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GROWTH DRIVEN BY DIFFUSION

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Abstract. A growth process driven by stationary diffusion field is considered to be a consequence of the mass conservation law. A correct expression for the growth velocity is derived and applied to a specific model of the perturbed sphere. It is studied in the linear regime, for which all corrections are consequently taken into account and graphically demonstrated. A critical discussion and confrontation with some statements in the literature is carried out.

1. INTRODUCTION

Many different growth processes like solidification, nucleation, aggregation, etc. have been intensively studied in the past few years, both theoretically and experimentally [1-4]. A common point of all of them is a sort of mathematical treatment used in their description, headed by the name "free and moving boundary problems" [5].
The term "free boundary problem" is commonly used when the boundary is stationary and a steady-state problem exists. Moving boundary problem, on the other hand, is associated with time dependent problem and the position of the boundary has to be determined as a function of time and space [5].
In all cases, however, two conditions are needed on the free or moving boundary, one to determine the boundary itself, and the other to complete the general "possedness" of the problem [6]. Suitable conditions on the fixed boundaries and, where appropriate, an initial condition has to be also prescribed as usually.
In this paper we would like to continue our study on growth processes driven by diffusion field [7] which could be treated equally well as "free" or "moving boundary" problem depends on the aspects one takes into account [5].
On the other hand, when started with conservation of mass, the whole analysis changes, in some sense, to dynamical system with the appropriate "setting", and, in this paper, we are very much involved in this approach. We concentrate on a stationary diffusion limited aggregation (SDL A) in a fashion presented only recently [7] with the special attention to an accuracy of the calculus. In other words, we would like to see what sort of features are being generated by the treatment on a certain level, and which of them are just the results of approximations made while dealing on a lower level of accuracy.

The paper is organized as follows:

(i) a general model for growth driven by diffusion is reconsidered (Section 2),
(ii) the general model is restricted to linear, "solvable" case (Section 3),
(iii) dynamical system describing the kinetics of the process is developed and solved analytically (Sections 3 and 4),
(iv) the evolution of the aggregate is consequently examined, and the most interesting cases are visualized (Section 4),
(v) a critical discussion and confrontation with some statements in the literature is carried out (Sections 2, 3 and 5).

2. GENERAL MODEL

Consider the growth of an object by the aggregation of Brownian particles which diffuse outside the object. The aggregated particles become a part of the object and do not migrate once they stick to a surface of the object. A simplified description of that process is based on the following picture (cf. figure 1)

Let \( c(\vec{r}) \) be a concentration field of the Brownian particles in an infinitely extended domain \( \Omega \). We assume that the explicit form of the function \( c(\vec{r}) \) is known [5]. Let \( C \) be a concentration of the object. Finally, let \( c_\Sigma \) be a concentration of particles on the interface \( \Sigma \), the surface bounding the volume \( V \) of the object. We assume that the condition

\[
c(\vec{r}) = c_\Sigma \quad \text{on} \quad \Sigma
\]  

(2.1)

is fulfilled. It is the continuity condition of the outside Brownian field.

On the other hand, we assume that there is a jump of the concentration for the inside field,

\[
C(\vec{r})|_\Sigma - c_\Sigma > 0. 
\]  

(2.2)
Let us analyze the mass conservation law (cf. figure 2).

At time $t$ the object has the volume $V(t)$ and at time $t_1 > t$ it has the volume $V(t_1)$. The mass contained in $V(t_1)$ at $t_1$ is

$$m(t_1) = \iiint_{V(t_1)} C(\bar{r}) dV.$$  \hfill (2.3)

The mass contained in $V(t_1)$ but at $t$ is

$$m(t) = \iiint_{V(t)} C(\bar{r}) dV + \iiint_{V(t_1) - V(t)} c(\bar{r}) dV.$$  \hfill (2.4)

The rate of change of the mass in the volume $V(t_1)$,

$$\frac{m(t_1) - m(t)}{t_1 - t} = \frac{1}{t_1 - t} \iiint_{V(t_1) - V(t)} \left[ C(\bar{r}) - c(\bar{r}) \right] dV.$$  \hfill (2.5)

equals the net mass flux through the surface $\Sigma(t_1)$,

$$\frac{m(t_1) - m(t)}{t_1 - t} = \iiint_{\Sigma(t_1)} \vec{j} \cdot d\vec{S}.$$  \hfill (2.6)

where

$$\vec{j} = -D \text{grad } c(\bar{r})$$  \hfill (2.7)

is the diffusional flux of Brownian particles, $D$ is a diffusion coefficient and $d\vec{S}$ is an inward normal to the surface $\Sigma(t_1)$.

In the limit $t_1 \rightarrow t$ we get

$$\frac{d}{dt} \iiint_{V(t)} \left[ C(\bar{r}) - c(\bar{r}) \right] dV = -D \iiint_{\Sigma(t)} \text{grad } c(\bar{r}) \cdot d\vec{S}.$$  \hfill (2.8)

where "\cdot" denotes the scalar product.
Eq. (2.8) is a mass conservation law and describes spatio-temporal evolution of the growing object. Let us notice that it has not a standard form and (2.8) is not equivalent to the well-known local conservation law

\[
\frac{\partial c}{\partial t} + \text{div } \vec{j} = 0. \tag{2.9}
\]

It is so because in the model presented here the concentrations \(C(r)\) and \(c(\vec{r})\) do not depend on time but the volume \(V(t)\) and the external surface \(\Sigma(t)\) of the growing object change with time.

In the Cartesian coordinate system and in the \((\theta, \phi)\)-parameterization, the surface \(\Sigma(t)\) is represented by the vector equation [8]

\[
\vec{r} = \vec{r} \cos \phi \sin \theta \, \vec{e}_x + \vec{r} \sin \phi \sin \theta \, \vec{e}_y + \vec{r} \cos \theta \, \vec{e}_z \tag{2.10}
\]

where the function

\[
\vec{r} = \vec{r}(\theta, \phi; t) \tag{2.11}
\]

specifies the surface \(\Sigma(t)\). In the spherical coordinate system \((r, \theta, \phi)\), \(\Sigma(t)\) is described by the equation

\[
r = \vec{r}(\theta, \phi; t) \tag{2.12}
\]

E.g., for a sphere of a radius \(R(t)\), one obtains \(\vec{r}(\theta, \phi; t) = R(t)\).

The surface element \(d\vec{S}\) in (2.8) can be expressed by the formula

\[
d\vec{S} = \vec{n} d\theta d\phi, \tag{2.13}
\]

where the inward normal [8]

\[
\vec{n} = \vec{n}(\theta, \phi; t) = \frac{\partial \vec{r}}{\partial \phi} \times \frac{\partial \vec{r}}{\partial \theta}. \tag{2.14}
\]

The symbol "\(\times\)" denotes the vector product and \(\vec{n}\) is given by eq. (2.10). We would like to stress on that \(\vec{n}\) in (2.14) is not a unit vector!

We can use eq. (2.13) and the expression for the volume element in the spherical coordinate system to convert (2.8) into the form

\[
\frac{d}{dt} \int_0^\pi d\theta \int_0^{2\pi} d\phi \int_0^{\vec{r}} dr \, r^2 \sin \theta \left[ C(r, \theta, \phi) - c(\vec{r}, \theta, \phi) \right] = \\
= \int_0^\pi d\theta \int_0^{2\pi} d\phi (-D \text{ grad } c(\vec{r}, \theta, \phi) \cdot \vec{n}) \tag{2.15}
\]
where \( \tilde{r} \) is the function (2.11). This equation can be recast as follows

\[
\left[ C(\tilde{r}, \vartheta, \phi) - c(\tilde{r}, \vartheta, \phi) \right] \frac{d\tilde{r}}{dt} = D \text{grad} \ c \circ \tilde{n}_o \tag{2.16}
\]

where \( \text{grad} \ c \) is taken on \( \Sigma(t) \) and

\[
\tilde{n}_o = \tilde{n}_o(\vartheta, \phi; t) = -\frac{1}{\tilde{r}^2} \sin \vartheta
\tag{2.17}
\]

is the outer normal to the surface \( \Sigma(t) \). In the spherical coordinate system,

\[
\tilde{n}_o = \tilde{e}_r - \frac{1}{\tilde{r}} \frac{\partial \tilde{r}}{\partial \vartheta} \tilde{e}_\vartheta - \frac{1}{\tilde{r} \sin \vartheta} \frac{\partial \tilde{r}}{\partial \phi} \tilde{e}_\phi. \tag{2.18}
\]

Its length \( |\tilde{n}_o| \) is given by

\[
|\tilde{n}_o|^2 = g_{ij} n^i n^j = 1 + \left( \frac{\partial \tilde{r}}{\partial \vartheta} \right)^2 + \left( \frac{\partial \tilde{r}}{\partial \phi} \right)^2 \tag{2.19}
\]

where \( g_{ij} \) is the metric tensor in the \( (r, \vartheta, \phi) \)-system and \( n^i(i = r, \vartheta, \phi) \) are components of the vector (2.18). It is seen that \( \tilde{n}_o \) is unit only when \( \Sigma(t) \) is a sphere. Otherwise, \( \tilde{n}_o \) is not unit.

From (2.16) and (2.18) we obtain

\[
\left[ C(\tilde{r}, \vartheta, \phi) - c(\tilde{r}, \vartheta, \phi) \right] \frac{d\tilde{r}}{dt} = D \text{grad} \ c = \frac{\partial c}{\partial \tilde{r}} - \frac{1}{\tilde{r}^2} \frac{\partial \tilde{r}}{\partial \vartheta} \frac{\partial c}{\partial \vartheta} - \frac{1}{\tilde{r}^2 \sin \vartheta} \frac{\partial \tilde{r}}{\partial \phi} \frac{\partial c}{\partial \phi} \bigg|_{\Sigma(t)} \tag{2.20}
\]

where in the right-hand side of this equation derivatives are taken on the surface \( \Sigma(t) \)(i.e., \( r = \tilde{r} \)). Eq.(2.20) is a differential equation for \( \tilde{r} = \tilde{r}(\vartheta, \phi; t) \) as a function of time, \( \vartheta \) and \( \phi \) are treated as parameters. As an initial condition \( \tilde{r}(\vartheta, \phi; t = 0) \) for (2.20) we can take an arbitrary shape of the object and (2.20) determines temporal and spatial evolution of the object. In the approach used here, we need to know the concentration field \( c(\tilde{r}) \) on the interface \( \Sigma \) and its gradient on \( \Sigma \) as well. From (2.20) it follows that to provide the growth process one needs the condition (2.2) which implies positive velocity of growth.

At this stage we should make two comments concerning eq.(2.16). In the literature there is some confusion on this subject. In refs. [3,9,10] the authors make use of the notion of the normal growth velocity \( V_n \). But \( V_n \) is not a projection of the vector velocity \( \tilde{v} \) on the direction of the normal vector \( \tilde{n}_o \) to the surface \( \Sigma(t) \). The natural definition of the vector velocity \( \tilde{v} \) is

\[
\tilde{v} = \frac{d\tilde{r}}{dt} \tag{2.21}
\]

where \( \tilde{r} \) is given by (2.10) and in the spherical coordinate system
\[ \vec{v} = \frac{d\vec{r}}{dt} \vec{e}_r = v_r \vec{e}_r \quad (2.22) \]

therefore \( v_r \) is a radial velocity.

Because \( V_n \) corresponds to \( d\vec{r}/dt = v_r \), therefore \( V_n \) should not be called the normal growth velocity.

The second remark concerns the expression for a growth velocity in the form \([7,11]\)

\[ v = \frac{D}{C - c_s} \frac{\partial c}{\partial n} \quad (2.23) \]

where \( c_s = c(\vec{r}, \theta, \phi) \) is the concentration on \( \Sigma(t) \) and \( \partial c/\partial n \) is the normal derivative of the concentration field at the interface \( \Sigma(t) \). Eq. \((2.23)\) is incorrect because

\[ \frac{\partial c}{\partial n} = \text{grad} \ c \circ \hat{n} \quad (2.24) \]

where \( \hat{n} \) is the unit outer normal to \( \Sigma(t) \). In the correct eq. \((2.16)\) we have \( \text{grad} \ c \circ \hat{n}_o \) with \( \hat{n}_o \) in \((2.18)\).

There is a question: what form of the concentration field \( c(\vec{r}) \) should we take? Because we have assumed that the object is immersed in an infinite system consisting of the Brownian particles, the state of the outside environment can be taken as a stationary state. In order to justify this choice, we can find upon some analogy to a "small" system in contact with a heat bath (thermostat) \([12]\). It is well known \([13]\) that although the "small" system interacts with a heat bath, the state of thermostat does not change with time because it is infinite. A heat bath is in a stationary state which is, e.g., the Gibbs state with temperature \( T \) and it is a stationary solution of the Liouville equation. The Gibbs state describes thermodynamic equilibrium in which mean values of dynamical variables are constant and their fluctuations are small (proportional to inverse of number of particles). In the case considered, a "small" system is the growing object and a heat bath is a system of an infinite number of Brownian particles.

An analogy to the Liouville equation is here the diffusion equation for concentration field \( c(\vec{r}) \). The stationary state of the Brownian particles is determined by the steady-state solution of the diffusion equation

\[ \frac{\partial c(\vec{r})}{\partial t} = D \text{ div grad} \ c(\vec{r}) = D\Delta c(\vec{r}) = 0 \quad (2.25) \]

with appropriate boundary conditions, e.g.,

\[ c(\vec{r}) \to c_\infty \text{ as } |\vec{r}| \to \infty \quad (2.26) \]

\[ c(\vec{r}) = c_\Sigma \text{ on } \Sigma. \quad (2.27) \]
Another boundary conditions can be considered as well, but (2.26) and (2.27) are based on physical background. In the problems on growing objects, the boundary condition (2.27) is the most significant because it appears directly in the evolution equation (2.20). We can assume that \( c_\Sigma \) is an equilibrium concentration on the surface \( \Sigma \) and this thermodynamic boundary condition has the form

\[
e_{\Sigma} = e_o \exp(\Gamma \kappa_{\Sigma})
\]

(2.28)

where \( \kappa_{\Sigma} \) is twice the mean curvature of the surface \( \Sigma \) (i.e., \( R_1^{-1} + R_2^{-1} \) with \( R_1 \) and \( R_2 \) being the principal radii of curvature), \( \Gamma \) is a capillary constant and \( e_o \) is a concentration on a flat surface. If \( \Gamma \kappa_{\Sigma} \ll 1 \) then one obtains the commonly used formula \([3,7,11]\)

\[
e_{\Sigma} = e_o(1 + \Gamma \kappa_{\Sigma})
\]

(2.29)

which is known to be the Gibbs–Thomson relation \([3]\).

3. SPECIFIC MODEL

A specific model is defined by an initial shape of the growing object, \( \Sigma(t_0) \), or by the function (2.11) and the constant \( c_\infty \) in (2.26). The second boundary condition (2.27) is determined by the function (2.11). For simplicity, we assume that \( C \) is constant.

Let

\[
\mathbf{r} = \mathbf{r}(t, \theta, \phi) = R(t) + \epsilon(t)Y_{l,m}^{m}(\theta, \phi)
\]

(3.1)

where at time \( t = t_0, R(t_0) \) and \( \epsilon(t_0) \) are given, \( Y_{l,m}^{m}(\theta, \phi) \) is a spherical harmonic. We assume that

\[
\epsilon(t) \ll R(t)
\]

(3.2)

which permits us to use perturbation calculations. The surface \( \Sigma(t) \) is a perturbed sphere. One should notice, at this point, that the boundary value problem (2.25–2.27) with condition (2.28), supported by the exactly calculated mean curvature \( \kappa_{\Sigma} \) of the perturbed sphere is an inhomogeneous one and as such can be solved by the Green's function method \([14]\).

The whole idea of the linear structural stability however, forces us to follow the regular perturbation scheme instead, i.e. if the perturbation for calculating \( \kappa_{\Sigma} \) expansion is used then with accuracy to terms of the first order in \( \epsilon \) \([3,7,11]\),

\[
\kappa_{\Sigma} = \frac{2}{R} + \epsilon \left( \frac{l - 1}{2} + \frac{l + 2}{R^2} \right) Y_{l,m}^{m}(\theta, \phi)
\]

(3.3)

and the solution of (2.25) with (2.26), (2.27) and (3.3) reads \([7,11]\)
\[ c(r, \theta, \phi) = -\frac{A(R)}{r} + \epsilon \frac{B(R)}{r^{l+1}} Y_l^m(\theta, \phi) + c_\infty \]  

(3.4)

where

\[ A(R) = (c_\infty - c_o)R - 2c_o \Gamma \]  

(3.5)

\[ B(R) = (l(l+1)c_o \Gamma R^{l-1} - (c_\infty - c_o)R^l \]  

(3.6)

It is assumed that \( c_\infty > c_o \) and \( A(R) > 0 \). It means that

\[ R > R^* = \frac{2\Gamma c_o}{c_\infty - c_o} \]  

(3.7)

where \( R^* \) is the critical nucleation radius, above which the object grows (for details, see ref. [11]). From eq.(2.20) we obtain the evolution of the perturbed sphere. The second and third terms in the right-hand side of eq.(2.20) are of order \( \epsilon^2 \) and therefore are neglected. Limiting ourselves to linear terms in \( \epsilon \) we get

\[ \left( C - c_o - \frac{2c_o \Gamma}{R} \right) \frac{dR}{dt} = D \frac{A(R)}{R^2} \]  

(3.8)

and

\[ \left( C - c_o - \frac{2c_o \Gamma}{R} \right) \frac{d\epsilon}{dt} - \epsilon \frac{(l-1)(l+2)c_o \Gamma}{R^2} \frac{dR}{dt} = -D \left( \frac{2A(R)}{R^3} + \frac{(l+1)B(R)}{R^{l+2}} \right) \epsilon \]  

(3.9)

Eq.(3.8) is identical as in refs. [7,11]. In eq.(3.9) a new term (the second one in the left-hand side of (3.9)) appears which is absent in corresponding equations in [7,11]. This term is of the same order as the others and there is no reasons to neglect it. Although it does not influence on the stability of the system, it is important in some domain of the parameter values and for small times (an early stage of the growth). A comparison of the evolution of the growing structure based on eq.(3.9) with and without (see ref. [7] or [11]) the second aforementioned term will be done in the last chapter.

4. ANALYSIS

The solution of eq.(3.8) is implicitly given by the expression

\[ R^2(t) - R^2(t_o) + \alpha [R(t) - R(t_o)] + \beta \ln[(R(t) - R^*)/(R(t_o) - R^*)] = 2D[(c_\infty - c_o)/(C - c_o)](t - t_o) \]  

(4.1)

where
\[ \alpha = 2R^* \frac{C - c_\infty}{C - c_o} \] (4.2)

\[ \beta = 2(R^*)^2 \frac{C - c_\infty}{C - c_o} \] (4.3)

and \( R^* \) is given by (3.7).

From (4.1) it follows that for long times (cf. figure 3)

\[ R^2(t) - R^2(t_o) \propto \text{const} (t - t_o) \] (4.4)

which is the well-known result in a conventional spherical colloidal growth theory and combustion [15,16].

Because \( R(t) \) is known, from (3.8) and (3.9) it follows that

\[ \frac{d\epsilon}{dR} = \frac{l - 1}{R} \left( 1 - \frac{1}{2} (l + 1)(l + 2) \frac{R^*}{R - R^*} + \frac{1}{2} (l + 2) \frac{R_o}{R - R_o} \right) \epsilon \] (4.5)

where \( R^* \) is given by (3.7) and

\[ R_o = \frac{2\Gamma c_o}{C - c_o} \] (4.6)

The solution of (4.5) has the form

\[ \frac{\epsilon(t)}{\epsilon(t_o)} = \left[ \frac{R(t)}{R(t_o)} \left( \frac{R(t)}{R(t_o)} \frac{R(t_o)}{R(t) - R^*} \right)^{\frac{1}{2}(l+1)(l+2)} \left( \frac{R(t)}{R(t_o)} - \frac{R_o}{R(t) - R_o} \right)^{\frac{1}{2}(l+2)} \right]^{(l-1)} \] (4.7)

If \( l = 0 \) then \( \epsilon(t) \) decreases with time. The perturbation for \( l = 0 \) is not interesting because \( Y_0^o \) is constant and the perturbed sphere (3.1) is in fact an ideal sphere. If \( l = 1 \) then \( \epsilon(t) = \epsilon(t_o) = \text{constant} \). This is probably due to the fact that the first order correction in \( \epsilon \) to the curvature disappears. The first significant correction to the curvature is of order \( (\epsilon/R)^2 \), and therefore a linear approximation in \( \epsilon \) loses its sense. The perturbations with \( l \geq 2 \) are more interesting. For these cases, \( \epsilon(t) \) increases with time according to a power law. From (4.7) it follows that

\[ \epsilon(t) \propto t^{\frac{1}{2}(l-1)} \] (4.8)
because \( R(t) \propto \sqrt{t} \). Representative examples of an evolution of \( \epsilon(t) \) are sketched in figure 4.

Below we consider three examples of the growth of the perturbed sphere. We should remember that our linear analysis is correct as long as the inequality (3.2) is fulfilled. Because \( \epsilon(t) \) increases faster than \( R(t) \), the condition (3.2) gives a restriction on times \( t \). It means that we can analyze a linear stage of the growth which is valid rather for "short" times. For convenience we choose the spherical harmonics in the form \( Y_i^m(\theta, \phi) = C_i^m P_i^m(\cos \theta) \cos m\phi \), where the constants \( C_i^m \) are such that \( \max | Y_i^m(\theta, \phi) | = 1 \), \( P_i^m(\cos \theta) \) represent the associated Legendre functions [17]. Below we present an evolution of the perturbed sphere for \( m = 0 \) and in the \( z-x \) plane. The case \( m \neq 0 \) can be treated exactly in the same way.

Note also, that we investigate perturbations beyond a linear regime, simply, to overcome difficulties in the visualization of the cluster growth.

4.1. A case \( l=2 \)

In this case, which seems to be to us, the first interesting in the description of the diffusion driven growth, the spherical harmonic \( Y_2^0(\theta, \phi) \) is represented by [17]

\[
Y_2^0 = (3 \cos 2\theta + 1)/4
\]  

(4.9)

A few stages of the evolution of the structure are visualized in figure 5, in \( z \) and \( x \)-coordinates which, in general, have the following form

\[
z(t) = \tilde{r}(t) \cos \theta
\]  

(4.10)

\[
x(t) = \tilde{r}(t) \sin \theta
\]  

(4.11)

where \( \tilde{r}(t) \) is given by (3.1).

4.2. A case for odd \( l \)-values

For a clear presentation of the evolution of the growing object the value \( l = 5 \) has been chosen. The function \( Y_5^0 \) is represented by [17]

\[
Y_5^0 = (63 \cos 5\theta + 35 \cos 3\theta + 30 \cos \theta)/128
\]  

(4.12)

The growth of the diffusive structure is now presented in figure 6.
4.3. A case for even l-values \((l>2)\)

In figure 7 we present a picture of the growth for \(l = 6\). In this case \(Y_6^o\) has the following form [17]

\[
Y_6^o = (231 \cos 6\vartheta + 126 \cos 4\vartheta + 105 \cos 2\vartheta + 50)/512
\]  
(4.13)

We also should mention that in this case \(\epsilon\) grows faster with time as in the preceding cases, namely

\[
\epsilon(t) \propto t^{5/2}
\]  
(4.14)

what one can observe in figure 7, and what influences on the growth of the object (cf. figure 7).

5. CONCLUDING REMARKS

The goal of this paper was to study the growth driven by diffusion. More precisely to say, the kinetics of the growth process was mostly under consideration, but two other important problems of that process i.e., its thermodynamics and geometrical (differential geometry) aspects have also been mentioned. Our approach, in fact, is not a quasi-stationary approximation of the problem. We have simply chosen the Laplacian field because of great practical importance of the stationary states, being also motivated by many experimental situations met [1].

At first, we would like to stress on that although a linear analysis of the problem is provided (cf. eqs. (3.2), (3.8) and (3.9)), results of other authors [4] show that an extended analysis with the presence of nonlinear terms in \(\epsilon\) does not make something essentially new, and the character of the process remains unchanged.

A frequently used formulation of the growth problems [3,4,11] is based on the following hierarchy

(i) diffusion equations as fundamental evolution equations
(ii) boundary conditions for these equations
(iii) mass (or energy) conservation law.

On the other hand, our approach follows a quite different scheme, namely

(1) mass conservation law as a fundamental evolution equation
(2) specification of the concentration field \(c(\vec{r})\) on the interface \(\Sigma\) (it is, in fact, equivalent to the point (ii))
(3) specification of a gradient of the concentration field \(c(\tau)\) on \(\Sigma\) (it is determined by a stationary diffusion equation with boundary conditions).

Let us notice that in many papers (cf. Section 2) the mass conservation law is used not in quite precise form, what is seen at once, when one compares eq. (2.16) and (2.23). From the mathematical point of view the problem is far from complete formulation, e.g., the initial conditions are not specified at all [4].

Moreover, in [4] one concludes that "morphological instabilities for free growth evolve according to a power law in agreement with WKB results and contrary to the exponential law found in a quasi-stationary approximation". It is obviously not true. We have considered a stationary concentration field, and from (4.7) it follows that instabilities evolve according to a power law.

It was also suggested [3,7,11] that in such systems a critical radius \(R_\circ(t)\) exists, above which \(\epsilon\) grows unboundedly in time and below which \(\epsilon\) dies out. Unfortunately, no such suggestions are confirmed in our investigations (cf. eq. (4.2)).

The last but not least problem we would like to comment on (connected to the new term appeared in eq. (3.9)) is the problem of a correction of the expression for \(\epsilon(t)\). The comparison of the solution of eq. (3.13) in [7] and eq. (4.7) leads to (figure 8)

\[
\frac{\epsilon(t)}{\delta(t)} = \left( \frac{R(t) - R_\circ R(t_\circ)}{R(t_\circ) - R_\circ R(t)} \right)^{\frac{1}{2(t+2)(t-1)}} \tag{5.1}
\]

where \(\delta(t)\) is explicitly given by eq. (3.9) with no the second left-hand additional term. It is easy to observe (see figure 8) that if the curvature of the growing object is positive then the evolution of the structure described by (3.12)-(3.13) in [7] is slower than in the case of an object following (3.8)-(3.9). If, in turn, the curvature of the structure remains negative then the situation in evolution of the object is completely different, namely the structure following (3.12)-(3.13) in [7] grows faster than in the case considered in this work. In that sense the above correction proved to be essential.

**Fig.8**

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6. REFERENCES


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CAPTIONS FOR ILLUSTRATIONS

FIG.1. The growing aggregate immersed in a concentration field.

FIG.2. Two instants $t$ and $t_1 > t$ in the structure growth.

FIG.3. The time dependence of $R(t)$ for a few representative values of the parameters: (a)—the supersaturation parameter $(c_\infty - c_o)/(C - c_o)$ decreases, (b)—when the critical nucleation radius $R^*$ increases.

FIG.4. Representative examples of an evolution of $\epsilon(t)$ for a few values of a spherical harmonics index $l$.

FIG.5. A few stages of the evolution of sphere perturbed by the spherical harmonics with $l = 2$.

FIG.6. A few stages of the evolution of sphere perturbed by the spherical harmonics with $l = 5$.

FIG.7. A few stages of the evolution of sphere perturbed by the spherical harmonics with $l = 6$.

FIG.8. A comparison of the evolution of the growing structure based on eq.(3.9) with and without the second term in the left-hand side of (3.9); the sphere is perturbed by $Y_{11}^0$. 
FIGURE 2
FIGURE 5