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Diffusion-assisted aggregation in crystal growth

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Abstract. When particles gather and form a stable pattern, their kinetic energy must be dissipated into the surrounding medium. This means that the medium plays an essential role in the pattern formation. Here I present a crystal growth theory that accommodates the dynamics of the medium, and I apply it to snowflake pattern formation. When the kinematic viscosity of the medium is sufficiently large, macroscopic velocity waves in the medium can be produced by the gathering particles. Then, the waves work as the long-range interaction and assist the formation of ordered patterns.

1. Introduction

Crystal growth is a non-equilibrium phenomenon, and it is difficult in general to elucidate the growth mechanism from only the final ordered structure. Different external conditions may change the course of the crystal growth, and bring about different crystal structures. In the biological world, similarly, it is generally difficult to understand how ordered patterns are formed. Even though they belong to the different worlds, we often recognize similar patterns. For example, the Belousov–Zhabotinskii reaction pattern [1] was originally discovered in chemical reactions. However, such a pattern was later found in the aggregation of the unicellular amoebae called *Dictyostelium discoideum* [2, 3]. Although different principles work in these two different systems, this case suggests the existence of a common pattern-formation algorithm. The motivation of this study comes from the desire to derive such a fundamental algorithm that rules both crystal growth and biological pattern formation.

Turing [4] discovered that a spatially stable pattern can be formed if two substances with different diffusion rates react with each other. Since his work, many studies on pattern formation have been conducted based on the coupled diffusion equations [5]. Obviously, these models assumed that the two kinds of substance are continuous materials. In biological systems, the continuous-cell-density model has been adopted. It is in principle a hydrodynamic approach. When cells are not treated discretely, we have fundamental difficulty in understanding the biological meaning of the pattern formation at a cellular level. Recently, I have developed a theory that can treat individual cells discretely and that reproduces *Dictyostelium* aggregation patterns successfully [6]. This cellular dynamics simulation corresponds to molecular dynamics simulation in the study of material science. Through the *Dictyostelium* aggregation study, I have clarified how diffusible chemical (cyclic adenosine 3′, 5′-monophosphate, cAMP) and the cell-adhesion molecules (secreted from amoebae) are used for the pattern formation. I have found that a combination of the slow amoeboid movement and fast chemical diffusion effectively helps in avoiding local minima during the optimization procedure for successful aggregation. *Dictyostelium* amoeba is

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known to have a tendency to move toward the higher-density area of such a chemical. This is known as chemotaxis. Diffusible chemicals and cell-adhesion molecules respectively work as the long-range interaction and the short-range interaction in this kind of cellular dynamics. Although there has been a lot of work on pattern formation based on the diffusion-limited aggregation theory of Witten and Sander [7], the model described above takes the opposite approach from theirs since diffusible molecules are essential for the formation of the ordered structures. In this article, I will construct a theory for crystal growth using a basic idea on robust biological pattern formation, and I will apply this theory to snowflake pattern formation.

2. Theory

As we know, diffusivity and viscosity are directly connected to each other through the Einstein relation [8]. I will use this relation here as a way to combine the biological pattern formation and the crystal growth. Since chemotactic movement of *Dictyostelium* amoebae was a principal driving force for the pattern formation, I assume here that individual-particle motion in the viscous substance produces a wave that helps the creation of a macroscopic pattern. Although such a wave is known to damp unless it is in the solid phase, it has the capability of changing particle velocity if it meets particles before it is damped completely. Furthermore, from the superposition of waves we can expect formation of macroscopic coherent waves. On the basis of these physical ideas, I have formulated this model as follows.

I assume that individual-particle velocity is changed not only through the interaction with other particles, but also through the Stokes friction [9] of the surrounding medium. The equations of motion become [10, 6]

$$m\frac{\mathrm{d}^2\boldsymbol{r}_i}{\mathrm{d}t^2} = -\frac{\partial U}{\partial \boldsymbol{r}_i} - 6\pi\eta R\left(\frac{\mathrm{d}\boldsymbol{r}_i}{\mathrm{d}t} - \boldsymbol{V}_{\boldsymbol{r}=\boldsymbol{r}_i}\right) \tag{1}$$

where

$$U = \frac{1}{2}\sum_{i\neq j}^{N}\phi(\boldsymbol{r}_i - \boldsymbol{r}_j)$$

where m, $\boldsymbol{r}_i$, and N are the particle mass, the positional vector, and the total number of particles, respectively; $6\pi\eta R$ is the Stokes friction coefficient, where R is the effective radius of a particle in the medium; ϕ is the interaction potential of two particles; $\boldsymbol{V}$ and η are respectively the velocity vector and the viscosity of the surrounding medium; $\boldsymbol{V}_{\boldsymbol{r}=\boldsymbol{r}_i}$ is the velocity of the medium at $\boldsymbol{r} = \boldsymbol{r}_i$. According to Newton's third law of motion, the medium is counteracted by an equal force in the opposite direction. Then, the equation of motion of this surrounding medium becomes

$$\rho\frac{\partial \boldsymbol{V}}{\partial t} = \eta\nabla^2\boldsymbol{V} + 6\pi\eta R\sum_{i=1}^{N}\left(\frac{\mathrm{d}\boldsymbol{r}_i}{\mathrm{d}t} - \boldsymbol{V}_{\boldsymbol{r}=\boldsymbol{r}_i}\right)\left(\frac{1}{\pi R^2}\right)^{3/2}\exp\left[-\frac{(\boldsymbol{r}-\boldsymbol{r}_i)^2}{R^2}\right] \tag{2}$$

where the medium is regarded as incompressible, and the linearization approximation is adopted for the velocity of the medium; ρ is the mass density of the medium. Here I used the relationship

$$\delta(\boldsymbol{r}) = \lim_{R\to 0}(\pi R^2)^{-3/2}\exp\left[-r^2/R^2\right]$$

without taking the $R \to 0$ limit to avoid numerical difficulty.

Equation (2) clearly shows that individual-particle motion becomes the source of the velocity wave in the medium, where $D = \eta/\rho$ (known as the kinematic viscosity) becomes the diffusion constant of the velocity of the medium, and is a key factor in determining whether a macroscopic velocity wave is formed. Using the Fourier expansion method [11], we can solve the above coupled equations numerically.

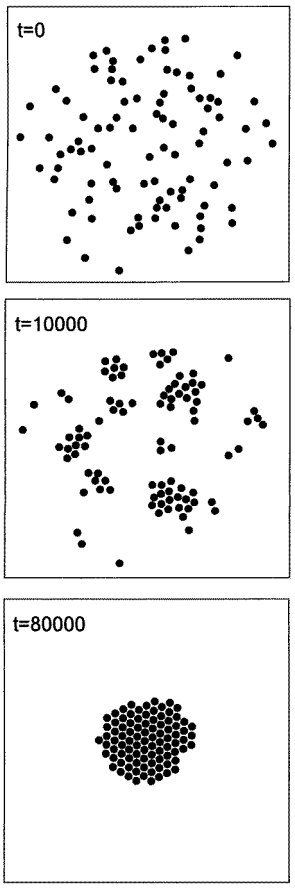

Figure 1. Triangular-lattice formation of 91 particles, where the time step is 6.2×10^{-16} s.

As a sample application, I applied the theory to snowflake pattern formation. Here, I assumed that water molecules ($m = 3.0 \times 10^{-23}$ g) were moving in the air ($\rho = (1.2$–0.6×10^{-3} g cm^{-3}, $\eta = 1.7 \times 10^{-4}$ g cm^{-1} s^{-1}), and I adopt the following approximate potential for water molecular interaction:

$$\phi(r) = \epsilon \frac{mn}{m-n}\left[\frac{1}{m}\left(\frac{\sigma}{r}\right)^m - \frac{1}{n}\left(\frac{\sigma}{r}\right)^n\right] \tag{3}$$

although a more realistic potential is known [12]. The potential given by equation (3) has a minimum value $-\epsilon$ at $r = \sigma$ for any m, n integer pairs. In this study I used $\sigma = 1.6$ Å, $R = 0.8$–1.6 Å and $\epsilon = 0.15$–1.5 kcal mol^{-1}. Since air mass density is very sensitive to altitude and temperature, snowflake pattern formation is strongly influenced by natural conditions through changes in the diffusion constant of the velocity of the medium. Since numerical simulation is still in the preliminary stages, I only show one of the computer

simulations in figure 1. Here, I conducted simulations for 91 particles including the dynamics of the medium in an area of $30\sigma \times 30\sigma$ with a time step of 6.2×10^{-16} s, and the following parameter values were used: $m = 9$, $n = 3$; $R = 0.8$ Å; $\epsilon = 0.30$ kcal mol^{-1}; $\rho = 1.2 \times 10^{-3}$ g cm^{-3}. One can see the formation of a nearly perfect triangular lattice.

3. Discussion

Biological systems utilize diffusible chemicals for robust pattern formation. I have shown in this article that the velocity wave produced by the moving particles in the medium can play the same role as that of the chemotaxis. The difference in the control mechanisms lies in whether the diffusible quantity is scalar or vector. In biological systems, individual cells control the production of diffusible chemicals by themselves, according to the cellular configuration. On the other hand, in crystal growth, the velocity field automatically disappears when a symmetrical stable pattern is formed. In *Dictyostelium* aggregation, individual-cellular motion controls the pattern formation when the density of the extracellular cAMP is low. But when it is high, extracellular cAMP flow controls the pattern formation. Similarly, in crystal growth, when the diffusion constant of the velocity vector is small, a macroscopic velocity wave of the medium cannot evolve and the pattern formation is controlled mainly by the individual-particle motion. But when the diffusion constant is big enough for macroscopic velocity waves to evolve, the velocity wave of the medium plays a significant role in the pattern formation.

In this article I have adopted a very simplified interaction potential for water molecules for the simulated study of snowflake pattern formation. This study is in its very early stages now. I will report more detailed results of the computer simulation study in the near future.

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