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# Kinetics of growth process controlled by convective fluctuations

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A model of the spherical (compact) growth process controlled by a fluctuating local convective velocity field of the fluid particles is introduced. It is assumed that the particle velocity fluctuations are purely noisy, Gaussian, of zero mean, and of various correlations: Dirac delta, exponential, and algebraic (power law). It is shown that for a large class of the velocity fluctuations, the long-time asymptotics of the growth kinetics is universal (i.e., it does not depend on the details of the statistics of fluctuations) and displays the power-law time dependence with the classical exponent 1/2 resembling the diffusion limited growth. For very slow decay of algebraic correlations of fluctuations asymptotically like $t^{-\gamma}$, $\gamma \in (0,1]$), kinetics is anomalous and depends strongly on the exponent $\gamma$. For the averaged radius of the crystal $\langle R(t)\rangle \sim t^{1-\gamma/2}$ for $0<\gamma<1$ or $\langle R(t)\rangle \sim (t \ln t)^{1/2}$ for $\gamma=1$.

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## I. INTRODUCTION

Growth processes occur at various levels of nature: from microscopic to macroscopic worlds, from inorganic to organic worlds, from inanimate to animated worlds, from physical through biological up to social worlds [1–3]. They have been studied both experimentally and theoretically. In physics, examples are aggregation processes, growth of clusters and crystals, grain growth, and the like. These are mostly irreversible processes in which objects are built up from elementary ingredients such as particles, molecules, or microaggregates. Growth from the vapor phase, from solution, or from melt is the most widespread method of crystal growing. Commonly used solvents are water, multicomponent aqueous or nonaqueous solutions, melts of some chemical components, colloidal suspensions, complex electrolytes, etc. Two aspects of the growth process have been intensively studied: a geometric structure of crystals (aggregates, clusters) and their growth kinetics. The former is related to the growth patterns (compact crystals, dendrites), the question of a (fractal or nonfractal) dimension and scaling properties of aggregates. The latter concerns the evolution of the interface dynamics, the velocity of the interface and its asymptotics at long times, the time increase of the crystal radius, existence of regimes with power-law growth behavior, and evaluation of the growth exponents. One can classify the growth process with respect to the growing object-surroundings interaction or properties of the solution: the particle-cluster or cluster-cluster aggregation, the reaction or diffusion limited growth, the kinetic or ballistic aggregation, the growth in external fields, under diffusive and/or convective flow, in deterministic or stochastic fields.

In most papers on the crystal growth, it is assumed that the crystal formation and mass transfer from surroundings to the crystal is achieved by an ordinary diffusive flow, i.e., by the particle self-diffusivity or by the particle gradient diffusivity (the so-called diffusion limited growth) [4,5]. However, the mass transfer can be maintained by natural or forced convection (the temperature difference method, the concentration-induced convection). Nevertheless, the purely convection limited growth has been rarely considered. Let us remark that even in the absence of natural convection in the liquid phase or in the melt, in some cases the local convective flow can appear because the change of density during the phase transition causes a flow in the liquid or in the melt towards the interface. In some practical applications the growth process may take place under conditions of an externally applied velocity field, which can be induced by the production of the liquid phase [6]. Therefore it is sensible to study the influence of convective flow on the growth process, see, e.g., Ref. [7]. In Ref. [8], the convective field consists of two parts: deterministic and random. The random part has been assumed to be Gaussian white noise and then the evolution equation of the solid-liquid interface is a Langevin-type equation. In that case, the kinetics is determined mainly by the deterministic convective flow. Here, we assume that the deterministic part is absent and only the fluctuating part occurs. Locally, it looks like a diffusion process of the Brownian particle. If fluctuations are modeled by Gaussian white noise then the long-time kinetics is the same as in the classical theory of the diffusion driven growth for which the evolution of crystal sizes is proportional to the square root of time. However, our approach gives an advantage over a standard approach: it allows to model the growth process driven not only by Markovian diffusion (the Wiener process) but also to include a wide class of non-Markovian diffusion processes. In the standard description, which couples the diffusion equations in the bulk phases with the interfacial boundary conditions, it is rather difficult to include non-Markovian diffusion processes, which are described by much more complicated evolution equations (e.g., integrodifferential equations) than the classical parabolic diffusion equation with a constant (state independent) diffusion coefficient.

In any modeling, the complexity of the process is usually reduced by supposing elementary processes to be dominant mechanisms responsible for geometry and kinetics of growth. Our approach is based on the mass conservation law from which a fundamental evolution equation is derived elsewhere [9,10]. This equation describes time evolution of the surface of the crystal and can be reduced to an extremely simple form for growing objects with *spherical* or perturbed spherical symmetry such as spherulites [11,12], droplike aggregates in ferrocolloids [13], or protein crystals [14]. The compact spherical growth (neglecting the possibilities of faceting or dendritic growth) has been studied from various points of view (see, e.g., Refs. [5,15,16]).

The rest of the paper is organized as follows. In the following section, we rederive an evolution equation for the solid-liquid interface. In Sec. III we present details of our model. As in Refs. [8,17], we consider the growth process driven by a convective velocity field [18]. In Sec. IV, we solve the corresponding master (Fokker-Planck) equation. In Sec. V, we present general results on asymptotic behavior of statistical moments of the radius of the growing aggregate. In Sec. VI, we describe several models of fluctuations. In Sec. VII, we analyze kinetics of the growth process and summarize the paper.

## II. EVOLUTION EQUATION OF INTERFACE

Consider one of the simplest models of growth of the crystal as a process of attachment of particles from isotropic medium that usually is liquid or gas. After the nucleation stage, a small crystal is formed. Particles of the surroundings perform a walk and when they arrive in contact with the crystal, they stick permanently. Then other particles arrive and stick to the crystal, and so on. An equation describing time-evolution of a growing object can be obtained using the mass conservation law for the crystal plus surroundings. Details are presented in Refs. [9,10]. Here, we rederive that equation. Let the medium be a saturated solution which is two component. The first component is a solvent and the second component consists of particles that will form the crystal. Denote the concentration of the second component in the solution by $c(\overline{r})$ (in units of $\mathrm{m}^{-3}$) and the density of the crystal that consists of particles of the second component by $C(\overline{r})$ [expressed in the same units as $c(\overline{r})$]. Let us analyze the mass conservation law (cf. Fig. 1). At time $t$ the crystal has a volume $V(t)$ and at the time $t_1 > t$ it has a volume $V(t_1) > V(t)$. The mass contained in $V(t_1)$ at $t_1$ is

$$m(t_1) = \int\int\int_{V(t_1)} C(\overline{r})dV. \tag{1}$$

The mass contained in the volume $V(t_1)$ but at earlier time $t$ consists of the crystal mass in $V(t)$ and the mass of particles of the second component of solution in the volume $V(t_1) - V(t)$, i.e.,

$$m(t) = \int\int\int_{V(t)} C(\overline{r})dV + \int\int\int_{V(t_1)-V(t)} c(\overline{r})dV. \tag{2}$$

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

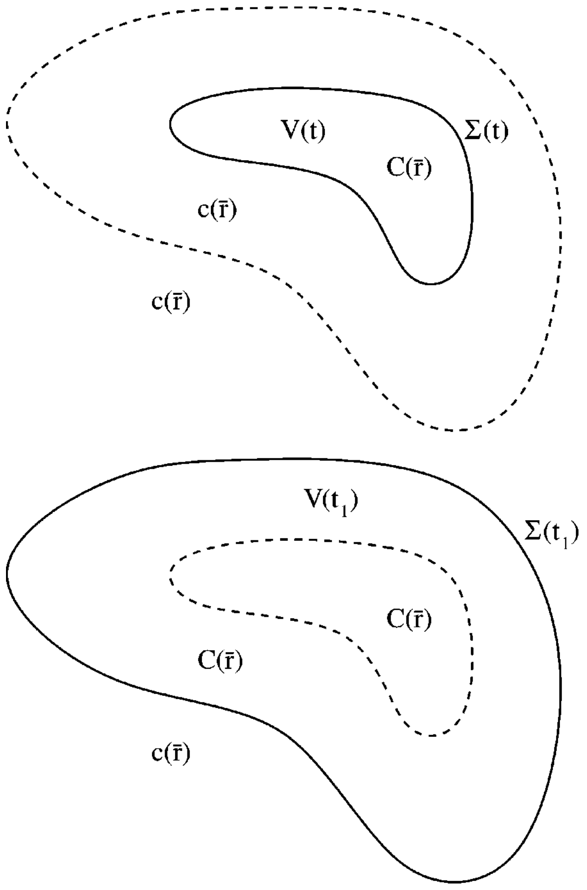

FIG. 1. The growing crystal of the density $C(\overline{r})$ immersed in the concentration field $c(\overline{r})$. The solid-liquid interfaces $\Sigma(t)$ and $\Sigma(t_1)$ at two instants $t$ and $t_1 > t$ of the growth process.

$$\frac{m(t_1)-m(t)}{t_1-t} = \frac{1}{t_1-t}\int\int\int_{V(t_1)-V(t)} [C(\overline{r}) - c(\overline{r})]dV \tag{3}$$

equals the net mass flux across the interface $\Sigma(t_1)$,

$$\frac{m(t_1)-m(t)}{t_1-t} = \int\int_{\Sigma(t_1)} \mathbf{j}\cdot d\mathbf{S}, \tag{4}$$

where $\cdot$ denotes the scalar product and

$$\mathbf{j} = \mathbf{j}(c(\overline{r})) \tag{5}$$

is the flux of particles whose dependence on the fluid concentration $c(\overline{r})$ follows from physics of the problem (examples will be given below) and $d\mathbf{S}$ is an inward normal to the surface $\Sigma(t_1)$. In the limit $t_1 \to t$, we get

$$\frac{d}{dt}\int\int\int_{V(t)} [C(\overline{r}) - c(\overline{r})]dV = \int\int_{\Sigma(t)} \mathbf{j}(c(\overline{r}))\cdot d\mathbf{S}. \tag{6}$$

This equation expresses the mass conservation law for growing objects. If the growing object has a (ideal or perturbed) symmetry, then Eq. (6) can be converted into a simpler and more tractable equation. In the spherical coordinate system Eq. (6) takes the form

$$\int_0^{\pi} d\vartheta \int_0^{2\pi} d\phi \frac{d}{dt}\int_0^{\tilde{r}} dr\, r^2 \sin\vartheta [C(r,\vartheta,\phi)-c(r,\vartheta,\phi)] = \int_0^{\pi} d\vartheta \int_0^{2\pi} d\phi\, \mathbf{j}(c(\tilde{r},\vartheta,\phi))\cdot \mathbf{n}, \tag{7}$$

where the function

$$\tilde{r} \equiv \tilde{r}(\vartheta,\phi;t) \tag{8}$$

specifies the interface $\Sigma(t)$ and **n** is the inward normal [19] to the surface. For example, for a sphere of radius $R(t)$, one obtains $\tilde{r}(\vartheta,\phi;t)=R(t)$. From Eq. (7) it follows that

$$\tilde{r}^{\,2} \sin\vartheta [C(\tilde{r},\vartheta,\phi)-c(\tilde{r},\vartheta,\phi)]\frac{d\tilde{r}}{dt} = \mathbf{j}(c(\tilde{r},\vartheta,\phi))\cdot \mathbf{n}. \tag{9}$$

One has to determine the following three functions.

(a) The density $C(\tilde{r},\vartheta,\phi)$ of the growing crystal on the surface $\Sigma(t)$.

(b) The concentration $c(\overline{r})$ of the saturated solution over the interface $\Sigma(t)$. It is determined from thermodynamical conditions and geometry of $\Sigma(t)$.

(c) The dependence of the flux **j** on the concentration $c(\overline{r})$ of the fluid.

Let us consider point (a). In the most cases one can assume that the crystal is homogeneous and the density is uniform,

$$C(\tilde{r},\vartheta,\phi)=\mathcal{C}=\text{const.} \tag{10}$$

As for point (b), the expression for $c(\tilde{r},\vartheta,\phi)$ has been derived under an assumption of local thermodynamical equilibrium near the interface $\Sigma(t)$. The concentration of solution over a crystal depends on the surface curvature due to the Gibbs-Thomson effect and is given by the formula [1,20]

$$c(\tilde{r},\vartheta,\phi)=c_0[1+\Gamma(\vartheta,\phi)\mathcal{K}(\tilde{r},\vartheta,\phi)], \tag{11}$$

where $\Gamma(\vartheta,\phi)$ is the capillary coefficient, $\mathcal{K}(\tilde{r},\vartheta,\phi)$ is twice the mean curvature of the surface $\Sigma(t)$ at the point $(\tilde{r},\vartheta,\phi)$, and $c_0$ is the concentration of the saturated solution over the flat surface (the equilibrium concentration for the planar interface), i.e., when the curvature of the interface is zero.

In turn, let us consider point (c). If the feeding of the growing object is purely convective then [18]

$$\mathbf{j}(c(\overline{r}))=c(\overline{r})\mathbf{v}(\overline{r}), \tag{12}$$

where $\mathbf{v}(\overline{r})$ is a velocity of convective particles.

For a purely parabolic diffusion field [18]

$$\mathbf{j}(c(\overline{r}))=-D \;\; \text{grad} \;\; c(\overline{r}), \tag{13}$$

where $D$ is the diffusion coefficient [in general, $D=D(c,\overline{r},t)$].

For a generalized diffusion case and in the high-friction limit $\mathbf{j}(c(\overline{r}))$ takes the form [21]

$$\mathbf{j}(c(\overline{r}))=\frac{1}{\kappa}c(\overline{r})\mathbf{F}(\overline{r})-D\,\text{grad}\,c(\overline{r}), \tag{14}$$

where $\mathbf{F}(\overline{r})$ is a force acting on particles of the fluid and $\kappa$ stands for a friction coefficient.

For the so-called hyperbolic diffusion (described by the telegrapher's equation) [22] the flux is determined by the equation

$$\tau_H\frac{\partial \mathbf{j}}{\partial t}+\mathbf{j}=-D\,\text{grad}\,c(\overline{r}), \tag{15}$$

where $\tau_H$ is the correlation time of the hyperbolic random walk. One can combine convective and diffusive fields or postulate other mechanisms for flow of the concentration fields outside the growing crystal, as, e.g., the nonlocality of the flux [cf. Eqs. (3) and (5) in Ref. [23]].

Equation (9) is our fundamental equation that describes time evolution of the interface $\Sigma(t)$ represented by the function $\tilde{r}(\vartheta,\phi;t)$. In some cases, it reduces to or can be approximated by a (partial or ordinary) differential equation [8–10].

## III. DESCRIPTION OF MODEL

From the mass conservation law, we obtained Eq. (9), which governs the long-time dynamics of the growth process. The mass transfer from the solution to the crystal is driven by the flux in the immediate vicinity of the interface. The theoretical models of the crystal growth have mostly considered the parabolic diffusive flux (13) and the mass conservation law has been expressed as a diffusion equation for the fluid particles. We propose an alternative description based only on the convective flux (12) instead of the diffusive flux (13). In the coexistence region, the crystal growth produces a depletion region in the vicinity of the solid-fluid interface changing the particle density. It causes a local flow of particles in the solution toward the interface. Consequently, even in the absence of the forced or natural convection in the fluid phase, the local flow velocity field occurs [7]. The effects of the local fluid convection is the object of this research. We make several simplifications assuming the spherical symmetry.

(i) The crystal is a sphere of radius $R=R(t)>0$. Then the function $\overline{r(\vartheta,\phi;t)}=R(t)$.

(ii) The convective field (12) is radial,

$$\mathbf{j}(c(\tilde{r},\vartheta,\phi))=-c(R)v(R,t)\mathbf{e}_r, \tag{16}$$

where $v(R,t)$ is the velocity of convective particles over the surface $R(t)$.

(iii) The Gibbs-Thomson relation (11) takes the form

$$c(\tilde{r},\vartheta,\phi)=c(R)=c_0\left[1+\frac{2\Gamma}{R}\right]. \tag{17}$$

Under these assumptions, Eq. (9) takes the form

$$\frac{dR}{dt}=A(R)v(R,t), \tag{18}$$

where

$$A(R)=\alpha\frac{R+2\Gamma}{R-R^*}, \quad R>R^*, \tag{19}$$

and

$$\alpha=\frac{c_0}{\mathcal{C}-c_0}, \quad R^*=2\Gamma\alpha. \tag{20}$$

The quantity $\alpha$ plays the role of the reciprocal of the "saturation" parameter and $R^*$ is the critical radius of the aggregate nucleus. When $R>R^*$ the aggregate grows. Otherwise, it recedes.

In the previous papers [8,17], we considered the case of the convective velocity field $v(R,t)$ composed of two parts: deterministic (induced by, e.g., the external force) and random (describing the local fluctuating flow). In a general case, the velocity field can fluctuate in space and in time. Here, we consider the velocity fluctuations of the fluid particles, which do not depend on the position in the space but only on time. In other way, the velocity field is purely noisy, i.e.,

$$v(R,t)=V(t), \tag{21}$$

where $V(t)$ stands for a stationary Gaussian (generally correlated) stochastic process with the first two moments

$$\langle V(t)\rangle=0, \quad \langle V(t)V(s)\rangle=K(|t-s|), \tag{22}$$

where $K(t)$ is a correlation function of the velocity fluctuations of the fluid particles. It implies that the deterministic part of the velocity field is zero and $V(t)$ describes fluctuations of the zero-mean convective field. In the approach proposed, the diffusive flux in the classical form (13) does not appear. Nevertheless, the mass transfer from the fluid to the crystal is not purely convective but implicitly it is diffusive because diffusion is induced by velocity fluctuations of the fluid particles in the vicinity of the interface. Notice that the fluid particles of the interface region will stick to the crystal if their velocity (and in consequence energy and momentum) is sufficiently large in order to overcome the potential barrier of the interface. In this picture, it can be achieved by fluctuations of the particle velocity.

## IV. SOLUTION OF MASTER EQUATION

Equation (18) in the form

$$\frac{dR}{dt}=A(R)V(t), \tag{23}$$

where $V(t)$ is a random function, is a Langevin-type equation with multiplicative noise. From the mathematical point of view, the function $R(t)$ represents a nonstationary stochastic process, which for correlated noise $V(t)$ is non-Markovian. Let $P(R,t)$ be a probability density that at time $t$ the crystal has a radius $R$. Then $P(R,t)$ obeys the following master equation

$$\frac{\partial}{\partial t}P(R,t)=-\frac{\partial}{\partial R}J(R,t), \tag{24}$$

where the probability current $J(R,t)$ is

$$J(R,t)=-D(t)A(R)\frac{\partial}{\partial R}A(R)P(R,t) \tag{25}$$

and the diffusion function

$$D(t)=\int_0^t K(s)ds. \tag{26}$$

To prove above, let us exploit the transform $R\rightarrow x$, where

$$x=\int^R\frac{dr}{A(r)}. \tag{27}$$

Then from Eq. (23) one obtains an additive noise equation for the stochastic process $x(t)$, namely,

$$\frac{dx}{dt}=V(t). \tag{28}$$

It is a particular case of the equation (3.28) in Ref. [24], for which the master equation for the probability density $p(x,t)$ of the transformed process $x(t)$ is derived [see the Eq. (3.30) in Ref. [24]]. Having the master equation for $p(x,t)$, one can obtain the master equation (24) remembering that $p(x(R),t)=A(R)P(R,t)$.

The master equation (24) has the same form as a forward Kolmogorov (Fokker-Planck) equation for the conditional probability density of the Markovian diffusion process. However, in general the process $R(t)$ is not Markovian. To solve this equation, we have to specify the initial and boundary conditions. We assume that at the initial moment $t=0$, the crystal is a sphere of radius $R_0$. It means that the initial condition is

$$P(R,0)=\delta(R-R_0) \tag{29}$$

and the phase space is $R\in[R_0,\infty)$. The left boundary condition is the reflecting one,

$$J(R_0,t)=0. \tag{30}$$

The solution of the problem (24) with Eqs. (29) and (30), which is normalized on $[R_0,\infty)$, reads

$$P(R,t)=\frac{1}{A(R)}\frac{1}{\sqrt{\pi\tau(t)}}\exp\left[-\frac{[x(R)-x(R_0)]^2}{4\tau(t)}\right], \tag{31}$$

where

$$x(R)=\frac{1}{\alpha}[R-(R^*+2\Gamma)\ln(R+2\Gamma)] \tag{32}$$

and

$$\tau(t)=\int_0^t D(s)ds. \tag{33}$$

The function $\tau(t)$ is a rescaled time for the growth process.

## V. LONG-TIME ASYMPTOTICS

The probability distribution (31) enables to determine the most probable value $R_m(t)$ of the radius of the growing crystal. It corresponds to the maximum of the probability density $P(R,t)$ and is determined by the equation

$$\left[R_m(t)-R_0-(R^*+2\Gamma)\ln\frac{R_m(t)+2\Gamma}{R_0+2\Gamma}\right]\times[R_m(t)-R^*]^2=2\alpha^2(R^*+2\Gamma)\tau(t). \tag{34}$$

For long time, $t\gg 1$, the most probable radius evolves as

$$R_m(t)\sim\tau^{1/3}(t). \tag{35}$$

The next characteristics of the growing process are statistical moments defined by

$$\langle R^n(t)\rangle=\int_{R_0}^{\infty}R^nP(R,t)dR \tag{36}$$

for integers $n=1,2,3,\ldots$ . Now, we prove that in the long-time limit, the statistical moments behave as

$$\langle R^n(t)\rangle\sim\tau^{n/2}(t). \tag{37}$$

*Proof.* Denote the integrand in Eq. (36) by

$$f_n(R,\tau)=\frac{R^n}{A(R)\sqrt{\pi\tau}}\exp\left[-\frac{[x(R)-x(R_0)]^2}{4\tau}\right]. \tag{38}$$

First, let us observe that

$$\lim_{R\to\infty}\frac{x(R)-x(R_0)}{R-R_0}=\frac{1}{\alpha} \tag{39}$$

and

$$\lim_{R\to\infty}\frac{R^n}{A(R)(R-R_0)^n}=\frac{1}{\alpha}. \tag{40}$$

So, it implies that the function $f_n(R,\tau)$ is bounded. More precisely, for any $\epsilon>0$ there is an $R_\epsilon>0$ such that the inequalities

$$\frac{\alpha-\epsilon}{\alpha+\epsilon}g_n(\tau(\alpha-\epsilon)^2,R-R_0)\leqslant f_n(R,\tau)\leqslant\frac{\alpha+\epsilon}{\alpha-\epsilon}g_n(\tau(\alpha+\epsilon)^2,R-R_0) \tag{41}$$

hold for $R\geqslant R_\epsilon$, where

$$g_n(a,y)=\frac{y^n}{\sqrt{\pi a}}\exp\left[-\frac{y^2}{4a}\right]. \tag{42}$$

Since

$$f_n(R,\tau)\leqslant\frac{R_\epsilon^n}{A_0\sqrt{\pi\tau}}, \tag{43}$$

where $A_0=\min A(R)>0$, then $f_n(R,\tau)\to 0$ uniformly on the interval $[0,R_\epsilon]$ when $\tau\to\infty$. Hence, one concludes that

$$\lim_{\tau\to\infty}\int_{R_0}^{R_\epsilon}\tau^{-n/2}f_n(R,\tau)dR=0 \tag{44}$$

and similarly

$$\lim_{\tau\to\infty}\int_{R_0}^{R_\epsilon}\tau^{-n/2}g_n(\tau(\alpha\pm\epsilon)^2,R-R_0)dR=0. \tag{45}$$

Let us denote

$$\int_0^\infty g_n(a,y)dy=a^{n/2}I_n, \tag{46}$$

where the constants $I_n$ are defined by the integral

$$I_n=\frac{1}{\sqrt{\pi}}\int_0^\infty x^n\exp\left[-\frac{x^2}{4}\right]dx. \tag{47}$$

From Eqs. (41), (44), and (45) it follows that

$$\frac{\alpha-\epsilon}{\alpha+\epsilon}(\alpha-\epsilon)^nI_n\leqslant\liminf_{\tau\to\infty}\int_{R_0}^{\infty}\tau^{-n/2}f_n(R,\tau)dR\leqslant\limsup_{\tau\to\infty}\int_{R_0}^{\infty}\tau^{-n/2}f_n(R,\tau)dR\leqslant\frac{\alpha+\epsilon}{\alpha-\epsilon}(\alpha+\epsilon)^nI_n. \tag{48}$$

Since $\epsilon$ is an arbitrary positive number, one can take $\epsilon$ small enough and then

$$\lim_{\tau\to\infty}\tau^{-n/2}\int_{R_0}^{\infty}f_n(R,\tau)dR=\alpha^nI_n. \tag{49}$$

In consequence, one obtains for long times the following asymptotics:

$$\langle R^n(t)\rangle \simeq \alpha^n I_n \tau^{n/2}(t), \tag{50}$$

which gives Eq. (37) and this completes the proof. ■

The most important is the first moment, i.e., the averaged radius of the crystal. From the relation (50) it follows that

$$\langle R(t)\rangle \simeq \frac{2\alpha}{\sqrt{\pi}}\tau^{1/2}(t). \tag{51}$$

The explicit form of time evolution of $\langle R(t)\rangle$ depends on the correlations of the velocity fluctuations of the fluid particles. It is worth to mention that the most probable radius $R_m(t)$ and the mean radius $\langle R(t)\rangle$ of the crystal display different asymptotics (35) and (51), respectively.

## VI. MODELS OF FLUCTUATIONS

In order to study the influence of statistics of fluctuations on kinetics of the growth process of crystals, one has to specify Gaussian fluctuations $V(t)$, i.e., their correlation function $K(t)$. Below, we present several models of such fluctuations. The nature and origin of fluctuations of a specific correlation function is related to interactions of the fluid particles. The simplest model assumes that fluctuations are uncorrelated (the correlation time is zero) but this idealization is never exactly realized and in many cases can be insufficient. Therefore one should consider velocity fluctuations of the nonzero correlation time [24,25].

### A. White noise

The first example of fluctuations is white noise for which the correlation function takes the form

$$K_1(t) = 2D_0\delta(t), \tag{52}$$

where $D_0 > 0$ is constant and $\delta(t)$ is the Dirac delta function. This case corresponds to the noncorrelated velocity fluctuations of the fluid particles. The diffusion function (26) has the form

$$D_1(t) = D_0 \tag{53}$$

and the function (33) is given by the relation

$$\tau_1(t) = D_0 t. \tag{54}$$

This case has been studied in Ref. [8].

### B. Ornstein-Uhlenbeck process

The second example is the Ornstein-Uhlenbeck stochastic process, which is exponentially correlated [24]. Its correlation function has the form

$$K_2(t) = \frac{D_0}{\tau_c}\exp\left(-\frac{t}{\tau_c}\right), \tag{55}$$

where $\tau_c$ is the correlation time of the velocity fluctuations. The corresponding diffusion function is given by

$$D_2(t) = D_0\left[1-\exp\left(-\frac{t}{\tau_c}\right)\right] \tag{56}$$

and in this case the function (33) reads

$$\tau_2(t) = D_0\left[t-\tau_c+\tau_c\exp\left(-\frac{t}{\tau_c}\right)\right]. \tag{57}$$

### C. 1/$t^2$ correlations

The third model defines special algebraically correlated fluctuations [25] for which

$$K_3(t) = \frac{D_0}{\pi}\frac{\tau_c}{\tau_c^2+t^2} \tag{58}$$

with the exponent 2. Asymptotically, for $t \gg \tau_c$, fluctuations exhibit the long-time tail $t^{-2}$. For this model

$$D_3(t) = \frac{D_0}{\pi}\arctan\left(\frac{t}{\tau_c}\right) \tag{59}$$

and

$$\tau_3(t) = \frac{D_0}{\pi}\left[t\arctan\left(\frac{t}{\tau_c}\right)-\frac{1}{2}\tau_c\ln\left(1+\frac{t^2}{\tau_c^2}\right)\right]. \tag{60}$$

### D. Power-law correlations

The last example also concerns the algebraically correlated stochastic process [25], namely,

$$K_4(t) = K_0\left(1+\frac{t}{\tau_c}\right)^{-\gamma}, \tag{61}$$

where $K_0 > 0$ is constant and the exponent $\gamma > 0$. However, this process is more general than Eq. (58). We have to distinguish several cases.

#### *1. The case $\gamma = 1$*

If $\gamma = 1$ then the diffusion function $D(t)$ increases logarithmically in time,

$$D_4(t) = A\tau_c\ln\left(1+\frac{t}{\tau_c}\right). \tag{62}$$

The function (33) is

$$\tau_4(t) = A\tau_c^2\left[\left(1+\frac{t}{\tau_c}\right)\ln\left(1+\frac{t}{\tau_c}\right)-\frac{t}{\tau_c}\right]. \tag{63}$$

#### *2. The case $\gamma \neq 1$*

If the exponent $\gamma \neq 1$ then

$$D_4(t) = \frac{A\tau_c}{1-\gamma}\left[\left(1+\frac{t}{\tau_c}\right)^{1-\gamma}-1\right]. \tag{64}$$

The form of the function (33) depends on $\gamma$. For $\gamma\neq 2$, it reads

$$\tau_4(t)=\frac{A\tau_c^2}{(1-\gamma)(2-\gamma)}\left[\left(1+\frac{t}{\tau_c}\right)^{2-\gamma}-(2-\gamma)\frac{t}{\tau_c}-1\right], \tag{65}$$

while for $\gamma=2$, it is given by

$$\tau_4(t)=A\tau_c^2\left[\frac{t}{\tau_c}-\ln\left(1+\frac{t}{\tau_c}\right)\right]. \tag{66}$$

## VII. KINETICS OF GROWTH PROCESS

Dependence of the growth rate upon the growth mechanism is the most important characteristic of the growth process. For the model considered, the growth mechanism depends on the velocity fluctuations, i.e., on the form of their correlation function. The correlation functions $K_2(t)$ and $K_3(t)$ have been normalized in such a way that when the correlation time $\tau_c$ tends to zero then

$$K_i(t)\to 2D_0\delta(t) \tag{67}$$

for $i=2,3$ and these two processes tend to Gaussian white noise. Moreover, let us notice that for long time, when $t\gg\tau_c$, the functions $\tau_i(t)\sim t$, $i=2,3$ (as for normal diffusion). For the exponent $\gamma>1$, the correlation function $K_4(t)$ exhibits the same features when we redefine the coefficient $K_0$, namely,

$$K_0=D_0\frac{\gamma-1}{2\tau_c}. \tag{68}$$

Indeed, if $\tau_c\to 0$ then $K_4(t)\to 2D_0\delta(t)$ and $\tau_4(t)\sim t$ for large times.

For these cases, in the long-time limit, the statistical moments display the power-law dependence,

$$\langle R^n(t)\rangle\sim t^{n/2} \tag{69}$$

with the exponent $n/2$ for the corresponding $n$th moment. In particular, the rate of growth is determined by evolution of the averaged radius of the crystal, which behaves as

$$\langle R(t)\rangle\sim t^{1/2}. \tag{70}$$

A feature such as the one presented in Eq. (70) is characteristic and generic for the diffusion limited growth. Here, we have not taken into account the Fick diffusive flux (13) of particles of surroundings. Instead, we consider a convective flux without a deterministic part and only with the fluctuating field. However, fluctuations indirectly induce diffusion. Therefore it is comprehensible that the relation (70) can be satisfied. Unfortunately, this argumentation can be incorrect. Indeed, let us consider the case of long-time (very slow decay of) correlations of fluctuations. For algebraic fluctuations, it is the case when the exponent $\gamma\in(0,1]$. In the limit of large time, the averaged radius increases faster than for the diffusion limited growth, namely,

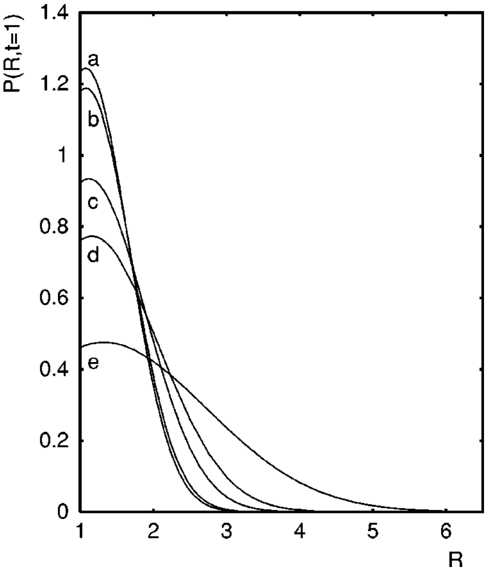

FIG. 2. Some selected examples of the probability distribution $P(R,t=1)$ of the growth process controlled by convective fluctuations of various correlations: (a) algebraic $K_3(t)$, (b) algebraic $K_4(t)$ with $\gamma=2$, (c) algebraic $K_4(t)$ with $\gamma=3$, (d) exponential $K_2(t)$, and (e) Dirac-delta $K_1(t)$. Values of the remaining parameters are $D_0=\alpha=R_0=\tau_c=1$ and $R^*=0.1$.

$$\langle R(t)\rangle\sim t^{1-\gamma/2}\quad\text{for}\quad 0<\gamma<1 \tag{71}$$

and

$$\langle R(t)\rangle\sim(t\ln t)^{1/2}\quad\text{for}\quad\gamma=1. \tag{72}$$

It means that the crystal grows faster. In consequence, long-time correlations induce anomalous kinetics. There the question appears: which feature of the velocity fluctuations is responsible for diffusivelike or anomalous kinetics. From above it is clearly seen that for all presented models, fluctuations that in the proper scaling tend to Gaussian white noise induce diffusivelike kinetics and those that do not tend to white noise lead to anomalous kinetics. Put differently, the power spectrum $S(\omega)$ of the former takes a finite value for all frequencies $\omega$ and, on the contrary, for the latter $S(\omega)\to\infty$ when $\omega\to 0$. The conjecture is that the mechanism responsible for anomalous kinetics is concealed in the low-frequency properties of the power spectrum of driving fluctuations: if for sufficiently low frequency the power spectrum can be arbitrary large then the growth kinetics is anomalous.

Now, let us present the details of the kinetics. Time evolution of the probability density (31) is similar for all models of fluctuations: it starts from the sharp Dirac-delta distribution, spreads out monotonically, its maximum $R_m(t)$ moves to larger values of $R$ according to Eq. (34) and finally $P(R,t)\to 0$ as $t\to\infty$. The influence of various correlations of fluctuations on the probability density is visualized in Fig. 2. At a fixed instant $t=\text{const}$, $P(R,t)$ is sharper for algebraic fluctuations in comparison with the remaining fluctuations. Although asymptotically the correlation functions $K_3(t)$ and

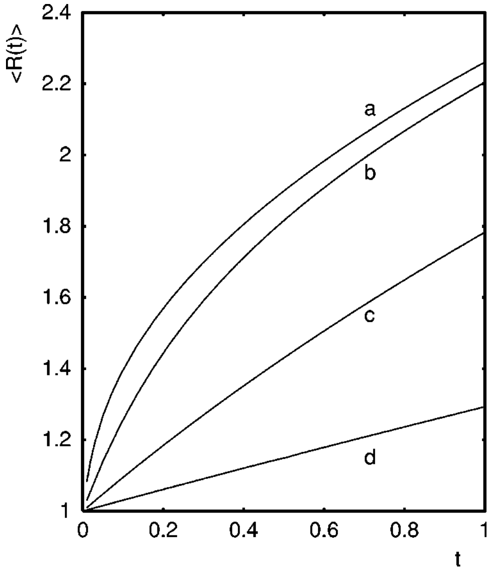

FIG. 3. The average radius $\langle R(t)\rangle$ of the crystal versus time $t$ for the growth driven by the Ornstein-Uhlenbeck fluctuations with the exponential correlation function $K_2(t)$ and for several values of the correlation time $\tau_c$: (a) $\tau_c=0.01$, (b) $\tau_c=0.1$, (c) $\tau_c=1$, and (d) $\tau_c=10$. Values of the remaining parameters are the same as in Fig. 1.

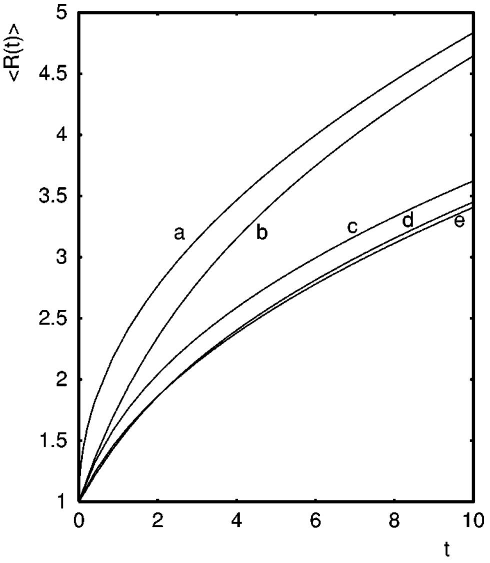

FIG. 4. Plots of the mean value of the radius $\langle R(t)\rangle$ against time $t$ for the process with the correlation function: (a) $K_1(t)$, (b) $K_2(t)$, (c) $K_4(t)$ for $\gamma=3$, (d) $K_3(t)$, and (e) $K_4(t)$ for $\gamma=2$. It is the case of fixed integrated intensity of fluctuations. Values of the remaining parameters are the same as in Fig. 1.

$K_4(t)$ with $\gamma=2$ behave in the same way as $t^{-2}$, the early stages of evolution are a little bit different.

In Fig. 3 we show how the growth kinetics is sensitive to variation of the correlation time $\tau_c$ of the Ornstein-Uhlenbeck fluctuations with a fixed integrated intensity $D_0$. Such a scaling describes for small correlation time $\tau_c$ a deviation from white noise. As the correlation time increases, the variance $\langle V^2(t)\rangle=K(0)=D_0/\tau_c$ of fluctuations decreases and the growth is slower. In the adiabatic limit $\tau_c\to\infty$, fluctuations approach zero amplitude and the rate of growth tends to zero. The influence of statistics of fluctuations on time evolution of the mean radius $\langle R(t)\rangle$ is presented in Fig. 4. It is the case of the fixed integrated intensity $D_0$. In contrast, the case with a fixed variance $\langle V^2(t)\rangle$ implies a different scaling and describes a radically different physical situation. One can observe it for algebraic fluctuations, cf. Figs. 4 and 5. Fluctuations with $\gamma=3$ can lead to a faster growth than with $\gamma=2$ (the case of the fixed intensity $D_0$, Fig. 4) or just the opposite, fluctuations with $\gamma=3$ can lead to a slower growth than with $\gamma=2$ [the case of the fixed variance $K(0)$, Fig. 5].

As we mentioned, in the case when the correlation function of fluctuations is or tends to the Dirac delta function, the asymptotics (70) is the same as for the diffusion limited growth. Let us compare the growth rates in both theories. For this aim, we rewrite Eq. (51) in the form

$$\langle R(t)\rangle^2\simeq\frac{4}{\pi}\left(\frac{\Omega c_0}{1-\Omega c_0}\right)^2 D_0 t, \tag{73}$$

where $\Omega=1/\mathcal{C}$ is the average volume occupied by a particle in its own crystal [1]. For the diffusion limited growth, we get [1,9,20]

$$R_d^2(t)\simeq 2\frac{\sigma\Omega c_0}{1-\Omega c_0}Dt, \tag{74}$$

where $\sigma$ is the saturation parameter [1] and $D$ is the diffusion coefficient of solute in the matrix, which is assumed to be the Stokes-Einstein diffusivity of particles in solution [4,23]. The diffusion constant $D_0$ that appears in the correlation function of the velocity fluctuations can be obtained from the theory of Brownian motion and is given by the Stokes-Einstein for-

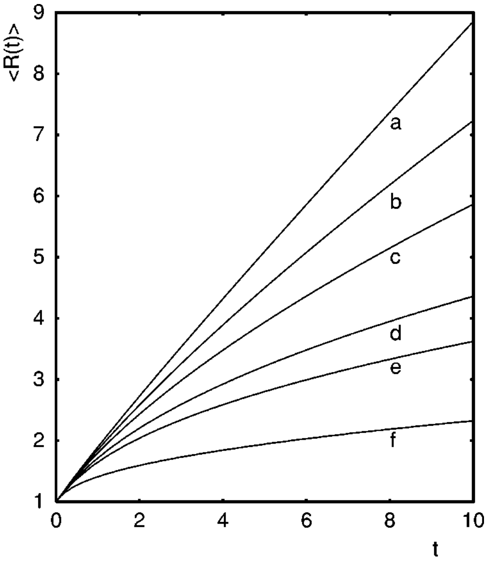

FIG. 5. Time evolution of the mean radius $\langle R(t)\rangle$ for the growth controlled by algebraically correlated fluctuations (61) for various values of the exponent $\gamma$: (a) 0.1, (b) 0.5, (c) 1, (d) 2, (e) 3, and (f) 10. It is the case of fixed variance of fluctuations. Values of the remaining parameters are $D_0=\tau_c=\alpha=R_0=1$ and $R^*=0.1$.

mula as well [21]. So, we can identify both diffusion coefficients $D_0$ and $D$ and neglect the small correction in the denominators. Then

$$\langle R(t)\rangle^2 \simeq \frac{\Omega c_0}{\sigma} R_d^2(t). \tag{75}$$

Typical values of the parameters are $\Omega c_0 = 10^{-1}$–$10^{-2}$ and $\sigma = 10^{-1}$–$10^{-2}$ (see pp. 109 and 123 in Ref. [1]). From this rough estimation we see that it is possible to prepare such conditions that both rates can be of the same order.

In summary, we have proposed a mechanism of normal and anomalous kinetics of growing crystals and investigated a large class of growth processes controlled by the fluctuating velocity field. A rich behavior in the growth kinetics is shown to appear due to various statistics of the velocity fluctuations of the fluid particles. On one hand, the growth process is insensitive to details of statistics of driving fluctuations and its kinetics is universal (like for diffusion driven growth). On the other hand, it can be very sensitive to a specific feature of fluctuations. We have identified such a feature and conditions for normal anomalous kinetics: the low-frequency behavior of the power spectrum of driving fluctuations of the velocity field outside the growing crystal. It can be discussed whether the concentration field $c(\overline{r})$ that affects the growth process is diffusion in the classical sense (13) or can be modeled by a fluctuating zero-mean convective field (12). It is difficult to unambiguously resolve this question by looking only at the average radius of growing crystals.

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