MESOSCALE AVERAGING OF NUCLEATION AND GROWTH MODELS

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Abstract. The aim of this paper is to derive a general theory for the averaging of heterogeneous processes with stochastic nucleation and deterministic growth. We start by generalizing the classical Johnson-Mehl-Avrami-Kolmogorov theory based on the causal cone to hetereogeneous growth situations. Moreover, we relate the computation of the causal cone to a Hopf-Lax formula for Hamilton-Jacobi equations describing the growth of grains. As an outcome of the approach we obtain formulae for the expected values of geometric densities describing the growth processes, in particular we generalize the standard Avrami-Kolmogorov relations for the degree of crystallinity.

By relating the computation of expected values to mesoscale averaging, we obtain a suitable description of the process at the mesoscale. We show how the variance of these mesoscale averages can be estimated in terms of quotients of the typical length on the micro- and on the mesoscale. Moreover, we discuss the efficient computation of the mesoscale averages in the typical case when the nucleation and growth rates are obtained from mesoscopic fields (such as e.g. temperature).

Finally, we give a short outlook to possible extension such as polycrystalline growth, which turns out to be rather straight-forward when starting from our general framework.

Keywords: Nucleation, Growth, Multiscale Models, Averaging, Hamilton-Jacobi equations.
Subject Classification (MSC 2000): 49L25, 60D05, 82C26, 92C15

1. Introduction. Nucleation and growth processes arise in a variety of natural and technological applications (cf. [12] and the references therein), such as e.g. solidification and phase-transition of materials (cf. e.g. [49]), semiconductor crystal growth (cf. [37]), biomineralization (cf. e.g. [48]), DNA replication (cf. e.g. [29]). The mathematical modelling of such processes can, roughly speaking, be divided into two parts:

- Models focussing on the geometric growth of objects, such as a part of theory of free boundary problems (cf. e.g. [1, 19, 45] and [44] as a collection of references), often completely disregarding nucleation phenomena or even the presence of multiple objects (e.g. crystals). Usually, such models are moving boundary problems with a law for the growth of a phase boundary in normal direction.
- Models focussing on the kinetics of nucleation, often completely disregarding the geometric aspect of the growth processes. Usually such models are mean-field or rate equations, often without spatial dependence (cf. e.g. [2, 4, 10, 26, 28, 32]).

The aim of this paper is to bridge between these two type of models, the microscopic front growth and the macroscopic average of many nuclei, by introducing mesoscale models that locally average the microscopic models in presence of a large number of grains. The special way of averaging allows to describe systems with a very high number of grains (for which it is impossible to simulate the growth of every single grain), but still provides information about local averages for geometric quantities such as contact interface densities. The starting point of averaging procedures are the global spatial averages derived by Kolmogorov [32], Avrami [2], and Johnson

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and Mehl [31] for constant growth rates and simple nucleation laws. These global averages have later been extended to time-dependence of the nucleation and growth process and certain other effects (cf. [11, 22, 23, 35]). First steps towards heterogeneous nucleation and growth processes have been made in [40], who derived a system of local rate equations by formal arguments, whose solution is actually close to the local averages we shall derive in this paper. The computation of local averages has been applied for the first time with partly formal arguments by the authors in the context of polymer crystallization (cf. [7, 8, 9, 34]). In this paper we shall derive such a local averaging approach in a mathematically rigorous way for an important and rather general class of nucleation and growth models and derive new error estimates for the averaged quantities.

The setup of this paper is the following: we shall consider a nucleation process in time and space, which is a stochastic Poisson process with rate $\alpha = \alpha(x,t)$. This nucleation process generates a sequence of random variables $X_k \in \mathbb{R}^d$ and $T_k \in \mathbb{R}^+$ describing the spatial location and time of the k-th nucleation event. The k-th nucleus shall be represented by the set $\Theta^k(t)$. Moreover, we assume that the growth of a nuclei occurs with a nonnegative normal velocity $G(x,t)$, i.e., the velocity of boundary points is determined by

$$V = Gn \qquad \text{on } \partial(\bigcup_k \Theta^k(t)), \tag{1.1}$$

where n is the unit outer normal. We shall consider the growth from a spherical nucleus from an infinitesimal radius $R \to 0$.

Without further notice we shall assume that α and G are bounded and continuous functions on $\mathbb{R}^d \times [0,T]$ with

$$g_0 := \inf_{x\in\mathbb{R}^d, t\in[0,T]} G(x,t), \qquad G_0 := \sup_{x\in\mathbb{R}^d, t\in[0,T]} G(x,t). \tag{1.2}$$

Moreover, we assume that G Lipschitz-continuous with respect to the spatial variable x.

As mentioned above, the case of particular interest is a three-scale situation in the growth process with respect to space, i.e., there exist

- A *macroscale* corresponding to a length L, in which the whole process takes place.
- A *microscale* corresponding to the length $\ell := G_0 T$ related to typical grain sizes obtained in the interval $[0,T]$
- A *mesoscale* corresponding to a length λ such that $\ell << \lambda << L$, which marks the finest resolution for the description that is of practical importance.

The paper is organized as follows: In Section 2 we shall introduce the causal cone, which describes the set of nucleation events leading to coverage of a point by the grains, and relate it to Hopf-Lax formulae for the solution of Hamilton-Jacobi equations modeling the growth. In Section 3 we introduce the stochastic model of the nucleation process and compute expected values of some random geometric measures such as the phase function and nucleation numbers. The efficient computation of approximations to these expected values in typical multiscale situations is discussed in Section 4. Section 5 is devoted to the estimation of variances of these random variables and perform a mesoscale averaging, which allows to bound the variances in terms of the relative scale $\frac{\ell}{\lambda}$. Finally, we discuss some extensions such as crystalline growth in Section 6.

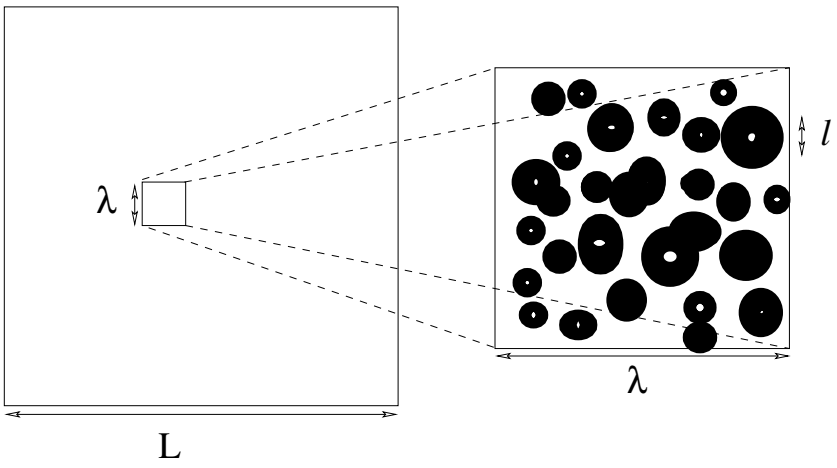

FIG. 1.1. *Sketch of macro- (L), meso- (λ), and microscale (ℓ) in a nucleation and growth process.*

2. Causal Cone and Hopf-Lax Formula. In this section we shall define the growth model in detail and verify its well-posedness. Moreover, we establish the connection between the total phase and the "freely grown grains", i.e., the objects obtained for a single nucleation. Finally, we introduce the causal cone, which we relate to Hopf-Lax-type formula backward in time.

2.1. The Growth Model. We start with a weak formulation of the growth model provided by the level set method. For this sake we assume that the nucleation times T_k and the nucleation locations X_k are given and fixed (i.e., we investigate single realizations of the stochastic nucleation process), such that $0 = T_1 \leq T_2 \leq ...$ Then we consider the following growth model: The function ϕ is determined as the unique continuous viscosity solution of

$$\frac{\partial \phi^R}{\partial t} + G|\nabla \phi^R| = 0 \qquad \text{in } \mathbb{R}^d \times \left((0,T) - \bigcup_k \{T_k\} \right), \tag{2.1}$$

subject to the initial condition

$$\phi^R(x,0) = b_{B_R(X_1)}(x) \qquad \forall x \in \mathbb{R}^d \tag{2.2}$$

and the intermediate conditions

$$\phi^R(x,T_k) = \min\{b_{B_R(X_K)}(x), \lim_{t \uparrow T_k} \phi^R\} \qquad \forall x \in \mathbb{R}^d. \tag{2.3}$$

Here $R > 0$ is a fixed radius and b_Ω denotes the signed distance function to a set Ω, i.e.,

$$b_\Omega(x) = \begin{cases} -d(x, \partial\Omega) & \text{if } x \in \Omega, \\ d(x, \partial\Omega) & \text{else,} \end{cases}$$

with d being the Hausdorff-distance. It is well-known that the computation of a viscosity solution for (2.1) is a weak formulation of the above geometric front-growth model (1.1) (cf. [3]) and the evolution of the phase is determined by

$$\Theta^R(t) = \{\ x \in \mathbb{R}^d \mid \phi^R(x,t) < 0\ \}. \tag{2.4}$$

We shall define the evolution with infinitesimal nucleation radius as the limit for $R \to 0$, i.e.,

$$\Theta(t) := \lim_{R\to 0} \Theta^R(t). \tag{2.5}$$

In order to prove the existence of the limit, we employ a Hopf-Lax formula, which yields a quasi-explicit formula for the solution of (2.1):

PROPOSITION 2.1. *Let ϕ^R be the unique viscosity solution of* (2.1) *in a time interval (T_{k-1}, T_k). Then*

$$\begin{aligned}\phi(x,t) = \inf\{\ \phi(y,T_{k-1}) \mid y \in \mathbb{R}^d, \exists \xi \in W^{1,\infty}([T_{k-1},t]) : \xi(T_{k-1}) = y, \xi(t) = x,\\ |\dot\xi(s)| \le G(\xi(s),s), s \in (T_{k-1},t)\ \}\end{aligned}$$

for all $t \in (T_{k-1}, T_k)$.

Proof. The result follows from a standard Hopf-Lax formula (cf. [24]). □

A consequence of the Hopf-Lax formula for the viscosity solution is a representation formula for the phase Θ^R:

LEMMA 2.2. *For $t \in [T_m, T_{m+1})$, the phase $\Theta^R(t)$ is determined by*

$$\begin{aligned}\Theta^R(t) = \bigcup_{k\le m} \{\ x \in \mathbb{R}^d \mid \exists y \in B_R(X_k), \exists \xi \in W^{1,\infty}([T_k,t]) : \xi(T_k) = y,\\ \xi(t) = x, |\dot\xi(s)| \le G(\xi(s),s), s \in (T_k,t)\ \}.\end{aligned}$$

Proof. We have $x \in \Theta^R(t)$ if and only if $\phi^R(x,t) < 0$, which holds if and only if one of the following two statements is true:

(i) $\exists \xi \in W^{1,\infty}([T_m,t]) : \xi(T_m) = X_k, \xi(t) = x, |\dot\xi(s)| \le G(\xi(s),s)$, for a.e. $s \in (T_m,t)$.

(ii) $\exists \xi \in W^{1,\infty}([T_m,t]) : \xi(T_m) \in \lim_{\tau\uparrow T_m} \Theta^R(\tau), \xi(t) = x, |\dot\xi(s)| \le G(\xi(s),s)$, for a.e. $s \in (T_k,t)$.

We may now inductively apply the above argument to $\xi(T_k)$ and so on, which finally implies the above represenation of $\Theta^R(t)$. □

The result in Lemma 2.2 allows to derive a representation formula for the limit phase $\Theta(t)$:

THEOREM 2.3. *The limit in* (2.5) *exists and the phase $\Theta(t)$ is determined by*

$$\begin{aligned}\Theta(t) = \bigcup_k \{\ x \in \mathbb{R}^d \mid \exists \xi \in W^{1,\infty}([T_k,t]) : \xi(T_k) = X_k, \xi(t) = x,\\ |\dot\xi(s)| \le G(\xi(s),s), s \in (T_k,t)\ \}\end{aligned}$$

Proof. From (2.2) we may conclude that $\Theta^R(t) \subset \Theta^{\tilde R}(t)$ for $R < \tilde R$ and thus, $\Theta(t) = \cap_R \Theta^R(t)$, which yields a well-defined limit. Consequently, for $x \in \Theta(t)$ and $R > 0$ arbitrary, there exists $k_R \in \mathbb{N}$ and $\xi^R \in W^{1,\infty}([T_{k_R},t])$ such that

$$\xi^R(T_{k_R}) = X_{k_R}, \xi^R(t) = x, |\dot\xi^R(s)| \le G(\xi^R(s),s), s \in (T_{k_R},t).$$

Since the number of nuclei is countable, there exists a subsequence (R^j) such that $k_{R^j} = \overline{k}$ for some $\overline{k} \in \mathbb{N}$. Moreover, for this subsequence (ξ^{R^j}) is uniformly bounded in $W^{1,\infty}([T_{\overline{k}},t])$ and therefore, there exists a subsequence converging in the weak-* topology (without restriction of generality (ξ^{R^j}) itself) to ξ. Using the compact

embedding of $W^{1,\infty}([T_{\overline{k}},t])$ into $C([T_{\overline{k}},t])$ we may conclude that $\xi^{R^j}(T_{\overline{k}}) \to X_{\overline{k}}$. Hence, the limit xi satisfies $\xi(T_{\overline{k}}) = X_{\overline{k}}$, $\xi(t) = x$, and

$$|\dot{\xi}(s)| \le G(\xi(s), s), \qquad s \in (T_{\overline{k}}, t),$$

which implies

$$\Theta(t) \subset \bigcup_k \{\ x \in \mathbb{R}^d \mid \exists \xi \in W^{1,\infty}([T_k,t]) : \xi(T_k) = X_k, \xi(t) = x, \\ |\dot{\xi}(s)| \le G(\xi(s),s), s \in (T_k,t)\ \}.$$

Vice versa, if x is an element of the set on the right-hand side of this inclusion, then $\xi(T_k) \in B_R(X_k)$ for any R and therefore $x \in \cap_{R>0}\Theta^R(t)$, which implies equality of the sets. □

2.2. The Freely Grown grains. Given the nucleation events (X_k, T_k), we can also define the evolution of a freely grown single grain $\Omega^k(t)$, which nucleates in X_k at time T_k and then grows with normal velocity G on $\partial\Omega^k(t)$. Using the same technique as in the previous section, we may conclude that

$$\Omega^k(t) = \{\ x \in \mathbb{R}^d \mid \exists \xi \in W^{1,\infty}([T_k,t]) : \xi(T_k) = X_k, \xi(t) = x, \\ |\dot{\xi}(s)| \le G(\xi(s),s), s \in (T_k,t)\ \} \tag{2.6}$$

for $t \ge T_k$ and $\Omega^k(t) = \emptyset$ for $t < T_k$.

It seems obvious that the total phase $\Theta(t)$ is the union of the freely grown grains, but this statement is not true for general growth laws like mean curvature motion. In our case, this statement holds and is a simple consequence of the representation formulae for $\Theta(t)$ and $\Omega^k(t)$.

COROLLARY 2.4. *The equality* $\Theta(t) = \bigcup_k \Omega^k(t)$ *holds for all* $t \in \mathbb{R}^+$.

Subject to the Hopf-Lax formula, Corollary 2.4 is a rather simple result, but it clarifies a discussion going on the literature on modelling crystallization processes for a long time (cf. [23, 47]), whether it makes sense to use freely grown grains (which do not correspond to physical objects in general) or not. Our result just states that from a rigorous mathematical viewpoint, it is equivalent to take the union of the freely grown or the union of the real grains to obtain the phase. Of course, we cannot expect this result to be true for more general growth laws, like curvature-dependent velocity. We will discuss such cases and their difficulties in Section 6.

For the freely grown grains, we can somehow revert time, i.e., derive a condition whether $x \in \Omega^k(t)$ for fixed $x \in \mathbb{R}^d$ and $t \in \mathbb{R}^+$.

PROPOSITION 2.5. *For* $(x,t) \in \mathbb{R}^d \times \mathbb{R}^+$, *the following two statements are equivalent:*

(i) $x \in \Omega^k(t)$.

(ii) There exists $\eta \in W^{1,\infty}([0, t-T_k])$ *such that* $\eta(t-T_k) = X_k, \eta(0) = x$, $|\dot{\eta}(s)| \le G(\xi(s), t-s), s \in (0, t-T_k)$.

Proof. The assertion follows immediately from the above Hopf-Lax-formula and a transformation of the time variable from s to $t-s$, and the use of the new variable $\eta(s) := \xi(t-s)$. □

2.3. The Causal Cone. So far, we have taken a Lagrangian approach and looked at the evolution of the grain away from the location they nucleated. Alternatively, we can use an Eulerian approach, i.e., fix a time t and a location a spatial x,

and investigate under which condition the point x will be covered by the phase $\Theta(t)$ at time t. This investigation is simplified significantly by the results of the previous section, which allow to look at the freely grown grains.

Looking at the possible nucleation events for which $x \in \Theta(t)$ leads in a natural way to the *causal cone* defined by

$$\mathcal{C}(x,t) := \{\ (y,s) \in \mathbb{R}^d \times [0,t] \mid \text{Nucleation of grain } \Omega \text{ at } y \text{ at time } s \text{ implies } x \in \overline{\Omega(t)}\ \}. \tag{2.7}$$

Here $\Omega(t)$ denotes a freely grown grain, and due to (2.4) $x \in \overline{\Omega(t)}$ implies that x is an element of the crystalline phase at time t. Motivated by Corollary 2.4 and Proposition 2.5 we introduce the set

$$\begin{aligned}\mathcal{C}_0(x,t) := \{\ (y,s) \in \mathbb{R}^d \times [0,t] \mid \exists \xi \in W^{1,\infty}([s,t]) : \xi(t) = x, \xi(s) = y,\\ |\dot{\xi}(\tau)| \le G(\xi(\tau),\tau), \tau \in (s,t)\ \}\end{aligned} \tag{2.8}$$

From Proposition 2.5 we know that $\chi(x,t) = 1$ if and only if $(X_k, T_k) \in \mathcal{C}_0(x,t)$ for some k, and hence,

$$\mathcal{C}_0(x,t) = \mathcal{C}(x,t). \tag{2.9}$$

Due to the change of the time direction, we may consider the causal cone as the space-time region covered by a grain growing backward in time with the given growth rate G.

The representation of the causal cone via the Hopf-Lax formula allows some immediate conclusions on its geometric structure:

PROPOSITION 2.6. *The causal cone $\mathcal{C}(x,t)$ can be decomposed in the form*

$$\mathcal{C}(x,t) = \bigcup_{s\in[0,t]} \mathcal{E}(x,t;s),$$

with $\mathcal{E}(x,t;s) \subset \mathbb{R}^d$ being a closed bounded set for each $s \in [0,t]$, $\mathcal{E}(x,t;t) = \{t\}$ and

$$\mathcal{E}(x,t;s_1) \supset \mathcal{E}(x,t;s_2), \qquad \text{if } s_1 \le s_2.$$

Proof. Let

$$\mathcal{E}(x,t;s) = \{\ y \in \mathbb{R}^d \mid (y,s) \in \mathcal{C}(x,t)\ \}.$$

Then the above decomposition for $\mathcal{C}(x,t)$ clearly holds, and for any sequence $y_k \in \mathcal{E}(x,t;s)$ converging to $y \in \mathbb{R}^d$ there exist motions ξ_k with $\xi_k(s) = y_k$, $\xi_k(t) = x$, and $|\dot{\xi}_k(\tau)| \le G(\xi_k(\tau),\tau) \le \sup G$. Hence, the sequence ξ_k is uniformly bounded in $W^{1,\infty}([s,t])$ and hence there exists a subsequence (without restriction of generality ξ_k itself) and some $W^{1,\infty}([s,t])$ such that $\dot{\xi}_k \to \dot{\xi}$ in the weak-* topology of $L^\infty([s,t])$ and, by compact embedding, $\xi_k \to \xi$ uniformly in $C([s,t])$. With this kind of convergence we may conclude

$$|\dot{\xi}(\tau)| \le \liminf_k |\dot{\xi}_k(\tau)| \le \lim_k G(\xi_k(\tau),\tau) = G(\xi(\tau),\tau)$$

and $x = \xi_k(t) \to \xi(t)$, $y_k = \xi_k(s) \to \xi(s)$. With the uniqueness of the limit we deduce $\xi(s) = y$ and $\xi(t) = x$. Thus, ξ is an admissible motion for y, which implies that $y \in \mathcal{E}(x,t;s)$ and consequently, the closedness of $\mathcal{E}(x,t;s)$.

Now let $|y-x| > (t-s)\sup G$. Then for each ξ with $\xi(s) = y$ and $|\dot{\xi}(\tau)| \leq G(\xi(\tau),\tau)$ we have

$$|\xi(t) - \xi(s)| \leq |\int_s^t G(\xi(\tau),\tau)\ d\tau| \leq (t-s)\sup G,$$

and hence $\xi(t) \neq x$. Consequently, $y \notin \mathcal{E}(x,t;s)$, which implies the boundedness of $\mathcal{E}(x,t;s)$.

Finally, let $y \in \mathcal{E}(x,t;s_2)$ and let ξ be an admissible motion with $\xi(s_2) = y$ and $\xi(t) = x$. Then, for any $s_1 \leq s$,

$$\xi_1(\tau) := \begin{cases} y & \text{if } \tau \leq s_2 \\ \xi(\tau) & \text{if } \tau > s_2 \end{cases}$$

is an admissible motion (since $\dot{\xi}_1 = 0$ or $\dot{\xi}_1 = \dot{\xi}$) with $\xi_1(s_1) = y$, $\xi_2(t) = x$ and hence, $x \in \mathcal{E}(x,t;s_2)$. □

Proposition 2.6 shows that $\mathcal{C}(x,t)$ has indeed the geometric structure of a cone in space-time with center (x,t). By standard comparison principles for ordinary differential equations, one can show that each admissible motion ξ satisfies

$$g_0|t-s| \leq |\xi(s) - \xi t| \leq G_0|t-s|.$$

Hence, the causal cone lies between two linear cones, i.e.,

$$\{\ (y,s) \mid |y-x| \leq g_0(t-s)\ \} \subset \mathcal{C}(x,t) \subset \{\ (y,s) \mid |y-x| \leq G_0(t-s)\ \}. \qquad (2.10)$$

2.4. Arrival Times and Nucleation Events. Due to the above reasoning we can define a "maximal" nucleation time S at y leading to coverage of x at time t, i.e.,

$$S(y;x,t) = \sup\{\ s \geq 0 \mid (y,s) \in \mathcal{C}(x,t)\ \} \qquad \text{if } (y,0) \in \mathcal{C}(x,t).$$

We shall set $S(y;x,t) = 0$ if $(y,0) \notin \mathcal{C}(x,t)$, since in this case a nucleation at y will never create a grain covering x at time t.

The Hopf-Lax formulas used to derive the causal cone offer the possibility to interpret maximal nucleation times from a geometric optics point of view (cf. [5]). Note that $S(y;x,t)$ corresponds to the time, when a front starting at x at time t and travelling (in negative time direction) with the Hamiltonian $H(x,t,p) := G(x,t)|p|$ arrives at y. It is well-known (cf. [42]) that (fixing x and t), the *arrival time* $\sigma = t - S$ is a (positive) viscosity solution of the *eikonal equation*

$$G(y,\sigma(y))|\nabla\sigma(y)| = 1, \qquad \sigma(x) = 0. \qquad (2.11)$$

LEMMA 2.7. *For fixed $y \in \mathbb{R}^d$, the arrival time $\psi(x,t) := S(y;x,t)$ is a viscosity solution of*

$$\frac{\partial\psi}{\partial t} - G|\nabla\psi| = 0, \qquad \psi(y,t) = t. \qquad (2.12)$$

Proof. We can rewrite the definition of the arrival time as

$$\begin{aligned} -S(y;x,t) &= \inf\{\ -s \leq 0 \mid (y,s) \in \mathcal{C}(x,t)\ \} \\ &= \inf\{-S(y;y,s) \mid \exists\ \xi \in W^{1,\infty}([s,t]) : \xi(t) = x, \xi(s) = y, \\ &\qquad |\dot{\xi}(\tau)| \leq G(\xi(\tau),\tau), \tau \in (s,t)\}. \end{aligned}$$

The latter is exactly a Hopf-Lax formula for the function $\eta(x,t) := -S(y;x,t)$, i.e., η is the viscosity solution of

$$\frac{\partial \eta}{\partial t} + G|\nabla \eta| = 0, \qquad \eta(y,t) = -t$$

and thus, $\psi = -\eta$ is the viscosity of (2.12) ∎

We can now consider a subset of the causal cone, namely the set of nucleation events which give a freely grown grain which arrives at x exactly at time t. From geometric intuition it seems clear that this set is just the boundary of the causal cone. The proof is again based on the Hopf-Lax formula:

THEOREM 2.8. *With the above assumptions and notation, the following properties are equivalent:*

(i) $S(y;x,t) = s$.
(ii) $(y,s) \in \partial\mathcal{C}(x,t)$.
(iii) $y \in \partial\mathcal{E}(x,t;s)$.

Proof. We start by showing that (i) implies (ii). Let $S(y;x,t) = s$, then $(y,s) \in \mathcal{C}(x,t)$, but $(y,\tau) \notin \mathcal{C}(x,t)$ for any $\tau > t$ and therefore (y,s) cannot be in the interior of $\mathcal{C}(x,t)$, thus it lies on the boundary.

As a second step we verify that (iii) implies (i). Let $y \in \partial\mathcal{E}(x,t;s)$, then by definition of the arrival time, $S(y;x,t) \geq s$. Now assume $S(y;x,t) > s$, then there exists $s_0 > s$ and an admissible motion ξ such that $\xi(t) = x$, $\xi(s_0) = y$. Let $|z-y| \leq R := g_0(s_0 - s)$. If we continue $\xi(\tau) = y + \frac{\tau - s_0}{s - s_0}(z-y)$ for $\tau \in [s, s_0]$, then we obtain an admissible motion ($|\dot{\xi}| \leq \frac{|z-y|}{s-s_0} \leq g_0 \leq G(\xi,\tau)$) with $\xi(s) = z$. Consequently, $B_R(y) \subset \partial\mathcal{E}(x,t;s)$, which contradicts $y \in \partial\mathcal{E}(x,t;s)$.

Finally, we show that (ii) implies (iii). Assume that $(y,s) \in \partial C(x,t)$ and assume there exists a ball $B_R(y) \subset \mathcal{E}(x,t;s)$ with positive radius around y. If $(y,s_0) \in \mathcal{C}(x,t)$ for any $s_0 \geq 0$, then by analogous reasoning as above we can extend a motion ξ such that $(z,\tau) \in \mathcal{C}(x,t)$ for $|z-y| \leq g_0(s_0 - \tau)$, and this is an open neighbourhood of (y,s). Hence, $(y,s) \notin \partial\mathcal{C}(x,t)$. If $(y,s_0) \notin \mathcal{C}(x,t)$ for any $s_0 \geq s$, then the arrival time S attends a local maximum in $B_R(y)$, i.e., $S(z;x,t) \leq s = S(y;x,t)$ and hence $\sigma(z) \geq \sigma(y)$ for all $z \in B_R(0)$ for the solution of the eikonal equation (2.11). Since positive viscosity solutions of the eikonal equation do not attain a minimum in a convex domain by a strong maximum principle (cf. [20]), the latter is a contradiction. ∎

Using further properties of the eikonal equation (2.11) we obtain some information on the properties of the boundaries in a geometric measure theory sense:

PROPOSITION 2.9 ([6]). *For almost every $s \in (0,t)$, the set $\partial\mathcal{E}(x,t;s)$ has finite Hausdorff-measure $\mathcal{H}^{d-1}$ and the set $\partial\mathcal{C}(x,t)$ has finite Hausdorff-measure $\mathcal{H}^d$.*

2.5. Examples. In the following we give some examples of the causal cones for special growth rates.

EXAMPLE. The simplest case of a growth model uses a constant growth rate $G(x,t) \equiv G_0$. In this case, from the above Hopf-Lax formula, we have

$$\mathcal{C}(x,t) = \{\ (y,s) \in \mathbb{R}^d \times \mathbb{R}_+ \mid \exists \xi \in W^{1,\infty}([s,t]) : \xi(t) = x, \xi(s) = y, \\ |\dot{\xi}(\tau)| \leq G_0 \tau \in (s,t)\ \}.$$

Due to the bound on the growth rate, each $(y,s) \in \mathcal{C}(x,t)$ satisfy

$$|y - x| = |\xi(s) - \xi(t)| \leq \int_s^t |\dot{\xi}(\tau)|\ d\tau \leq G_0(t-s).$$

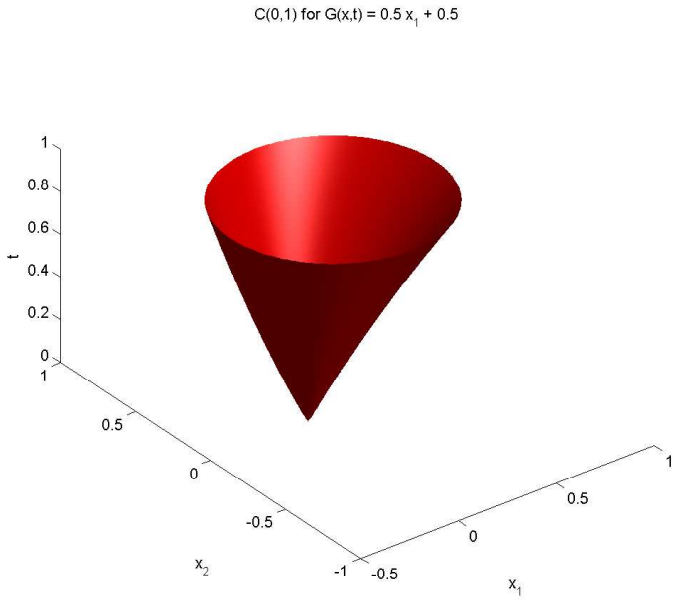

FIG. 2.1. *Illustration of the causal cone* $\mathcal{C}(0,1)$ *for growth rate* $G(x,t) = 0.5x_1 + 0.5$.

Vice versa, if $|y-x| \le G_0(t-s)$, then $\xi(\tau) := y + \frac{\tau-s}{t-s}(x-y)$ is an admissible motion ($|\dot{\xi}(\tau)| = G_0$) and hence, $(y,s) \in \mathcal{C}(x,t)$. This shows that the causal cone is exactly a linear cone given by

$$\mathcal{C}(x,t) = \{\ (y,s) \in \mathbb{R}^d \times \mathbb{R}_+ \mid |y-x| \le G_0(t-s)\ \}.$$

EXAMPLE. For the case of a spatially homogeneous growth rate $G(x,t) \equiv G_1(t)$ the causal cone has been computed explicitely by Eder [22, 23]. It is easy to see that $\mathcal{C}(x,t)$ remains a linear cone, in this case with a radius that does not necessarily grow linearly in time,

$$\mathcal{C}(x,t) := \{\ (y,s) \in \mathbb{R}^d \times \mathbb{R}_+ \mid |y-x| \le \int_s^t G_1(\tau)\ d\tau\ \}.$$

EXAMPLE. In [41], the growth of a grain with a time-homogeneous growth rate $G(x,t) \equiv G_2(x)$ has been considered for linear functions $G_2(x) = ax + b$ and spatial dimension $d = 2$ ($a \in \mathbb{R}^2$, $b \in \mathbb{R}^+$). Without restriction of generality one can assume that $a = (a_1, 0)$, and by solution of a problem in the calculus of variation, analogous to [41] the causal cone is obtained as

$$\mathcal{C}(x,t) := \{(y,s) \in \mathbb{R}^d \times \mathbb{R}_+ \mid$$
$$(y_1 - x_1 + \frac{a_0}{b} - \frac{b}{a_0}\cosh(a_0(s-t)))^2 + (y_2 - x_2)^2 \le (\frac{b}{a_0}\sinh(a_0(s-t)))^2\},$$

i.e., the sections $\mathcal{E}(x,t;s)$ are still spherical, but the radius is growing in time and the center is shifting. For a special choice ($p = q = 0.5$) the resulting causal cone is illustrated in Figure 2.1.

3. Models for Stochastic Nucleation. In the following we consider the nucleation process is random in space and time, and as a consequence the whole nucleation and process will be stochastic and occur on an underlying probability space $(\Phi, \mathcal{A}, \mathbb{P})$

The nucleation process is modelled as a stochastic marked point process (MPP, cf. [13, Section 2.10]) N defined as a random measure on the class of Borel sets $\mathcal{B}(\mathbb{R}_+) \times \mathcal{B}(D)$ given by

$$N = \sum_{n=1}^{\infty} \epsilon_{T_n, X_n},$$

where

- D is a compact subset of $\mathbb{R}^d$, the physical space
- T_n is an $\mathbb{R}_+$-valued random variable representing the time of birth of the $n-$th nucleus,
- X_n is a D-valued random variable representing the spatial location of the nucleus born at time T_n,
- $\epsilon_{t,x}$ is the Dirac measure on $\mathcal{B}(\mathbb{R}_+) \times \mathcal{B}(D)$ such that for any $t_1 < t_2$ and $B \in \mathcal{B}(D)$,

$$\epsilon_{t,x}([t_1, t_2] \times B) = \begin{cases} 1 & \text{if } t \in [t_1, t_2], x \in B, \\ 0 & \text{otherwise .} \end{cases}$$

By computing

$$N(A \times B) = \sharp\{T_n \in A, X_n \in B\}, \qquad \forall\ A \in \mathcal{B}(\mathbb{R}_+), B \in \mathcal{B}(D)$$

we obtain the (random) number of nuclei born during the time interval A in the region B.

We will assume in the following that the nucleation process in the free space is a space-time inhomogeneous Poisson process with intensity

$$\nu_0(dx \times dt) = P(N(dx \times dt) = 1) = \alpha(x, t)\ dx\ dt \tag{3.1}$$

independent of the past history. The nucleation rate $\alpha(x, t)$ is a given deterministic field, also known as the *free space intensity*. The

On the other hand, let us denote by $\Omega(t; X_n, T_n)$ the set covered at time t by the grain nucleated at T_n in X_n and growing freely (according to the above growth model), and again by

$$\Theta(t) = \bigcup_{T_n \le t} \Omega(t; X_n, T_n)$$

the region union of the random grains, which is now a *random closed set* (RACS).

The well known theory of Choquet-Matheron [33] shows that it is possible to assign a unique probability law associated with a random closed set $\Xi \subset \mathbb{R}^d$ on the measurable space $(\mathcal{F}, \sigma_{\mathcal{F}})$ of the family of closed sets in $\mathbb{R}^d$ endowed with the σ-algebra generated by the hit-or-miss topology, by assigning its *hitting function* H_Ξ. The hitting function of Ξ is defined as

$$H_\Xi : K \in \mathcal{K} \mapsto \mathbb{P}(\Xi \cap K \neq \emptyset).$$

More precisely, we define a random closed set Ξ as a random object

$$\Xi : (\Phi, \mathcal{A}, \mathbb{P}) \to (\mathcal{F}, \sigma_{\mathcal{F}}).$$

Moreover, we denote by $\mathcal{K}$ the family of compact sets in $\mathbb{R}^d$.

In our case, using the above analysis of the growth process, it is possible to show [17] that a unique probability measure $\mathbb{P}_\Theta$ can be associated with the germ-grain process $\Theta = \Theta(t), t \in \mathbb{R}_+$. From now on, in a canonical sense, we shall denote by $\mathbb{P}$ this probability measure, and by $\mathbb{E}$ (respectively $\mathbb{V}$), expectations (respectively variances) with respect to this probability, whenever they exist as finite values.

3.1. Stochastic Geometric Measures. In the following we discuss the quantitative description of the geometric process Θ, which can be obtained in terms of mean densities of volumes, surfaces, edges, and vertices (at the respective Hausdorff dimensions), based on the analysis in [14, 43]. Let $\Theta(t)$ be a $d-$dimensional random closed set having boundary of Hausdorff dimension $d-1$, with integer d.

The *mean local volume density* and *mean local surface density*, respectively, of the random closed $\Theta(t)$ at point x are defined by

$$\rho(x,t) := \lim_{r\to 0} \frac{\mathbb{E}[\mathcal{H}^d(\Theta(t) \cap B_r(x))]}{\mathcal{H}^d(B_r(x))} \tag{3.2}$$

$$S_V(x,t) := \lim_{r\to 0} \frac{\mathbb{E}[\mathcal{H}^{d-1}(\partial\Theta(t) \cap B_r(x))]}{\mathcal{H}^d(B_r(x))}, \tag{3.3}$$

provided that the limits exist and are a.e. finite.

It is easy to see that

$$\rho(x,t) = H_{\Theta(t)}(\{x\}) = \mathbb{P}(\{x \in \Theta(t)\}) = \mathbb{E}(\chi(x,t)), \quad x \in E,$$

where $H_{\Theta(t)}(\{x\})$ is the hitting function for the singleton $K = \{x\}$.

In practice, no further nucleation may occur in the space already occupied, the *actual birth rate* will be given by

$$\nu(dx \times dt) = P(N(dx \times dt = 1 | \Theta(t-)) = \alpha(x,t)(1 - \chi(x,t_-))\ dx\ dt,$$

where $\Theta(t-) = \bigcup_{s<t} \Theta(s)$ and $\chi(x,t_-) = \sup_{s<t} \chi(x,s)$. The corresponding (deterministic) measure defined by the expected values

$$\Lambda([0,t] \times B) := \mathbb{E}[N([0,t] \times B)], \qquad t \geq 0,\ B \in \mathcal{B}(D),$$

is the (deterministic) *intensity measure* of the nucleation process N.

Using the above definitions and continuity of ρ in time we obtain the identities

$$\begin{aligned}
\Lambda(dt \times dx) &= \mathbb{E}[N(dt \times dx)] \\
&= \mathbb{E}[\nu(dt \times dx)] \\
&= \mathbb{E}[\alpha(x,t)(1 - \chi(x,t_-))\ dt\ dx] \\
&= \alpha(x,t)\mathbb{E}[(1 - \chi(x,t_-))]dt\ dx \\
&= \alpha(x,t)(1 - \rho(x,t))dt\ dx.
\end{aligned}$$

We can also associate a local density to the nucleation process N given by

$$\begin{aligned}
L(x,t) &:= \lim_{\mathcal{H}^d(B)\to 0} \frac{\mathbb{E}[N([0,t] \times B)]}{\mathcal{H}^d(B)} \\
&= \lim_{\mathcal{H}^d(B)\to 0} \frac{\int_B \int_0^t \alpha(y,s)(1 - \rho(y,s))\ ds\ dy}{\mathcal{H}^d(B)} \\
&= \int_0^t \alpha(x,s)(1 - \rho(x,s))\ ds.
\end{aligned}$$

Below it will be convenient to use *extended densities*, which are obtained by considering all nuclei born with the free space intensity and the corresponding freely grown grains. Note that we have shown above that the union of the freely grown crystals still equals $\Theta(t)$. The *mean extended volume density* $\rho^*(x,t)$ is defined by

$$\int_B \rho^*(x,t)\ dx = \mathbb{E}\left[\sum_{T_j \le t} \mathcal{H}^d(\Omega(t;X_j,T_j)\cap B)\right]$$

for any $B \in \mathcal{B}(\mathbb{R}^d)$. Since we have $x \in \Omega(t;X_j,T_j)$ if and only if $(X_j,T_j) \in \mathcal{C}(x,t)$, we obtain

$$\mathbb{E}\left[\sum_{T_j \le t} \mathcal{H}^d(\Omega(t;X_j,T_j)\cap B)\right] = \mathbb{E}[\int_B N(\mathcal{C}(x,t))\ dx] = \int_B \mathbb{E}[N(\mathcal{C}(x,t))]\ dx,$$

and thus, since the nucleation is a Poisson process with intensity α

$$\rho_*(x,t) = \mathbb{E}[N(\mathcal{C}(x,t))] = \int_{\mathcal{C}(x,t)} \alpha(y,s)\ d(y,s) = \int_0^t \int_{\mathcal{E}(x,t;s)} \alpha(y,s)\ dy\ ds. \quad (3.4)$$

Correspondingly we may define the *mean extended surface density* $S_*(x,t)$ by

$$\int_B S_*(x,t)\ dx = \mathbb{E}\left[\sum_{T_j \le t} \mathcal{H}^{d-1}(\partial\Omega(t;X_j,T_j)\cap B)\right]$$

. for any $B \in \mathcal{B}_{\mathbb{R}^d}$.

3.2. The Volume Density. It seems obvious that ρ will be influenced by the nature of the nucleation and growth processes. However, the probability that the point x is not covered by time t may be expressed in terms of the probability that no nucleation event occurs inside the causal cone (see also [9]),

$$\begin{aligned} p(x,t) &:= 1-\rho(x,t) = \mathbb{P}(x \notin \Theta(t)) \\ &= \mathbb{P}[\text{no nucleation event in } \mathcal{C}(x,t)] = \mathbb{P}[N(\mathcal{C}(x,t)) = 0], \end{aligned} \quad (3.5)$$

where p is called the *porosity*. Since the nucleation process is a Poisson-process, we have

$$p(x,t) = \mathrm{e}^{-\nu_0(\mathcal{C}(x,t))} = \mathrm{e}^{-\rho_*(x,t)}$$

and hence,

$$\rho(x,t) = 1 - e^{-\rho_*(x,t)}. \quad (3.6)$$

For small free volume density ρ_*, the first order terms on the right-hand side dominate and thus, $\rho(x,t) \approx \rho_*(x,t)$. For increasing ρ_*, there is an obvious saturation effect yielding $\rho(x,t) << \rho_*(x,t)$. This relation can also be express as an evolution equation for the (volume) density:

$$\frac{\partial \rho}{\partial t}(x,t) = (1-\rho(x,t))\frac{\partial \rho_*}{\partial t}(x,t). \quad (3.7)$$

For small free volume density ρ_*, the first order terms on the right-hand side dominate and thus, $\rho(x,t) \approx \rho_*(x,t)$. For increasing ρ_*, there is an obvious saturation effect yielding $\rho(x,t) << \rho_*(x,t)$. We mention that equation (3.7) can be derived under rather general conditions in terms of hazard theory (cf. [16]), it turns out that the hazard rate can be identified as

$$h(x,t) := -\frac{\partial}{\partial t} \ln p(x,t) = \frac{\partial \rho_*}{\partial t}(x,t).$$

We finally consider the nucleation density n defined via

$$\int_B n(x,t)\ dx = \mathbb{E}[\Lambda([0,t) \times B)], \qquad \forall\ B \in \mathcal{B}(\mathbb{R}^d).$$

From the above computation of Λ in terms of ρ and α we obtain the nucleation density n as

$$n(x,t) = \int_0^t (1 - \rho(x,s))\alpha(x,s)\ ds. \tag{3.8}$$

Note that the nucleation density satisfies

$$\frac{\partial n}{\partial t} = (1-\rho)\alpha = (1-\rho)\frac{\partial n_*}{\partial t},$$

where n_* is the free nucleation density given by

$$n_*(x,t) = \int_0^t \alpha(x,s)\ ds.$$

This relation between the nucleation densities of the real process and the free process is an analogue to the relation (3.7) between the volume densities of the real and free process.

4. Computation of the Evolving Volume Density. We now turn our attention to the computation of the volume density, respectively its time evolution via partial differential equations. Above we already derived the relation (3.7) between the real and free volume densities, and as an obvious next step we therefore consider the time derivative of the free volume density ρ_*.

PROPOSITION 4.1. *Let ρ_* be defined by* (3.4) *and let the standard assumptions on the nucleation and growth rates be satisfied. Then ρ_* is continuously differentiable with respect to t and*

$$\frac{\partial \rho_*}{\partial t}(x,t) = G(x,t) \int_0^t \int_{\partial \mathcal{E}(x,t;s)} \alpha(y,s)\ d\mathcal{H}^{d-1}(y)\ ds. \tag{4.1}$$

Proof. With the arrival times defined above, we have $\mathcal{E}(x,t;s) = \{y \mid S(y;x,t) \geq s\}$. Then, (3.4) and a change of integration order yield

$$\begin{aligned}\rho_*(x,t) &= \int_0^t \int_{\{y\ \mid\ S(y;x,t) \geq s\}} \alpha(y,s)\ dy\ ds \\ &= \int_{\mathbb{R}^d} \int_0^{S(y;x,t)} \alpha(y,s)\ ds\ dy.\end{aligned}$$

Due to the regularity of the functions involved, we can simply compute the time derivative (using the standard formula for derivatives of parameter-dependent integrals) as

$$\begin{aligned}\frac{\partial \rho_*}{\partial t}(x,t) &= \int_{\mathbb{R}^d} \frac{\partial S}{\partial t}(y;x,t)\alpha(y,S(y;x,t))\ dy \\ &= G(x,t)\int_{\mathbb{R}^d} |\nabla_x S|(y;x,t)\alpha(y,S(y;x,t))\ dy,\end{aligned}$$

where we have inserted (2.12) that is satisfied by S almost everywhere. Finally, the co-area formula (cf. [25, Thm. 3.2.12]) implies with Proposition 2.9 that

$$\begin{aligned}\frac{\partial \rho_*}{\partial t}(x,t) &= G(x,t)\int_0^t \int_{\{y\ |\ S(y;x,t)=s\}} \alpha(y,s)\ d\mathcal{H}^{d-1}(y)\ ds \\ &= G(x,t)\int_0^t \int_{\partial\mathcal{E}(x,t;s)} \alpha(y,s)\ d\mathcal{H}^{d-1}(y)\ ds.\end{aligned}$$

□

The result of Proposition 4.1 can be interpreted as a generalized Steiner formula (cf. [30]) or as a shape derivative of a volume integral on a moving domain (cf. [21]), but under our very general regularity assumptions it does not follow from the known results. Note that the extended surface density is appearing the evolution formula as

$$S_*(x,t) = \int_0^t \int_{\partial\mathcal{E}(x,t;s)} \alpha(y,s)\ d\mathcal{H}^{d-1}(y)\ ds.$$

Finally, we consider a special example corresponding to the case originally introduced by Kolmogorov [32]:

EXAMPLE. Let $G(x,t) = G_0$ and $\alpha(x,t) = \alpha_0$ be constant. In this case the causal cone has been determined as an example above and since α is constant we obtain

$$\rho_*(x,t) = \int_{\mathcal{C}(x,t)} d\Lambda(y,s) = \alpha_0|\mathcal{C}(x,t)| = \frac{\omega_d \alpha_0 G_0^d}{d+1}\ t^{d+1},$$

where ω_d is the volume of the unit ball in $\mathbb{R}^d$. Abbreviating $\gamma = \frac{\omega_d\alpha_0 G_0^d}{d+1}$, we conclude from (3.6) that

$$\rho(x,t) = 1 - \ \exp\ (-\gamma t^{d+1}), \tag{4.2}$$

which widely is known as *(Johnson-Mehl-) Avrami-Kolmogorov formula* (cf. [18, 23, 27, 38, 46, 50] and the references therein).

4.1. Differential Equations in Spatial Dimension One. For nucleation and growth processes in spatial dimension one ($d = 1$) one can easily show by a comparison result for ordinary differential equations that

$$\mathcal{E}(x,t;s) = [a(x,t;s), b(x,t;s)],$$

where $a(x,t;t) = b(x,t;t) = x$ and

$$\frac{\partial a}{\partial s}(x,t;s) = G(a(x,t;s),s), \qquad \frac{\partial b}{\partial s}(x,t;s) = -G(b(x,t;s),s), \qquad \forall\ s \in [0,t].$$

Hence, the free volume density is given by

$$\rho_*(x,t) = \int_0^t \int_{a(x,t;s)}^{b(x,t;s)} \alpha(y,s)\ dy\ ds$$

and its time derivative is (due to Proposition 4.1) given by

$$\frac{\partial \rho_*}{\partial t}(x,t) = G(x,t) \int_0^t \left[\alpha(a(x,t;s),s) + \alpha(b(x,t;s),s)\right]\ ds$$

We now define the functions

$$\begin{aligned} v(x,t) &:= \int_0^t \alpha(a(x,t;s),s)\ ds, \\ w(x,t) &:= \int_0^t \alpha(b(x,t;s),s)\ ds. \end{aligned}$$

The first derivatives of v can be computed as

$$\begin{aligned} \frac{\partial v}{\partial t}(x,t) &:= \alpha(a(x,t;t),t) + \int_0^t \frac{\partial \alpha}{\partial y}(a(x,t;s),s)\frac{\partial a}{\partial t}(x,t;s)\ ds \\ &= \alpha(x,t) + \int_0^t \frac{\partial \alpha}{\partial y}(a(x,t;s),s)\frac{\partial a}{\partial t}(x,t;s)\ ds, \\ \frac{\partial v}{\partial x}(x,t) &:= \int_0^t \frac{\partial \alpha}{\partial y}(a(x,t;s),s)\frac{\partial a}{\partial x}(x,t;s)\ ds. \end{aligned}$$

Now we have

$$\begin{aligned} \frac{\partial}{\partial s}\frac{\partial a}{\partial t}(x,t;s) &= \frac{\partial G}{\partial y}(a(x,t;s),s)\frac{\partial a}{\partial t}(x,t;s), \\ \frac{\partial}{\partial s}\frac{\partial a}{\partial x}(x,t;s) &= \frac{\partial G}{\partial y}(a(x,t;s),s)\frac{\partial a}{\partial x}(x,t;s), \end{aligned}$$

i.e., both $\frac{\partial a}{\partial t}(x,t;.)$ and $\frac{\partial a}{\partial x}(x,t;.)$ are solutions of the same linear ordinary differential equation. From the relation $a(x,t;t) = x$ we deduce (by differentiating with respect to x and t) that

$$\frac{\partial a}{\partial x}(x,t;t) = 1, \qquad \frac{\partial a}{\partial t}(x,t;t) = -\frac{\partial a}{\partial s}(x,t;t) = -G(x,t).$$

Hence, the initial value for $\frac{\partial a}{\partial x}(x,t;.)$ is just a multiple of the initial value for $\frac{\partial a}{\partial t}(x,t;.)$ and by uniqueness of solutions, we conclude

$$\frac{\partial a}{\partial t}(x,t;s) = -G(x,t)\frac{\partial a}{\partial x}(x,t;s), \qquad \forall\ s \in [0,T].$$

Together with the above relations for $\frac{\partial v}{\partial t}$ and $\frac{\partial v}{\partial x}$ this finally yields the partial differential equation

$$\frac{\partial v}{\partial t} + G\frac{\partial v}{\partial x} = \alpha \qquad \text{in } \mathbb{R}^d \times (0,T)$$

with initial value $v(x,0) = 0$. By analogous reasoning for b we can derive the equation

$$\frac{\partial w}{\partial t} - G\frac{\partial w}{\partial x} = \alpha \qquad \text{in } \mathbb{R}^d \times (0,T)$$

with initial value $w(x,0) = 0$.

We now summarize the equations we have derived so far. If we insert the above formula for $\frac{\partial \rho_*}{\partial t}$ and the definitions of v and w into (3.7), we end up with the closed system

$$\begin{aligned} \frac{\partial \rho}{\partial t} &= G(1-\rho)(v+w) && \rho(.,0) = 0 \\ \frac{\partial v}{\partial t} + G\frac{\partial v}{\partial x} &= \alpha && v(.,0) = 0 \\ \frac{\partial w}{\partial t} - G\frac{\partial w}{\partial x} &= \alpha && w(.,0) = 0 \end{aligned} \tag{4.3}$$

for ρ, v, and w. Note that this system of partial differential equations generalizes the system of rate equations derived by Schneider et. al. [40] in the one-dimensional case, which can be rewritten as

$$\begin{aligned} \frac{\partial \rho}{\partial t} &= G(1-\rho)(v+w) && \rho(.,0) = 0 \\ \frac{\partial v}{\partial t} &= \alpha && v(.,0) = 0 \\ \frac{\partial w}{\partial t} &= \alpha && w(.,0) = 0. \end{aligned} \tag{4.4}$$

At a suitable space and time scaling it can indeed be shown that (4.4) is a limit of (4.3) for small growth rate G and large nucleation rate α (cf. [7]).

4.2. Approximation of the Volume Density in Mesoscopic Fields. We now consider a multi-dimensional situation, where the computation of the volume density can be rather involved due to the possibly complicated structure of the causal cone. For the sake of simplicity we restrict our attention to the case $d = 3$ (but analogous and even simpler reasoning is possible for $d = 1, 2$, too). The causal cone $\mathcal{C}(x,t)$ can be computed by a single simulation of growth process backward in time and subsequent integration of the nucleation rate α over $\mathcal{C}(x,t)$. However, for general growth rates G such an approach for the computation of the averaged quantities is rather inefficient. In order to determine the values of ρ on a grid, one has to compute the causal cone separately for each grid point if the grid fineness is larger than ℓ (since the causal cones are disjoint). On the other hand, a grid fineness smaller than ℓ would lead to an unreasonably high number of unknowns, in particular if one is interested in mesoscopic approximations.

We investigate a typical multiscale situation, where the nucleation and growth rate are derived from meso- or macroscopic fields, for example as functions of temperature as in solidification and phase-change processes (cf. e.g. [8, 49]). Consequently we assume

$$\sup_{(x,t)} |\nabla G(x,t)| \le \frac{C_G G_0}{\lambda} = \frac{C_G}{T}\left(\frac{\ell}{\lambda}\right), \qquad \sup_{(x,t)} |\nabla \alpha(x,t)| \le \frac{C_\alpha \alpha_0}{\lambda} = \frac{C_\alpha \alpha_0}{T G_0}\left(\frac{\ell}{\lambda}\right) \tag{4.5}$$

for some constants $C_G, C_\alpha \in \mathbb{R}^+$ of order one, where α_0 is assumed to be the maximal value of the nucleation rate α. Since the spatial variation of G is small on the microscale related to the diameter of the causal cone, it seems natural to derive an approximation by ignoring this variation, i.e., we define

$$\mathcal{C}^1(x,t) := \{(y,s) \in \mathbb{R}^d \times \mathbb{R}_+ \mid \exists \xi \in W^{1,\infty}([s,t]) : \xi(t) = x, \xi(s) = y, \\ |\dot{\xi}(\tau)| \leq G(x,\tau), \tau \in (s,t)\}. \tag{4.6}$$

The approximation $\mathcal{C}^1(x,t)$ is a linear cone, more precisely

$$\mathcal{C}^1(x,t) = \{(y,s) \in \mathbb{R}^d \times \mathbb{R}_+ \mid |y-x| \leq \int_s^t G(x,\tau)\ d\tau\}.$$

Correspondingly we define the first-approximation to ρ and ρ_* as

$$\rho^1(x,t) := 1 - \exp(-\rho_*^1(x,t)), \qquad \rho_*^1(x,t) := \int_{\mathcal{C}^1(x,t)} \alpha(y,s)\ d(y,s). \tag{4.7}$$

We start by computing the evolution of ρ_*^1: First of all, since

$$\begin{aligned}\rho_*^1(x,t) &= \int_0^t \int_{|y-x| \leq \int_s^t G(x,\tau)\ d\tau} \alpha(y,s)\ dy\ ds \\ &= \int_0^t \int_0^{\int_s^t G(x,\tau)\ d\tau} \int_{\mathcal{S}^3} \alpha(x + r\nu, s)\ r^2\ d\nu\ dr\ ds,\end{aligned}$$

we obtain from the transport theorem that

$$\frac{\partial \rho_*^1}{\partial t}(x,t) = G(x,t) \int_0^t \int_{\mathcal{S}^3} \alpha\left(x + R(x,t,s)\ \nu, s\right)\ \left(R(x,t,s)\right)^2\ d\nu\ ds,$$

with $R(x,t,s) := \int_s^t G(x,\tau)\ d\tau$. Now define

$$\varphi_1(x,t) := \int_0^t \int_{\mathcal{S}^3} \alpha\left(x + R(x,t,s)\ \nu, s\right)\ \left(R(x,t,s)\right)^2\ d\nu\ ds,$$

then we can compute a further time derivative as

$$\begin{aligned}\frac{\partial \varphi_1}{\partial t}(x,t) = 2G(x,t) &\int_0^t \int_{\mathcal{S}^3} \alpha\left(x + R(x,t,s)\ \nu, s\right)\ R(x,t,s)\ d\nu\ ds + \\ G(x,t) &\int_0^t \int_{\mathcal{S}^3} \nabla\alpha\left(x + R(x,t,s)\ \nu, s\right) \cdot \nu \left(R(x,t,s)\right)^2\ d\nu\ ds\end{aligned}$$

Since we expect the gradient of α_0 to be small at the spatial scale corresponding to the size of the causal cone, we ignore the second integral for the moment and take a closer look at the first part, namely

$$\varphi_2(x,t) = 2 \int_0^t \int_{\mathcal{S}^3} \alpha\left(x + R(x,t,s)\ \nu, s\right)\ R(x,t,s)\ d\nu\ ds,$$

with time derivative

$$\begin{aligned}\frac{\partial \varphi_2}{\partial t}(x,t) = 2G(x,t) &\int_0^t \int_{\mathcal{S}^3} \alpha\left(x + R(x,t,s)\ \nu, s\right)\ d\nu\ ds + \\ 2G(x,t) &\int_0^t \int_{\mathcal{S}^3} \nabla\alpha\left(x + R(x,t,s)\ \nu, s\right) \cdot \nu R(x,t,s)\ d\nu\ ds\end{aligned}$$

Taking again the first term only, we have

$$\varphi_3(x,t) := 2\int_0^t \int_{\mathcal{S}^3} \alpha\left(x + R(x,t,s)\ \nu, s\right)\ d\nu\ ds$$

and

$$\frac{\partial \varphi_3}{\partial t}(x,t) = 2\int_{\mathcal{S}^3} \alpha\left(x + R(x,t,t)\ \nu, t\right)\ d\nu + 2G(x,t)\int_0^t \int_{\mathcal{S}^3} \nabla\alpha\left(x + R(x,t,s)\ \nu, s\right)\cdot \nu\ d\nu\ ds.$$

Since $R(x,t,t) = 0$ we obtain the identity

$$2\int_{\mathcal{S}^3} \alpha\left(x + R(x,t,t)\ \nu, t\right)\ d\nu = 2\alpha\left(x,t\right)\int_{\mathcal{S}^3}\ d\nu = 8\pi\alpha(x,t).$$

It seems reasonable to ignore all the gradient terms and to define an approximation ρ^0 as the solution of the system of differential equations

$$\begin{aligned} \frac{\partial \rho^0}{\partial t} &= (1-\rho^0)\frac{\partial \rho^0_*}{\partial t} = G(1-\rho^0)\frac{\partial \psi_1}{\partial t}, \\ \frac{\partial \psi_1}{\partial t} &= G\psi_2, \\ \frac{\partial \psi_2}{\partial t} &= G\psi_3, \\ \frac{\partial \psi_3}{\partial t} &= 8\pi\alpha, \end{aligned} \tag{4.8}$$

with homogeneous initial values for all variables. Here the variables ψ_j are thought of as approximations to ϕ_j. Note that (4.8) is the three-dimensional case of the rate equations proposed in [40].

In order to compare the extended volume ρ_* and the approximation ρ^1_*, ρ^0_* in a reasonable way, we rescale the extended densities by a typical size $\alpha_0\ell^d T$, i.e., we consider the rescaled variables

$$\tilde{\rho}_* := \frac{\rho_*}{\alpha_0\ell^3 T}, \qquad \tilde{\rho}^k_* := \frac{\rho^k_*}{\alpha_0\ell^3 T}.$$

In the same way we rescale the variables ϕ_j and ψ_j to

$$\tilde{\varphi}_j := \frac{\phi_j}{\alpha_0\ell^{3-j} T}, \qquad \tilde{\psi}_j := \frac{\psi_j}{\alpha_0\ell^{3-j} T}.$$

We start by estimating the difference between $\tilde{\varphi}_3$ and $\tilde{\psi}_3$, using the estimats for G and $\nabla\alpha$, as

$$\begin{aligned} |\tilde{\varphi}_3(x,t) - \tilde{\psi}_3(x,t)| &= \frac{1}{\alpha_0 T}|2\int_0^t G(x,\tau)\int_0^\tau \int_{\mathcal{S}^3} \nabla\alpha(x + R(x,\tau,s)\nu, s)\cdot\nu\ d\nu\ ds\ d\tau| \\ &\le \frac{2C_\alpha G_0}{\lambda T}|\int_0^t\int_0^\tau \int_{\mathcal{S}^3} d\nu\ ds\ d\tau| = \frac{4\pi C_\alpha G_0 t^2}{\lambda T}. \end{aligned}$$

For the difference between $\tilde{\varphi}_2$ and $\tilde{\psi}_2$ we can derive a similar estimate, taking into account that the error consists of two terms, namely the ignored integral involving $\nabla\alpha$ and the integral of $\tilde{\varphi}_3 - \tilde{\psi}_3$. By a simple application of the triangle inequality we obtain

$$\begin{aligned}|\tilde{\varphi}_2(x,t) - \tilde{\psi}_2(x,t)| &= \frac{1}{\ell}\Big| \int_0^t G(x,\tau)(\tilde{\varphi}_3(x,\tau) - \tilde{\psi}_3(x,\tau))\ d\tau\Big| \\ &\quad + \frac{1}{\alpha_0 \ell T}\Big|2\int_0^t G(x,\tau)\int_0^\tau \int_{\mathcal{S}^3} \nabla\alpha(x + R(x,\tau,s)\nu, s)\cdot\nu\ R(x,\tau,s)\ d\nu\ ds\ d\tau\Big| \\ &\leq \frac{4\pi C_\alpha G_0^2 t^3}{3\lambda\ell T} + \frac{4\pi C_\alpha G_0^2 t^3}{3\lambda\ell T} = \frac{8\pi C_\alpha G_0^2 t^3}{3\lambda\ell T}.\end{aligned}$$

By completely analogous reasoning we deduce

$$|\tilde{\varphi}_1(x,t) - \tilde{\psi}_1(x,t)| \leq \frac{2\pi C_\alpha G_0^3 t^4}{3\lambda\ell^2 T}$$

and, finally,

$$|\tilde{\rho}_*^1(x,t) - \tilde{\rho}_*^0(x,t)| \leq \frac{2\pi C_\alpha G_0^4 t^5}{15\lambda\ell^3 T} \leq \frac{2\pi C_\alpha}{15}\frac{\ell}{\lambda}.$$

Hence, the additional error made when ignoring the terms with $\nabla\alpha$ in the derivatives is of first order with respect to the relative scale $\frac{\ell}{\lambda}$.

A natural next step is to estimate the difference between ρ_* and ρ_*^1. For this sake we inspect the causal cone section $\mathcal{E}(x,t;s)$. For each $y \in \mathcal{E}(x,t;s)$ we can find an arc ξ such that $\xi(t) = x$, $\xi(s) = y$, and

$$|\dot{\xi}(\tau)| \leq G(\xi(\tau),\tau) \leq G(x,\tau) + \frac{C_G G_0}{\lambda}|\xi(\tau) - x|.$$

Since on the other hand, we have $G(\xi(\tau),\tau) \leq G_0$, we can estimate $|\dot{\xi}(\tau)| \leq G_0$ and hence, $|\xi(\tau) - x| \leq G_0(t-\tau)$. Inserting the latter estimate on the right-hand side above, we obtain

$$|\xi(s) - x| \leq \int_s^t |\dot{\xi}(\tau)|\ d\tau \leq R(x,t,s) + \frac{C_G G_0^2 (t-s)^2}{2\lambda} := R_+(x,t;s).$$

This shows that $\mathcal{E}(x,t;s) \subset B(x; R_+(x,t,s))$, where $B(x;R)$ denotes the ball around x with radius R. By similar reasoning we can deduce the inclusion $\mathcal{E}(x,t;s) \supset B(x; R_-(x,t,s))$ with

$$R_-(x,t,s) = R(x,t,s) - \frac{C_G G_0^2 (t-s)^2}{2\lambda}.$$

Hence, the relative volume between $\mathcal{E}(x,t;s)$ and $B(x,R(x,t,s))$ can be estimated by

$$\begin{aligned}&|\mathcal{E}(x,t;s) \setminus B(x,R(x,t,s))| + |B(x,R(x,t,s)) \setminus \mathcal{E}(x,t;s)| \\ &\quad \leq \frac{4\pi}{3}(R_+(x,t;s)^3 - R(x,t;s)^3) \\ &\quad \leq \frac{2\pi C_G G_0^2 (t-s)^2}{\lambda} R_+(x,t;s)^2 \leq \frac{2\pi C_G G_0^2 (t-s)^2}{\lambda}\left(G_0(t-s) + \frac{C_G \ell G_0 (t-s)}{2\lambda}\right)^2.\end{aligned}$$

With the integral representations of ρ_* and ρ_*^1 we can further estimate

$$\begin{aligned}
&|\rho_*(x,t) - \rho_*^1(x,t)| \\
&\quad \le \frac{1}{\alpha_0 \ell^3 T} \Big| \int_0^t \left(\int_{\mathcal{E}(x,t;s)} \alpha(y,s)\, dy\, ds - \int_{B(x,;R(x,t,s))} \alpha(y,s)\, dy \right) ds \Big| \\
&\quad \le \frac{1}{\ell^3 T} \Big| \int_0^t \frac{2\pi C_G G_0^4 (t-s)^4}{\lambda} \left(1 + \frac{C_G \ell}{2\lambda}\right)^2 ds \Big| \\
&\quad \le \frac{2\pi C_G}{5} \left(1 + \frac{C_G \ell}{2\lambda}\right)^2 \frac{t}{T} \frac{\ell}{\lambda} \le \frac{2\pi C_G}{5} \left(1 + \frac{C_G \ell}{2\lambda}\right)^2 \frac{\ell}{\lambda}
\end{aligned}$$

From the triangle inequality we obtain the following result:

THEOREM 4.2. *Let G and α satisfy* (1.2) *and* (4.5). *Then, with the above definitions of ρ_* and the approximation ρ_*^0 as above, the estimate*

$$\left\| \tilde{\rho}_* - \tilde{\rho}_*^0 \right\|_\infty \le \frac{2\pi C_\alpha}{15} \left[1 + 3 \left(1 + \frac{C_G \ell}{2\lambda} \right)^2 \right] \frac{\ell}{\lambda} \tag{4.9}$$

holds.

Theorem 4.2 confirms that ρ_*^0 is indeed a first-order approximation of the extended volume density ρ_*. The difference in the volume densities can be estimated by

$$\left\| \rho - \rho^0 \right\|_\infty \le \left\| e^{-\rho_*} - e^{-\rho_*^0} \right\|_\infty \le (\alpha_0 \ell^3 T) \left\| \tilde{\rho}_* - \tilde{\rho}_*^0 \right\|_\infty .$$

Note that the constant $\alpha_0 \ell^3 T$ is a bound for the number of nucleations in a microscale cell in the time interval $[0, T]$, which is usually small or of order one.

5. Variance and Mesoscale Averaging. In the following we discuss the variance of the random variable $\chi(x,t) := I_{\Xi(t)}(x)$, taking the values 0 or 1 only, and the variance of a local averaging on a mesoscale, which yields error estimates for corresponding mesoscale quantities.

5.1. Variance of the Volume Density. The volume density $\rho(x,t)$ is the expected value of the random variable $\chi(x,t)$. Hence, $\chi(x,t)^2 = \chi(x,t)$ and we obtain for the local variance

$$v(x,t) = \mathbb{E}[\chi(x,t)^2] - \mathbb{E}[\chi(x,t)]^2 = \mathbb{E}[\chi(x,t)] - \mathbb{E}[\chi(x,t)]^2 = \rho(x,t)(1 - \rho(x,t)).$$

Since $\rho(x,t) \in [0,1]$, we conclude that $\rho(x,t)(1-\rho(x,t)) \le \frac{1}{4}$ and hence, we have derived the following result:

THEOREM 5.1. *For each $(x,t) \in \Omega \times [0,T]$, the random variable $\chi(x,t)$ has a variance $v(x,t) \in [0, \frac{1}{4}]$.*

In general, we cannot expect a very low variance at a single point x, but we may expect a lower variance for local spatial averages of χ. Given $A \subset \Omega$, we have introduce the random variable

$$m_A(t) := \frac{1}{|A|} \int_A \chi(x,t)\, dx.$$

Due to the linearity of the integral we conclude $\mathbb{E}[m_A(t)] = \int_A \rho(x,t)\, dx$. The variance

of m_A can be estimated (in a pessimistic way) via the Cauchy-Schwarz inequality

$$\begin{aligned}\mathbb{E}\left[(m_A(t)-\mathbb{E}[m_A(t)])^2\right] &= \mathbb{E}\left[\left(\frac{1}{|A|}\int_A(\chi(x,t)-\rho(x,t))\,dx\right)^2\right]\\ &\le \frac{1}{|A|}\mathbb{E}\left[\int_A(\chi(x,t)-\rho(x,t))^2\,dx\right]\\ &= \frac{1}{|A|}\int_A v(x,t)\,dx \le \frac{1}{4}.\end{aligned}$$

Clearly, with such a pessimistic estimate the variance is not decreased, since we have not introduced information about the possible dependence or independence of the random variables $\chi(x,t)$ at different locations. This will be done in the following section within a local averaging procedure.

5.2. Error Estimates for Mesoscale Averaging. In the following we shall consider local averages of the volume density at the mesoscale. We assume that $\lambda = 3N\ell$ with $\ell \ge G_0T$. We perform the local averaging over a cell

$$A(z) = \{z\} + [-\frac{\lambda}{2},\frac{\lambda}{2}]^d, \tag{5.1}$$

i.e., we are interested in the average volume density

$$\hat{\rho}(z,t) := m_{A(z)}(t). \tag{5.2}$$

The local cell $A(z)$ can be decomposed into subcells

$$A_i = \{z_i\} + [-\frac{\ell}{2},\frac{\ell}{2}]^d, \qquad i = 1,\dots(3N)^d, \tag{5.3}$$

such that the interior of A_i and A_j are pairwise disjoint and

$$A(z) = \bigcup_i A_i.$$

Now define random variables $X_i(t) := m_{A_i}(t)$. From the results of the previous section we know that $\mathbb{E}[X_i(t)] = \int_{A_i}\rho(x,t)\,dx$ and that the variance of $X_i(t)$ can be estimated via $\mathbb{V}[X_i(t)] \le \frac{1}{4}$.

LEMMA 5.2. *Let $0 \le t \le T$ and $|z_i - z_j|_1 \ge (d+2\sqrt{d})\lambda$. Then the random variables $X_i(t)$ and $X_j(t)$ are independent.*

Proof. Let $x_i \in A_i$ and $x_j \in A_j$. Then, $|z_i - z_j|_1 \ge (d+2\sqrt{d})\lambda$ implies $|x_i - x_j| > 2G_0T$ and hence, from (2.10) we can conclude that $\mathcal{C}(x_i,t)\cap\mathcal{C}(x_j,t) = \emptyset$ and since $\chi(x,t)$ only depends on the nucleation in $\mathcal{C}(x,t)$, we may conclude that $\chi(x_i,t)$ and $\chi(x_j,t)$ are independent. Since $x_i \in A_i$ and $x_j \in A_j$ are arbitrary, we may also conclude that the integrals of χ with respect to $x_i \in A_i$ and with respect to $x_j \in A_j$ are independent, and thus, $X_i(t)$ and $X_j(t)$ are independent. ∎

THEOREM 5.3. *Let the nucleation and growth process satisfy the standard assumptions and let $\ell = G_0T < \lambda$. Then we have*

$$\mathbb{V}[\hat{\rho}(z,t)] \le \frac{1}{4N^d} = \frac{M(d)^d}{4}\left(\frac{\ell}{\lambda}\right)^d, \qquad \forall (z,t)\in\Omega\times[0,T],$$

with $M(d)$ being any real number such that $k(d) \geq d + 2\sqrt{d}$

Proof. Due to Lemma 5.2 we can find $(M(d))^d$ disjoint index sets

$$I_k \subset \{1, \ldots, (M(d)N)^d\}$$

such that

$$\{1, \ldots, (M(d)N)^d\} = \bigcup_{k=1}^{M^d} I_k, \qquad |I_k| = N^d,$$

and such that X_i and X_j are independent if $i \in I_k$ and $j \in I_k$ for some k. Now we define random variables $Y_k := \sum_{i \in I_k} N^{-d} X_i(t)$. The mean value of Y_k is given by

$$\mathbb{E}[Y_k] = \mathbb{E}\left[\sum_{i \in I_k} N^{-d} X_i(t)\right] = \sum_{i \in I_k} \frac{1}{N^d |A_i|} \int_{A_i} \rho(x,t)\, dx = \frac{1}{|B_k|} \int_{B_k} \rho(x,t)\, dx.$$

Since the X_i are independent for $i \in I_k$ with variance bounded by $\frac{1}{4}$ we obtain

$$\mathbb{V}[Y_k] = \mathbb{V}\left[\sum_{i \in I_k} N^{-d} X_i(t)\right] = \mathbb{V}\left[\sum_{i \in I_k} N^{-d} X_i(t)\right] = N^{-2d} \sum_{i \in I_k} \mathbb{V}[X_i(t)] \leq \frac{1}{4N^d}.$$

With the above notation, we have

$$\hat{\rho}(z,t) = (M(d))^{-d} \sum_{k=1}^{(M(d))^d} Y_k$$

and hence,

$$\mathbb{V}[\hat{\rho}(z,t)] = (M(d))^{-2d} \mathbb{V}\left[\sum_{k=1}^{(M(d))^d} Y_k\right] \leq (M(d))^{-d} \sum_{k=1}^{(M(d))^d} \mathbb{V}[Y_k] \leq \frac{1}{4N^d},$$

which completes the proof. □

Note that with the Chebyshev inequality, Theorem 5.3 implies

$$\mathbb{P}\left[\left|\frac{1}{A(z)} \int_{A(z)} (\chi(x,t) - \rho(x,t)) dx\right| > \epsilon\right] \leq \frac{M(d)^d}{4\epsilon^2} \left(\frac{\ell}{\lambda}\right)^d.$$

The variance estimate can also be interpreted in a different way, since $\ell = G_0 T$ yields a certain time dependence of the estimate. In particular we obtain

$$\mathbb{V}[\hat{\rho}(z,T)] \leq \frac{M(d)^d}{4} \left(\frac{G_0 T}{\lambda}\right)^d,$$

and therefore we have to expect that the variance grows in time like T^d.

6. Extensions. In the following we consider some possible extensions of the mesoscale averaging to further situations of interest. We shall not develop a detailed theory for these cases, but only outline the major analogies and differences to the growth considered above.

6.1. Anisotropic Growth. In anisotropic growth, which appears for many materials with an underlying crystal structure such as metals or semiconductors, the form of the normal velocity G in the growth model (1.1) has to be changed to

$$G = H(x,t,n), \qquad H : \mathbb{R}^d \times R_+ \times \mathcal{S}^d \to \mathbb{R}_+,$$

where $\mathcal{S}^d$ is the unit sphere in $\mathbb{R}^d$. Such growth situations appear e.g. for $d = 2$ on crystalline substrates, where the dependence of H is determined by the underlying crystal structure of the substrate. The function H can be extended to a one-homogeneous function on $\mathbb{R}^d \times R_+ \times \mathbb{R}^d$ via

$$H(x,t,p) := |p| H(x,t,\frac{p}{|p|}).$$

We shall assume that $H(x,t,.)$ is a convex function for all (x,t). In this case, the level set formulation of the growth model is given by $\Omega(t) = \{\phi(.,t) \leq 0\}$ for ϕ being the viscosity solution of the Hamilton-Jacobi equation

$$\frac{\partial \phi}{\partial t} + H(x,t,\nabla\phi) = 0.$$

For convex Hamiltonian H, one can still derive a Hopf-Lax formula (cf. [24]) of the form

$$\begin{aligned} \phi(x,t) = \inf\{\ \phi(y,0) \mid \exists \xi \in W^{1,\infty}([0,t]) : \xi(t) = x, \xi(0) = y, \\ |\dot{\xi}(\tau)| \leq \sup_{|\nu|=1} H(\xi(\tau),\tau,\nu), \tau \in (0,t)\ \}. \end{aligned} \tag{6.1}$$

The causal cone can be defined in the same way as in the isotropic growth situation above, and using (6.1) one can also derive an analogous Hopf-Lax representation of the causal cone as

$$\begin{aligned} \mathcal{C}(x,t) = \{\ (y,s) \in \mathbb{R}^d \times \mathbb{R}_+ \mid \exists \xi \in W^{1,\infty}([s,t]) : \xi(t) = x, \xi(s) = y, \\ |\dot{\xi}(\tau)| \leq \sup_{|\nu|=1} H(\xi(\tau),\tau,\nu), \tau \in (s,t)\ \}. \end{aligned}$$

The basic ideas and results of mesosale averaging such as the Avrami-Kolmogorov formula remain unchanged in the anisotropic setting, the only difference is the slightly more complicated computation of the causal cone.

6.2. Polycrystalline Growth. A challenging example in modern semiconductor processing is the growth of polycrystalline structures on amorphous substrates (cf. e.g. [39]). In these processes, a crystalline material is deposited on an amorphous substrate and crystals nucleate randomly. Since the material is crystalline, each nuclei has a special orientation, which is a random variable in the nucleation process. Hence, nucleation should be modeled as a Poisson process in $D \times \mathbb{R}^+ \times \mathcal{S}^d$ with a rate $\alpha = \alpha(x,t,\nu)$ for $\nu \in \mathcal{S}^d$.

The initial orientation of the nuclei determines the subsequent anisotropic growth of the crystal, i.e., the level set formulation of the growth of the j-th grain becomes $\Omega_j(t) = \{\phi_j(.,t) \leq 0\}$

$$\frac{\partial \phi_j}{\partial t} + H_\nu(x,t,\nabla\phi_j) = 0,$$

with Hamiltonian (respectively normal velocity for the front growth) depending on the initial orientation. Thus, the growth of a grain nucleated at (X, T) will in general be different for different values of the random variable ν. Since the nucleation event is now described by a random variable on $\mathbb{R}^d \times \mathbb{R}_+ \times \mathcal{S}^d$, we have to define the causal cone as a subset of this larger set, i.e.,

$$\begin{aligned}\mathcal{C}(x,t) := \{(y,s,\nu) \in \mathbb{R}^d \times \mathbb{R}_+ \times \mathcal{S}^d \mid \text{Nucleation of grain } \Omega \text{ at } y \text{ at time } s \\ \text{with orientation } \nu \text{ implies } x \in \overline{\Omega(t)}\}. \end{aligned} \tag{6.2}$$

The mesoscale averaging can then be performed by analogous reasoning as above and one obtains that (3.7) holds with

$$\begin{aligned}\rho_*(x,t) = \mathbb{E}[N(\mathcal{C}(x,t))] &= \int_{\mathcal{C}(x,t)} \alpha(y,s,\nu)\ d(y,s,\nu) \\ &= \int_{\mathcal{S}^d} \int_0^t \int_{\mathcal{E}(x,t;s,\nu)} \alpha(y,s,\nu)\ dy\ ds\ d\nu, \end{aligned} \tag{6.3}$$

with the section

$$\mathcal{E}(x,t;s,\nu) = \{\ y \in \mathbb{R}^d \mid (y,s,\nu) \in \mathcal{C}(x,t)\ \}.$$

Again, the major change in the mesoscopic averaging occurs with respect to the causal cone, which is now an object of higher dimension and consequently more difficult to compute.

Example. In order to make the above statements more concrete, we consider a special case of cubic anisotropy with constant growth rate $\alpha(x,t,\nu) \equiv \alpha_0$. We assume that the nucleating grain is an infinitesimally small cube with main axis in direction ν (and its unit normals $\nu_1^\perp$, $\nu_2^\perp$), and that the growth appears with a constant velocity G_0 in the directions of the main axis, so that the grain remains a cube until impingement. More precisely, a freely grown grain Ω^k nucleated at location X_k, time T_k, and orientation ν_k is given by

$$\Omega^k(t) = \{\ x \in \mathbb{R}^d \mid |x - X_k|_{\nu_k} \leq G_0(t - T_k)\ \},$$

where the anisotropic norm $|.|_\nu$ is given by

$$|y|_\nu = \max\{|y \cdot \nu|, |y \cdot \nu_1^\perp|, |y \cdot \nu_2^\perp|\}.$$

As a consequence we can compute the causal cone

$$\mathcal{C}(x,t) = \{(y,s,\nu) \in \mathbb{R}^d \times \mathbb{R}_+ \times \mathcal{S}^3 \mid |x-y|_\nu \leq G_0(t-s)\}$$

and its sections

$$\mathcal{E}(x,t;s) = \{(y,\nu) \in \mathbb{R}^d \times \mathbb{R}_+ \times \mathcal{S}^3 \mid |x-y|_\nu = G_0(t-s)\}.$$

With (6.3) we derive in this special case

$$\rho_*(x,t) = \int_{\mathcal{S}^d} \int_0^t \int_{\mathcal{E}(x,t;s,\nu)} \alpha(y,s,\nu)\ dy\ ds\ d\nu = 4\pi\alpha_0 \int_0^t 8G_0^3(t-s)^3\ ds = 8\pi\alpha_0 G_0^3 t^4.$$

Hence, the degree of crystallinity can be computed explicitely as

$$\rho(x,t) = 1 - \exp\left(-8\pi\alpha_0 G_0^3 t^4\right), \tag{6.4}$$

which is the polycrystalline equivalent of the classical Avrami-Kolmogorov formula (4.2).

Acknowledgements. Stimulating discussions on the subject of the paper are acknowledged to Alessandra Micheletti (University Milano) and on polycrystalline growth to Hajdin Ceric (Technical University Vienna) and Peter Smereka (University Michigan).

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