already occupied, and E_b is the bond energy.

The semilocal model is much simpler than the non-local model, having fewer parameters (no hop rates, no concentration). The semilocal model also avoids problems caused by the finite size of the lattice. A semilocal model is justified if the growth is slow enough (the aggregate must be in quasi-equilibrium with the gas).

4.2 Computation of the Electric Field

As we see the computation of the local electric fields is the crucial step in determining hopping probabilities. When computing this field we neglect the random field of the gas. The field of the growing cluster can be computed straightforwardly using the superposition principle, for the electrostatic potential

$$U(x, y) = \frac{e}{a} U'(x, y) \quad (15)$$

where $U' = \sum_i \frac{q_i}{|\vec{r}_i(x, y)|}$ is the *dimensionless* electrostatic potential, $\vec{r}_i(x, y) = (x - x_i)\hat{a}_0 + (y - y_i)\hat{a}_1$, the summation is performed over the particles in the cluster, (x_i, y_i) are dimensionless lattice coordinates of the cluster's particles, and q_i is the charge of the i -th cluster's particle expressed as a fraction of a single charge. For the field intensity

$$\begin{aligned} \vec{E}(x, y) &= \frac{e}{a^2} \vec{E}'(x, y) \\ \vec{E}'(x, y) &= \sum_i q_i \vec{r}_i(x, y) / |\vec{r}_i(x, y)|^3 \end{aligned} \quad (16)$$

The computation of these sums can be optimized (by a factor of 2-6, depending on computer architecture, compiler, and other factors) by building

tables of precomputed values for intersite interactions. For instance, for the electrostatic potential we precompute the values

$$U'_{ij} = \frac{1}{\sqrt{(i\hat{a}_1 + j\hat{a}_2)^2}}$$

store them in a 2D array, and use these precomputed values as follows

$$U(x, y) = \frac{e}{a} \sum q_i U'_{x-x_i, y-y_i} \quad (17)$$

Similarly, one can optimize the computation of $\vec{E}(x, y)$.

The last step in computing the field is finding q_i , that is the distribution of charge on the cluster. We have considered 3 kinds of charge distributions:

1. fixed charges: particles which carried a charge while in the gas carry the same charge when in the cluster. Obviously, such charge distribution can be used only in charge conserving models.
2. uniform charge distribution.
3. conducting charge distribution.

In cases 1 and 2 finding values of q_i is trivial. In case 3, one needs to solve a system of algebraic equations:

$$\sum_{j=0}^{N_c-1} a_{ij} q_j = 1 \quad (18)$$

where $a_{ij} = U_{x_i-x_j, y_i-y_j}$ for $i \neq j$, and $a_{ii} = 4/a$ (for the purpose of computing the self potential we treat particles as disks of radius $a/2$ and $i = 0 \dots N_c - 1$). After solving the system (18), we rescale $\{q_i\}$ to satisfy $\sum q_i = \alpha N_c$.

We also note that cases 1 and 2 (and, to some extent, case 3) allow us to employ a very important optimization. Computation of both sums (15) and (17) takes an $O(N_c)$ time, where N_c is the size of the cluster. However, for every lattice site (x, y) most of the terms in these sums do not change between field recomputations, this allows us to use the following caching technique. First, we introduce the “cluster time”, a counter which is incremented whenever a change in the cluster (addition of a new particle, or a hop of an edge particle) occurs. We also keep a “changelog”, that is a buffer which contains last changes in the cluster along with the times when those changes occurred (we used a circular buffer, so that if the buffer is full, then a new change replaces the oldest available change; the buffer size was usually set to 100 changes). Obviously, keeping such a changelog adds only a small ($O(1)$) overhead to the “cluster change” operation. Also we keep a table of cached values, for instance for electrostatic potential; this is an array $C_u(N_L \times N_L)$, where N_L is the size of the lattice, a cell $C_u(n, m)$ keeps the last computed value of the potential at the site (n, m) and the “time” when the computation was done. When a current value of potential at the site (n, m) is needed, we can use the last computed value with correction due to changes which have occurred *after* that last computation, then we update $C_u(n, m)$. If the cached value is too old (that is if some of the changes in the changelog have already been discarded), then the potential is recomputed “from scratch” using Eq. (15) or Eq. (17).

Maintaining and updating the cache table adds only a small $O(1)$ time overhead to every “compute field” operation, and $O(N_L^2)$ of memory overhead

to the whole program. But this optimization changes the computation time for sums (15) and (17) from $O(N_c)$ to effectively $O(1)$ and thus speeds the computation enormously.

The case of a conducting cluster is obviously more computationally intensive than other cases, as we need to solve the set of equations (18) whenever the cluster changes. This typically involves an $O(N_c^3)$ computation time for a single cluster change, and therefore, a simulation of the growth of the cluster of size N will require at least $O(N^4)$ time. However, even though an addition of a particle changes the charge distribution everywhere, the largest changes occur near the newly added particle. Hence, instead of solving Eq. (18) by a generic Gaussian elimination algorithm, one can employ one of the iterative solving algorithms and use the previously found solution as the starting point for iterations. In our simulation we used a conjugate gradient algorithm [33, 34] which effectively reduced the time required for finding charge distribution from $O(N_c^3)$ to $O(N_c^2 \log N_c)$; the observed speedup factors for growth of a 1000-particle cluster were about 10-15.

4.3 Discussion of Results

The models and optimization techniques are of general interest and can be applied to the simulation of a variety of growth phenomena in which the need to take into the account the long-ranged cluster's field arises.

However, can we simulate the growth of seahorse like clusters using the microscopic Monte-Carlo simulations? The most encouraging results were

obtained using a charge non-conserving semilocal growth model with a conducting charge distribution.

So far we have introduced 5 parameters which control the behavior of the model: temperature T , bond energy E_b , walker polarizability χ , lattice constant a , relative number of charged particles α . However, we can rewrite the rules for our model, so that only 2 independent parameters will appear in the equations: interaction constant $\gamma = \chi\alpha^2e^2/(2a^4kT)$ and bond constant $\gamma_b = E_b/(kT)$. Eq. (14) then becomes

$$P_i = A \exp(\gamma E_i'^2 + \gamma_b K_i) \quad (19)$$

Eq. (16) for $\vec{E}'$ and Eq. (18) for q_i remain the same, but the rescaling condition changes to $\sum q_i = N_c$.

Thus our model is now complete: given a cluster, we compute simultaneously all P_i for the cluster boundary and select the constant prefactor A so that the $\max\{P_i\} \ll 1$. Effectively, by choosing A , we choose the time scale of our simulations. While the result for any specific run will depend on the choice of A , any conclusions we draw from the run should not depend on A . That is, if we change A , we should still be able to arrive at the same conclusion.

Fig. 14 represents a set of results for different values of bond energy and interaction constant. First we see that this model does demonstrate a 2-arm instability: there is a whole range of parameters where all shapes have only 2 main arms. On some of the clusters one can also see the branches which "died" due to competition. We also note, that at least in some cases, the main

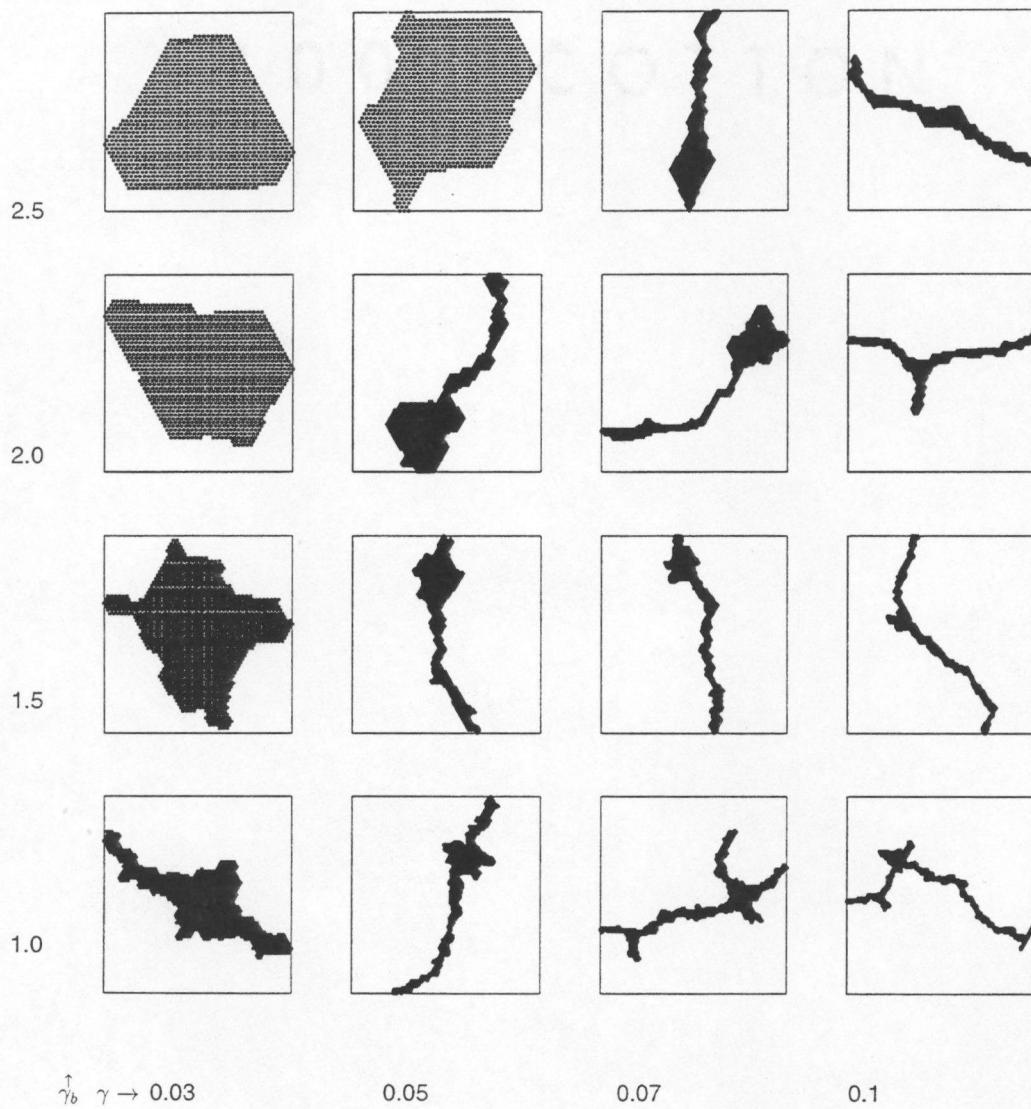


Figure 14: The results of Monte-Carlo simulation for different values of interaction constant γ (x axis) and bond constant γ_b (y axis). Semilocal, charge non-conserving model with conducting charge distribution. 1200 particles in each cluster.

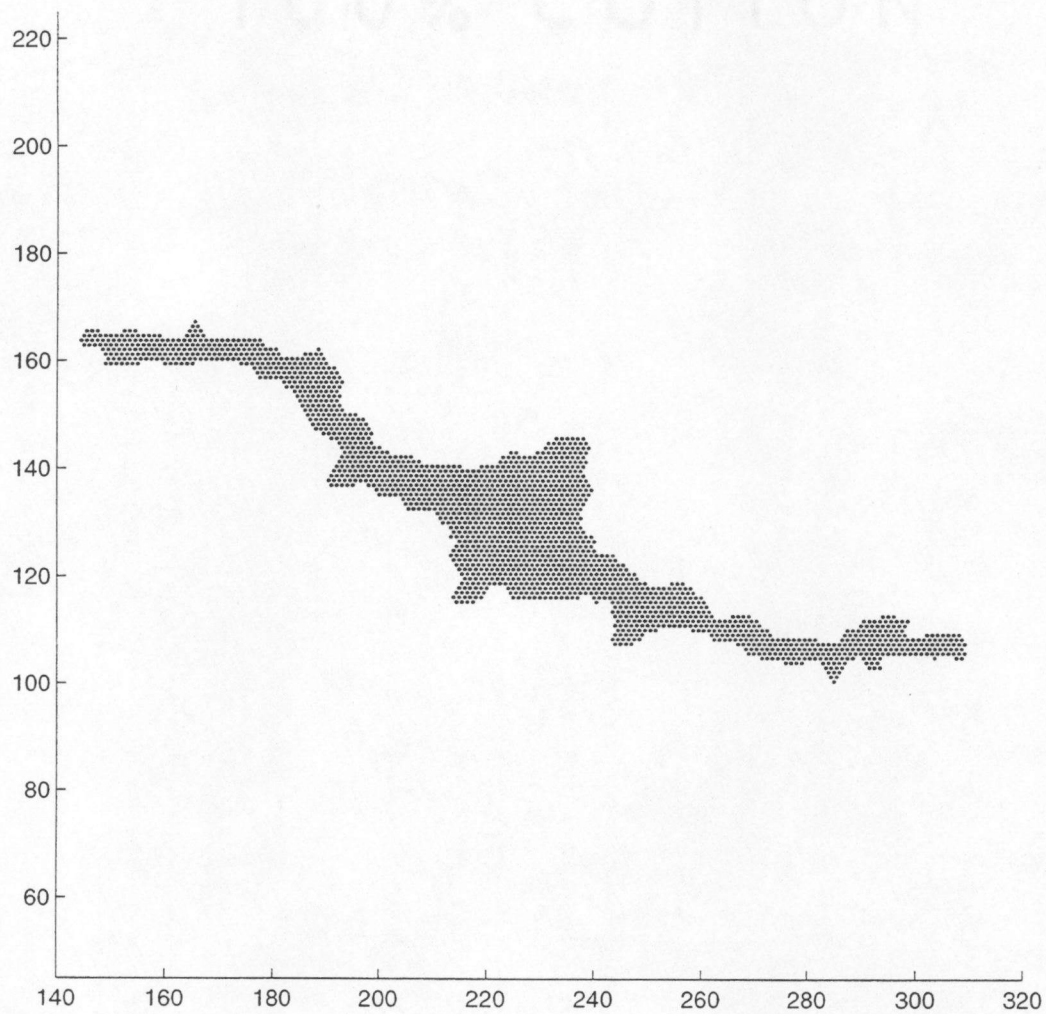


Figure 15: The results of growth for $\gamma = 0.03$, $\gamma_b = 1.0$. 2000 particles, lattice length units. The cluster clearly has some chirality.

arms are curved and the external edges of the main arms are more irregular (i.e. covered by small “bumps”) than the inner edges. This may indicate that the observed curvature in these clusters arises due to the interaction between the main arms and these bumps. Fig. 15 shows one of the clusters (the one at the lower left corner of the “map”) at an “older” age. The cluster clearly has some chirality. However, reruns at the same values of parameters but with different random number seeds show that this chirality is not very robust; some resulting clusters do have some weak chirality, and some do not. Thus, the result presented in Fig. 15 is encouraging, but not conclusive.

We conclude that, despite the fact that Monte Carlo simulations failed to produce S-shaped clusters consistently, they did lead to the appearance of some of the geometrical features of the seahorse clusters (existence of only 2 main arms, some signs of branch curvature and of chirality). It is obvious that the formation of main arms curved in opposite directions is hindered by the strong noise inevitably present in any Monte Carlo simulation. Simulations of much larger scale are needed to reduce the effects of the noise; such simulations would probably require more sophisticated numerical techniques. Simple parallelizing of the code and employing parallel computers is not sufficient, because in most of the outlined above models, the computation time increases non-linearly as a function of number of particles in the cluster (e.g. for a conducting cluster in a quasi-equilibrium semilocal model the computation time is $t \propto N^3 \log(N)$; thus, increasing the cluster size by a factor of 10^2 would require increasing the computing power by a factor of 10^6). Also it is likely that employing a lattice can hinder the effects we have

been looking for (branches “prefer” to follow one of the lattice axes, rather than curl).

5 Conclusions

In this work we suggest a novel mechanism for spontaneous chiral symmetry breaking during 2D aggregation. This mechanism does not rely on the presence of microscopic chirality but rather results from the existence of a long-ranged electrostatic interaction in the system. This interaction leads to a strong competition and repulsion between growing branches and eventually gives rise to a broken left/right symmetry. We explored several approaches to simulation of growth in the presence of an electrostatic interaction: tree models, continuum models, and Monte-Carlo simulations. Especially encouraging results were obtained using the continuum model; simulated growth often led to clusters which possess the same geometrical properties as experimentally observed “seahorses” [9, 10]. The results of our simulations in the presence of the external electric field are also in good agreement with the experimental results. Further work and further experiments are needed to clarify the connection between our model and the “seahorse” experiments. It is possible that there exist other growth phenomena which break the left/right symmetry and can be described by our model.

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Appendices

A Derivation of Some Electrostatics Results

A.1 The Field near the Edge of the Conducting Ellipse

Let us consider a solid conducting ellipsoid with semiaxes a, b, c carrying the total charge Q . The electrostatic potential of such an ellipsoid [35] is given by

$$V(\xi) = \frac{Q}{2} \int_{\xi}^{\infty} ((a^2 + t)(b^2 + t)(c^2 + t))^{-1/2} dt \quad (20)$$

where Q is the total charge of the ellipsoid and $\xi = \xi(x, y, z)$ is the largest of three roots of the cubic equation:

$$\frac{x^2}{a^2 + \xi} + \frac{y^2}{b^2 + \xi} + \frac{z^2}{c^2 + \xi} = 1 \quad (21)$$

Using Eqs. (20), (21), one can obtain the expression for the field intensity in the x-y plane

$$E^2(\xi) = Q^2 \frac{(a^2 + \xi)(b^2 + \xi)}{(c^2 + \xi)(x^2(b^2 + \xi)^2 + y^2(a^2 + \xi)^2)} \quad (22)$$

where ξ satisfies

$$\frac{x^2}{a^2 + \xi} + \frac{y^2}{b^2 + \xi} = 1 \quad (23)$$

In the degenerate case of a 2D ellipse $c = 0$ and the field $\vec{E}$ diverges near the edge where $(x/a)^2 + (y/b)^2 = 1$, and $\xi = 0$. We can deal with this divergence by replacing the field at the edge, by the field at a fixed distance from the edge. An obvious choice for this distance is the sticking distance δ , introduced earlier.

If the ellipse boundary is parameterized as $x = a \cos \phi$, $y = b \sin \phi$, then the unit vector normal to the boundary is given by

$$\hat{n}(\phi) = (b^2 \cos^2 \phi + a^2 \sin^2 \phi)^{-1/2} (b \cos \phi, a \sin \phi) \quad (24)$$

and points at distance δ can be parameterized as follows

$$\vec{r}(\phi) = \vec{r}_0(\phi) + \hat{n}(\phi)\delta = ((a + \delta_0 b) \cos \phi, (b + \delta_0 a) \sin \phi) \quad (25)$$

where $\delta_0 = \delta(b^2 \cos^2 \phi + a^2 \sin^2 \phi)^{-1/2}$. Now, using Eq. (23) one can compute

$$\xi = \xi(\phi) = 2\delta ab(b^2 \cos^2 \phi + a^2 \sin^2 \phi)^{-1/2}$$

and substituting expressions for ξ , x , and y into Eq. (22), and assuming $c \sim \delta \ll a$ one gets

$$E^2(\phi) = \frac{Q^2}{2\delta ab} (b^2 \cos^2 \phi + a^2 \sin^2 \phi)^{-1/2} \quad (26)$$

This solves the problem of finding the field at distance δ from the edge of a conducting ellipse.

A.2 The Self-Induced Potential for a 2D Uniformly Charged Rectangle

Let us consider a uniformly charged 2-dimensional rectangle of length $L = 2l$, and width $W = 2w$, ($l \geq w$), carrying a charge density σ . The electrostatic potential in the center of such a rectangle

$$\begin{aligned} U(0,0) &= \sigma \int_{-w}^w dy \int_{-l}^l \frac{dx}{\sqrt{x^2 + y^2}} = 4 \sigma \int_0^w dy \ln(x + \sqrt{x^2 + y^2}) \Big|_{x=0}^{x=l} \quad (27) \\ &= 4 \sigma \left(\int_0^w dy \ln(1 + \sqrt{(y/l)^2 + 1}) + \int_0^w dy (\ln l - \ln y) \right) \end{aligned}$$

The second integral in Eq. (27) can be easily computed:

$$\int_0^w dy (\ln l - \ln y) = w \ln l - (y \ln y - y)|_{y=0}^{y=w} = w \ln l - w \ln w = w \ln(l/w)$$

To evaluate the first integral in Eq. (27) we note that within the integration range $y/l \leq 1$, hence, one can expand the integrand in terms of powers of (y/l) ; keeping only the lowest order terms, one gets

$$\begin{aligned} \int_0^w dy \ln(1 + \sqrt{(y/l)^2 + 1}) &\approx \int_0^w dy \ln(1 + 1 + 1/2 (y/l)^2) \\ &= \int_0^w dy (\ln 2 + \ln(1 + 1/4 (y/l)^2)) = w \ln 2 + \int_0^w dy (1 + 1/4 (y/l)^2) \\ &= w(\ln 2 + 1 + 1/12 (w/l)^2) \end{aligned}$$

So, finally, we get

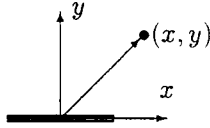
$$U(0, 0) = 4 \sigma w (\ln(2l/w) + 1 + \frac{1}{12} (w/l)^2) = 2\sigma W (\ln(2L/W) + 1 + \frac{1}{12} (W/L)^2) \quad (28)$$

The last equation is derived assuming that the ratio W/L is small, therefore, the worst case is achieved when $W = L$ (i.e. the case of a uniformly charged square). Then the approximate Eq. (28) yields $U(0, 0) = 3.5530 \sigma W$ while the numerical integration of the exact Eq. (27) yields $U(0, 0) = 3.5254 \sigma W$. Thus even in the worst case $W = L$, the relative error of Eq. (28) is smaller than 1%.

A.3 Field of a 1D Uniformly Charged Rod

Let us find the electrostatic potential of a uniformly charged rod of length l and carrying a 1D charge density λ . The system of coordinates is chosen so

that the origin is in the middle of the rod and the x-axis is parallel to the rod:



Then the electrostatic potential at the arbitrary point (x, y) is given by

$$U(x, y) = \int_{-l/2}^{l/2} \lambda d\xi / \sqrt{y^2 + (x - \xi)^2} = \lambda \ln \frac{l/2 - x + \sqrt{(l/2 - x)^2 + y^2}}{\sqrt{(l/2 + x)^2 + y^2} - (l/2 + x)} \quad (29)$$

A.4 1D Conducting Charge Distributions

The charge distribution on conducting bodies is governed by the equation

$$V = \text{const.} \quad (30)$$

It is known from elementary electrostatics that for a 3D conductor all the charge is concentrated on the conductor's surface and is distributed so as to satisfy Eq. (30). When a 3D body degenerates into a 2D body, the charge remains distributed over the whole surface of the conductor. However what happens when a 2D body degenerates into a 1D-body? It turns out that for a 1D loop of an arbitrary shape one can solve Eq. (30) analytically and arrive at an unexpected result: the 1D charge density is the same everywhere along the conducting loop and does *not* depend on loop's shape.

Let us consider a 1D closed loop defined by the equations $x = x(\phi)$, $y = y(\phi)$ $\phi \in [a, b]$, then $x(a) = x(b)$, $y(a) = y(b)$. We are looking for a charge distribution $\lambda(x, y) = \lambda(\phi)$ which makes the electrostatic potential

constant everywhere on the loop $V(x, y) = V(\phi) = V_0$. The constant V_0 is of no interest for us as we can later rescale $\lambda(\phi)$ as follows: $\lambda_{true}(\phi) = \alpha\lambda(\phi)$ where $\alpha = Q_{total} / \oint \lambda(\phi) dl(\phi)$ where the integral is taken over the whole loop and Q_{total} is the total charge of the loop which is assumed to be known.

At this point we note that while the problem of finding 1D charge density on a 1D loop is physically well defined, the mathematical problem posed above is ill-defined as the potential at a charged 1D conductor diverges logarithmically near the conductor. We can bypass this difficulty by assuming that our 1D wire has in fact some finite width w and then considering what happens when $w \rightarrow 0$.

Assuming that $\lambda(x, y)$ is a well-behaved function of x and y , we can split our loop into small segments of length l_i centered at (x_i, y_i) and having the linear charge density λ_i . Now we replace the continuous equation $V(x, y) = V_0$ by a set of equations $V(x_i, y_i) = V_0$. This immediately leads to a set of linear algebraic equations:

$$\sum_{j=0}^{N-1} U_{ij} \lambda_j = 1 \quad (31)$$

(with $V_0 = 1$). We note that the off-diagonal coefficients U_{ij} (which can be computed via Eq. (29)) do not depend on w , while the diagonal elements $U_{ii} \approx \ln(2l_i/w) + 1$ (Eq. (28)). Obviously, $U_{ii} \rightarrow +\infty$ when $w \rightarrow 0$, but this immediately means that for small enough w , solution of Eq. (31) is given by $\lambda_i = 1/U_{ii}$. Then we obviously get

$$\lim_{w \rightarrow 0} \frac{\max\{\lambda_i\}}{\min\{\lambda_i\}} = \lim_{w \rightarrow 0} \frac{\max\{V_{ii}\}}{\min\{V_{ii}\}} = \lim_{w \rightarrow 0} \frac{\max\{\ln(l_i/w)\}}{\min\{\ln(l_i/w)\}} = 1$$

Therefore, when $w \rightarrow 0$, $\lambda_i \rightarrow \lambda_0$ for all i , where the constant λ_0 is determined

by the normalization condition $\lambda_0 = Q_{total}/L$ and L is the total length of the loop. Thus we see that for a 1D conducting loop the linear charge density becomes constant and does not depend on the overall shape of the loop.

The proof above holds only for a closed smooth loop (for which we can assume the smoothness of $\lambda(x, y)$, and interpolate this function using the discrete set of points). For 1D conductors with sharp tips the proof remains valid only far enough from the tips; near the tips the charge distribution is determined by the tip's shape and thus should be considered as a 3D charge distribution rather than 1D.

B Charge Aggregation in Equilibrium Growth

In this section we will consider the question of charge aggregation during the near-equilibrium growth. In particular, we will derive the equation which governs the charge aggregation during the early stages of growth when the cluster still preserves its circular shape.

The growth due to neutral particles

$$G_n(x, y, t) = N_c^{(0)} p_s G_T \exp(-U_n(x, y, t)/(kT)) \quad (32)$$

where $U_n(x, y, t) = -\chi E^2(x, y, t)/2$ is the potential energy of a neutral particle at a distance δ_s from the cluster's edge. For a circular cluster of radius R $E(x, y)$ is given by Eq. (26), that is $E^2(x, y) = Q^2/(2\delta R^3)$.

The growth due to charged particles is

$$G_c(x, y, t) = N_c^{(0)} p_s G_T \exp(-U_c(x, y)/(kT)) \quad (33)$$

where $U_c(x, y) = eV(x, y)$ and $V(x, y)$ is the electrostatic potential at the edge of the cluster; for a circular conducting cluster $V(x, y) = \pi Q/(2R)$ [35].

In the equations above we assumed that the sticking probabilities p_s and the prefactors G_T are the same for charged and neutral particles and therefore

$$G_c/G_n = \exp(-(\chi E^2(x, y)/2 + V(x, y)e)/kT) \frac{N_c^{(0)}}{N_n^{(0)}} < \frac{N_c^{(0)}}{N_n^{(0)}} = \alpha \ll 1$$

Thus the radius R of the cluster is determined by

$$dR = (G_c + G_n)dt \approx G_n dt \quad (34)$$

We see that the growth of the cluster is, indeed, mainly determined by the neutral particles and the effects due to charged particles can be taken into account by changing the total charge of the cluster $Q(t)$ properly during the growth.

Obviously, the time dependence $Q(t)$ is given by

$$dQ = \left(\frac{e}{\delta^2}\right) 2\pi R G_c dt \quad (35)$$

($2\pi R G_c dt$ is the area change due to charged particles per time dt and δ^2 is the area occupied by a single particle). Now, dividing Eq. (35) by Eq. (34) we get

$$\frac{dQ}{dR} = 2\pi R e / \delta^2 \frac{G_c}{G_n} = 2\pi R (\alpha e / \delta^2) \exp(U_n(x, y) - U_c(x, y) / (kT)) = \quad (36)$$

$$2\pi R (\alpha e / \delta^2) \exp(-(\chi E^2(x, y) / 2 + V(x, y) e) / kT)$$

Now we note that

$$\left| \frac{U_n}{U_c} \right| = \frac{Q}{\pi R^2} \frac{\chi}{2\delta e} = \frac{\bar{\sigma} \chi}{2\delta e} = \frac{\alpha \chi}{2\delta^3},$$

$\alpha \simeq 0.1 \ll 1$, the molecular polarizability $\chi \leq 10^{-22} \text{ cm}^3$ while intermolecular distance $\delta \simeq 10^{-7} \text{ cm}$; therefore it is very safe to assume that $|U_n/U_c| \ll 1$. In addition, $U_n < 0$ while $U_c > 0$. Therefore we conclude from Eq. (36) that the quadratic regime $Q = \pi R^2 \alpha e / \delta^2$ (which corresponds to a constant average charge density $\sigma(t) = \bar{\sigma}$) is maintained as long as $U_c/kT = \pi Q e / (2RkT) = \pi^2 \alpha e^2 R / 2kT \delta^2 \ll 1$ which corresponds to $R/\delta \ll 2kT / (\pi^2 \alpha e^2 / \delta)$.

For room temperature $kT \simeq 4 \cdot 10^{-14} \text{ erg}$ while $e^2/\delta \simeq 2.5 \cdot 10^{-12}$ and therefore the above condition becomes $R/\delta \ll 0.1$. Thus we see that equilibrium growth alone can not maintain the constant average charge density.

However, as was noted earlier this assumption is not very important for our model.

Vita

Ilya Sandler was born in Gorky, USSR (now Nizhny Novgorod, Russia) on July 10, 1970. He graduated with honors from High School No. 36 in June, 1987. He entered the Department of General and Applied Physics of the Moscow Institute of Physics and Technology (MIPT) in August, 1987. After 6-year course of study, he graduated from MIPT with honors in June, 1993 and received his Diploma of Engineer-Physicist (equivalent to a Master of Science Degree in Physics).

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