Kinetics of phase transformations with heterogeneous correlated-nucleation

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HIGHLIGHTS

- 3D-phase transition with heterogeneous correlated nucleation is modeled, analytically.
- Second order terms in correlation functions provide good approximation of the kinetics.
- Differently from Poissonian nucleation, the present formulation makes use of actual nucleation rate.
- The model is suitable for studying electrodeposition where correlation effects are important.

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ABSTRACT

We develop a stochastic approach for describing the kinetics of 3D-phase transformations ruled by time-dependent correlated nucleation at solid surfaces. The kinetics is expressed as a series of correlation functions and, at odds with modeling based on Poisson statistics, it is formulated in terms of actual nucleation rate. It is shown that truncation of the series up to second order terms in correlation functions provides a very good approximation of the kinetics. The time evolution of both total amount of growing phase and surface coverage by the new phase have been determined. The theory is applied to describe progressive nucleation with parabolic growth under time dependent hard-disk correlation. This approach is suitable for describing electrochemical deposition by nucleation and growth where correlation effects are significant. In this ambit the effect of correlated nucleation on the behavior of kinetic quantities used to study electrodeposition has also been investigated.

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1. Introduction

Theoretical modeling of phase transformations taking place by nucleation and growth with correlated nuclei has in recent years attracted considerable interest from researchers [1–8]. This nucleation process occurs in diffusional growth where diffusion field gives rise to reduced nucleation probability around growing nuclei [9,10]. Correlated nucleation is also induced in stress-driven transformations where the strain field imparts a certain degree of spatial order to the nuclei [11,12]. Until now, the problem has been tackled in the case of homogeneous and isotropic phase transformations in 2D and 3D space, namely in systems that are translationally invariant and isotropic in the whole space where the transformation takes place. These models share the same hypotheses with the celebrated Kolmogorov–Johnson–Mehl–Avrami (KJMA) theory [13–15], with an exception to the nucleation process which is not random throughout the untransformed phase. The KJMA theory,

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originally developed for first order phase transitions, has been applied to several scientific fields which range from Materials Science to Electrochemistry [16–22] and from Biology to Pharmaceutics [23–25], just to cite a few examples.

The simplest nucleation process is called site saturation (or simultaneous) where all nuclei start growing at the same time [26]. The case of simultaneous nucleation has been firstly modeled in Refs. [2,3] for 2D transformations with hard-disk correlation among nuclei. The analytical solution has been found to be in good agreement with computer simulations on 2D lattice [2,3]. Also, computer simulations of non-random distribution of nuclei in either a periodic or a cluster arrangement have been performed for simultaneous nucleation in Ref. [7]. Recently, the problem has been studied in more general way in Ref. [8] for spatially-decaying correlation and site saturation nucleation. The more involved case of non-simultaneous nucleation has been tackled in Refs. [4–6] for both time-independent and time-dependent hard-disk correlations. In order to study the stochastic process of dots linked to nucleation, the modelings above quoted make use of correlation-functions. In addition, worthy to note is the alternative approach proposed in Ref. [4] which exploits a differential method, with properly defined extended quantities, recovering Avrami's kinetics in the random case [14].

The possibility to deal with spatial correlation is also significant in connection with the growth law of nuclei. On one hand, the KJMA theory does not apply to parabolic-type growths because of the overgrowth of phantom nuclei [14,27]. On the other hand, the possibility to describe correlated nucleation allows one to formulate the theory in terms of *actual* nuclei that are spatially correlated. As a consequence, the restriction on the growth law above mentioned is relaxed since phantom nuclei are eliminated from the formulation of the theory [28–30].

Besides the growth in homogeneous systems, it is also of importance the transformation in 3D systems where nucleation is constrained on a surface. For instance, such a process is encountered in Materials Science in the ambit of nucleation and growth at grain-boundaries and interfaces [11,31,32]. It also takes place in film growth by condensation of gas phase at solid surfaces, as studied to a certain extent in the literature [33]. Another technique widely employed to grow films on substrates is based on electrochemical nucleation and growth, where deposition takes place from the liquid phase. In this case the growth is ruled by the diffusion of species in the solution. On the experimental side, the kinetics of deposition is studied by recording chronoamperometric curves which are linked to the amount of deposited species through Faraday's law [9,22]. It follows that in these systems the modeling of the current-time behavior requires the determination of the kinetics of film growth in terms of total *amount* of deposited material. Until now this modeling has been limited to the case of nucleation which is compliant with the KJMA approach [34]. However, as anticipated above, correlation effects among nuclei are significant in electrochemical nucleation. Due to diffusional growth by mass transport in solution, *actual nuclei* are spatially correlated to an extent that is greater than that occurring in KJMA-type transformations. Experimental data on spatial distribution of actual nuclei in electrochemical deposition are well described by the exclusion zone model for nucleation [9,35–38], namely by considering a region around each nucleus, with size greater than the nucleus size (projected on surface), where further nucleation is prevented. It is also in this field that the present work finds application.

The kinetic theory for phase transformations with time dependent non-Poissonian heterogeneous nucleation has not been proposed so far. The purpose of the present work is to bridge the gap between theoretical modeling of phase transformations ruled by heterogeneous nucleation with random and correlated nuclei. With respect to the random case the present theory has also the advantage to be formulated in terms of actual nucleation rate, a quantity which is experimentally accessible.

The paper is organized as follows. The first section is devoted to correlation functions and probability theory. In the second one the theory is employed to model the kinetics of 3D diffusional growth of hemispheres. The third section is devoted to the presentation and discussion of the numerical results. In the last section an application to electrochemistry is presented, by studying the impact of correlation on chronoamperometric curves. To improve the presentation of the subject matter, the majority of the mathematical computations have been reported in the "Supplementary Material" section.

2. Results and discussion

2.1. Correlation-function-based theory

It has been demonstrated that for a 2D or 3D phase transformations, occurring by nucleation and growth, the fraction of the untransformed phase, $P(t)$, can be expressed in terms of either f-functions or correlation functions [30] according to

$$P(t) = 1 - \int_0^t I(t_1) \, dt_1 \int_{\Delta_{1t}} f_1(\mathbf{r}_1) \, d\mathbf{r}_1 + \int_0^t I(t_1) \, dt_1 \int_0^{t_1} I(t_2) \, dt_2 \int_{\Delta_{1t}} d\mathbf{r}_1 \int_{\Delta_{2t}} f_2(\mathbf{r}_1, \mathbf{r}_2) \, d\mathbf{r}_2 - \cdots$$

$$= 1 + \sum_{m=1}^{\infty} \frac{(-)^m}{m!} \int_0^t I(t_1) \, dt_1 \ldots \int_0^t I(t_m) \, dt_m \int_{\Delta_{1t}} d\mathbf{r}_1 \ldots \int_{\Delta_{mt}} f_m(\mathbf{r}_1, \ldots, \mathbf{r}_m) \, d\mathbf{r}_m, \tag{1}$$

where $\Delta_{it} \equiv \Delta(t_i, t)$ $(i = 1, 2, \ldots, m)$ is the domain (a disk or a sphere for transitions in 2D or 3D space) transformed at time t by a nucleus born at time t_i. The last expression in Eq. (1) holds for f_m functions symmetric with respect to the exchange of nucleus coordinates, $\mathbf{r}_i$. In Eq. (1) $[I(t_1) \, dt_1 d\mathbf{r}_1] [I(t_2) \, dt_2 d\mathbf{r}_2] \ldots [I(t_m) \, dt_m d\mathbf{r}_m] f_m(\mathbf{r}_1, \ldots, \mathbf{r}_m)$ is the probability of finding a nucleus born between times t_i and $t_i + dt_i$ in the volume element $d\mathbf{r}_i$ at $\mathbf{r}_i$, irrespective of the position of the others $N - m$ nuclei, with N total number of nuclei. For instance, $f_2(\mathbf{r}_1, \mathbf{r}_2)$ is the radial distribution function for the pair of nuclei (1,2). For a homogeneous and isotropic system $f_1(\mathbf{r}_1) = 1$ and $f_2(\mathbf{r}_1, \mathbf{r}_2) = f_2(|\mathbf{r}_1 - \mathbf{r}_2|)$. In Eq. (1), $P(t)$ is the