

# Kinetics of island density in thin film growth in the framework of statistical mechanics of rigid disks

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The paper centers on the evaluation of the function  $n(\Theta)=N(\Theta)/N_0$ , that is the normalized number of islands as a function of coverage  $\Theta \in [0,1]$ , given  $N_0$  initial nucleation centers (dots) having any degree of spatial correlation. A mean field approach has been employed: the islands have the same size at any coverage. In particular, as far as the random distribution of dots is concerned, the problem has been solved by considering the contribution of binary collisions between islands only. With regard to correlated dots, we generalize a method previously applied to the random case only. In passing, we have made use of the exclusion probability reported in [S. Torquato, B. Lu, and J. Rubinstein, *Phys. Rev. A* **41**, 2059 (1990)], for determining the kinetics of surface coverage in the case of correlated dots, improving our previous calculation [M. Tomellini, M. Fanfoni, and M. Volpe, *Phys. Rev. B* **62**, 11300 (2000)].

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## I. INTRODUCTION

For describing the evolution of thin film morphologies several physical processes have to be considered, among others the atom condensation and evaporation, the adatom surface diffusion, the nucleation, and the island growth. During the last decades significant advances have been done in modeling, taking advantage of both analytical and numerical approaches, the initial stage of film formation, namely the nucleation and the growth processes in the low coverage regime.<sup>1,2</sup> The methods range from the classical mean field rate equations to the scaling theories which are found to be suitable tools for describing both experimental and kinetic Monte Carlo results.<sup>3</sup> In order to go beyond the early stage of the growth, it is mandatory to tackle another physical process, that is the collision among the growing clusters. In the case of diffusionless clusters this process is actually linked to the cluster growth only. As a consequence an island which is in general a collection of connected clusters stems from one or more nucleation events. As regards the film morphology two mechanisms can be distinguished: the *impingement* and the *coalescence*. In the former no redistribution of matter among clusters occurs after a collisional event and the clusters retain their individuality. Conversely, in the latter mechanism redistribution of matter does occur with conservation of both mass and shape.

The process of coalescence has been modeled, for the first time, by Vincent,<sup>4</sup> who proposed an analytical solution for the island density kinetics on the basis of the Poisson distribution. Briscoe and Galvin developed a statistical theory for island coalescence which is in good agreement with the behavior of the island density decays obtained by computer simulations.<sup>5</sup> As far as the impingement mechanism is concerned, it has been faced in a certain details in Ref. 6. Specifically, the exact solution for the normalized number density of islands, as a function of surface coverage  $n(\Theta)$

$=N(\Theta)/N_0$ , where  $N(\Theta)$  is the number density of islands at coverage  $\Theta$  and  $N_0 \equiv N(0)$ , has been determined in the form of a series, the so-called *collision series*. This computation holds in the case of Poissonian simultaneous nucleation and in the entire range of the surface coverage ( $0 < \Theta < 1$ ). By means of Monte Carlo (MC) simulations it was also shown that the first three terms well approximate the series.<sup>7</sup> It is worth noting, in passing, that the continuum percolation threshold in 2D is achieved at about  $\Theta=0.7$ .<sup>8</sup> Besides, at the percolation threshold a certain number of isolated objects exists as the MC simulations and the exact computation of the first three terms of the collision series<sup>6</sup> witness. It is the number density of these islands (whose size is finite) which gives account of the small tail of the  $n(\Theta)$  kinetics at large coverages ( $\Theta > 0.7$ ).

Coalescence and impingement mechanisms of 2D and 3D islands have been extensively studied, through Monte Carlo simulations, as a function of the nucleus shape.<sup>8</sup> This work clearly demonstrates that, independently of the collision mechanism governing the film formation, the  $n(\Theta)$  kinetics is, in fact, the same, in spite of the fact that in the time domain the two mechanisms give rise to completely different kinetics. As a consequence, the behavior of  $n(\Theta)$  is expected to be the same also in the intermediate cases, namely the *partial coalescence*.<sup>8</sup> The universal behavior of the  $n(\Theta)$  kinetics can be successfully exploited for determining, from experimental data, the nucleation density at saturation. To this end it is sufficient to measure island densities in the high coverage regime ( $\Theta > 15\% - 20\%$ ), when islands are sufficiently large and atomic resolution microscopy is not required. An application of this approach to the growth of both diamond on Si substrate and quaterthiophene films on silica substrate has been recently presented in Refs. 9 and 10.

Thanks to the universal behavior of the normalized island density,  $n(\Theta)=N(\Theta)/N_0$ , also the nonsimultaneous nucleation case can be tackled. To this purpose one resorts to the

classical mean field rate equations for both island and adatom densities. These equations can be integrated provided the rate coefficient for island collisions is evaluated.<sup>11</sup> As a matter of fact this coefficient is a function of  $n(\Theta)$ .<sup>6</sup> The universal behavior of this function, together with the key role it plays in the rate equation approach to film growth, motivated further analytical studies. Recently, on the ground of a mean field approximation a semi-analytical approach has been developed which leads to island density kinetics that is in excellent agreement with the numerical simulation over the whole range of coverage. The method leads to<sup>12</sup>

$$n(\Theta) = \left( \frac{(\pi/4)^{1/2} - \Theta^{1/2}}{W_0(\Theta)} \right)^2, \quad (1)$$

where the function  $W_0(\Theta) = (\ln[1/(1-\Theta)])^{1/2} \int_0^\infty (1-\Theta)^{\xi(2+\xi)} d\xi$  has to be evaluated numerically.

The models discussed so far refer to the case in which nuclei are distributed at random throughout the whole surface. However, in nucleation processes ruled by adatom diffusion there exists a zone, around each nucleus, where the nucleation rate is reduced.<sup>11</sup> In other words, the nucleation events do not occur at random on the entire surface and this brings about the establishment of a degree of spatial correlation among nuclei.

One of the motivations of the present article is therefore the extension of the aforementioned analytical approach to the more realistic case of spatially correlated nuclei. Like in the random distribution of nuclei, also in this case rate equations can be employed to deal with nonsimultaneous nucleation. In this instance it is worth noting that rate equations are suitable for describing kinetic Monte Carlo results of correlated nucleation.<sup>13</sup> However, for want of theoretical modeling, in Ref. 13 the  $n(\Theta)$  function has been determined numerically through Monte Carlo simulations (MC).<sup>14</sup>

The paper is organized as follows. In the first section we propose a novel analytical approach based on the statistical mechanics of rigid disks, for the evaluation of the  $n(\Theta)$  kinetics in the random case. The rate coefficient for island collision is also computed, analytically. In the second section the method presented in Ref. 12 will be employed to tackle the impingement process in simultaneous nucleation of spatially correlated nuclei.

## II. RESULTS AND DISCUSSION

### A. Random distribution of nuclei

The following analytical approach for computing  $n(\Theta)$  is based on a mean field approximation, in the sense that at any given coverage (time), all islands have the same shape and appropriate size (disks in the case in point). This means that we are actually dealing with a sort of coalescence mechanism, yet, due to the universal behavior of the  $n(\Theta)$  function, the result of the computation can be applied to the impingement case as well. Collisions involving more than two islands will be neglected.

Let us denote by  $dP$  the probability that an island is involved in a binary collision. Since we are dealing with binary collision the changing rate of the island number is just equal

to the rate of “dimer” formation; this rate is equal to half the rate at which *an island* undergoes a collision event. Therefore the relation holds

$$\frac{dN}{N} = -\frac{1}{2}dP, \quad (2)$$

where  $N$  stands for the number density of islands. A simple closure of Eq. (2) is achieved by setting  $dP = 2\pi N(2R)d(2R)$ ,  $R$  being the radius of the islands, that is by considering the radial distribution function of the disks to be equal to one. For  $\Theta = N\pi R^2$ , to a first approximation one receives  $dN/N \approx -2d\Theta$  or<sup>15</sup>

$$n(\Theta) = e^{-2\Theta}. \quad (3)$$

As will soon be clear this is a poor description of  $n(\Theta)$  over the entire range of coverage; it describes the kinetics in the low coverage regime only. In fact, in the limit  $\Theta \rightarrow 0$  the kinetics becomes  $n(\Theta) \sim 1 - 2\Theta$  as already derived in Ref. 8.

The reason of this inaccuracy lies in the fact that the radial distribution function of a system of impenetrable disks is not equal to one except in the limit of large particle separation. A more suitable choice of the probability for binary collision is indispensable in order to model the island density kinetics over the whole range of coverage. To this end the results achieved on the thermodynamic system of rigid spheres<sup>16–18</sup> can be properly exploited. In particular we will make use of the results and the notation of Ref. 18.

$E_v(r)$  is the probability of finding a region of area  $\pi r^2$  centered at some arbitrary point empty of island centers;  $E_p(r)$  is the probability that given an island (its center) at some arbitrary point, the region of area  $\pi r^2$  encompassing the central island is empty of island centers. The respective density probability functions are attained by the derivatives of the exclusion probabilities  $E_v(r)$  and  $E_p(r)$ :  $H_v(r) = -\partial E_v(r)/\partial r$  and  $H_p(r) = -\partial E_p(r)/\partial r$ . The expression of the exclusion probability  $E_v(r)$ , for a system of particles not necessarily correlated through hard core potentials, has been derived in Refs. 18 and 19.

On the ground of the definition of the exclusion probability one gets  $dP = H_p(\sigma)d\sigma$ , where  $\sigma = 2R$  is the average value of the island diameter. The rate equation for binary collision then becomes

$$\frac{dN}{N} = -\frac{1}{2}H_p(\sigma)d\sigma. \quad (4)$$

In the thermodynamic limit, “voids” and “islands” exclusion probabilities are linked by the relationship<sup>18</sup>

$$E_p(r) = \frac{E_v(r)}{E_v(\sigma)}, \quad (5)$$

which holds for  $r \geq \sigma$ . Equation (5) shows that for a system of hard disks  $E_p(\sigma) = 1$ . Furthermore, in the same limit<sup>20</sup>

$$H_p(r) = \frac{8\Theta}{\sigma} \left( a_0 \frac{r}{\sigma} - a_1 \right) E_p\left(\frac{r}{\sigma}\right), \quad (6)$$

where  $a_0 = (1 + b_0\Theta)/(1 - \Theta)^2$ ,  $a_1 = b_1\Theta/(1 - \Theta)^2$ , and  $E_p(x) = \exp\{-\Theta[4a_0(x^2 - 1) - 8a_1(x - 1)]\}$ .

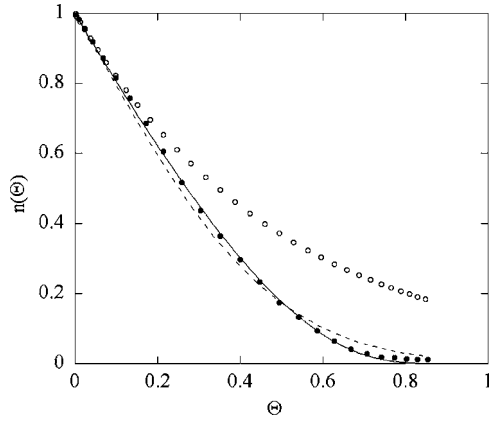


FIG. 1. Kinetics of island impingement as a function of surface coverage in the case of simultaneous nucleation of randomly distributed nuclei. The Monte Carlo result and the analytical solution [Eq. (8)] are shown as dots and full line, respectively. The solution Eq. (11) is reported as a dashed line. The behavior of Eq. (3) is displayed as open circles.

By using Eq. (6) in the kinetic equation (4), we eventually get

$$\frac{dN}{N} = - \frac{2(1-a\Theta)}{(1-\Theta)^2} d\Theta = - \frac{d\Theta}{\tau_c(\Theta)}, \quad (7)$$

where  $d\Theta = \frac{1}{4}\pi Nd(\sigma^2)$  is the increment of surface fraction covered by islands,  $a = b_1 - b_0$ , and  $\tau_c(\Theta)$  is the characteristic collision-time function. The definition of the time constant as given by Eq. (7) is in fact required in order to treat the nonsimultaneous nucleation by means of rate equations.<sup>21,13</sup> The integration of Eq. (7) can be performed analytically and gives

$$n(\Theta) = (1-\Theta)^{2a} \exp\left(-\frac{2(1-a)\Theta}{1-\Theta}\right). \quad (8)$$

The validity of our approach has been tested by using Monte Carlo (MC) simulations of island density decays in film growth ruled by the impingement mechanism.<sup>8</sup> In Fig. 1 Eq. (8) [for  $a = 0.564 - 0.128 = 0.436$  (Ref. 20)] has been compared to the MC simulation. Remarkably, the agreement between the simulation and the analytical result is excellent. In any case also the kinetics for  $a = 0.5 - 0 = 0.5$  (Ref. 22) is in very good agreement with the simulation (not shown).

Another analytical but less precise approach is based on the exclusion probability already derived by us in Ref. 23. By only retaining the Heaviside contribution in the radial distribution function of hard disks and decoupling the multiple integral which gives the argument of the exponential of the  $E_v(r)$  function,<sup>23</sup> we found

$$E_v(r) = \exp\left[-\pi Nr^2\left(1 + \frac{1}{2}\pi Nr^2\chi_{[0,\sigma]}(r) + \frac{1}{2}\pi N\sigma^2\chi_{(\sigma,\infty)}(r)\right)\right], \quad (9)$$

where  $\chi_A(x)$  is equal to one if  $x \in A$  and is equal to zero if  $x \notin A$ . It is worth noting that this expression has been suc-

cessfully employed for modeling the kinetics of the surface coverage in the case of spatially correlated nucleation (see the end of the paper and Ref. 23). From Eq. (9) on account of Eq. (5) we get

$$\begin{aligned} H_p(\sigma) &= - \frac{\partial_r E_v(r)|_\sigma}{E_v(\sigma)} \\ &= - \left. \frac{\partial \ln E_v(r)}{\partial r} \right|_\sigma = 2\pi N\sigma \left(1 + \frac{3}{4}N\pi\sigma^2\right), \end{aligned} \quad (10)$$

that, once inserted in Eq. (4), yields the kinetics

$$n(\Theta) = e^{-(2\Theta+3\Theta^2)}. \quad (11)$$

As shown in Fig. 1 this kinetics is in a pretty good agreement with the MC simulation over the entire range of coverage.<sup>24</sup> In the same figure is also displayed the behavior of the solution Eq. (3). As appears, the modeling based on this last approximation is inadequate for describing the kinetics in the whole range of surface coverage; in fact it is in agreement with the MC output only at the very beginning of the kinetics.

## B. Spatially correlated nuclei

The kinetics of island density in the case of Dirac delta (or heterogeneous) correlated nucleation can be determined by the same method as that employed in Ref. 12. Although the exclusion probability computed in Ref. 19 allows, in principle, to treat any kind of correlation, here it is introduced in such a way that nucleation in a circular region of radius  $R_{hc}$  around each nucleus is prevented.<sup>25</sup> It goes without saying that during the growth the radius of the cluster can exceed  $R_{hc}$ . Let us introduce the extended surface,  $\Theta_e = \pi N_0 R^2$ , where  $R$  stands for the nucleus radius and the quantity  $\Theta^* = \pi N_0 R_{hc}^2$  as a measure of the correlation degree of the system. The average value of the edge-to-edge distance among islands is given in terms of the exclusion probability,  $E_v(x; \Theta^*)$ , that is the probability that no nucleation centers fall in a disk of radius  $x$  centered at an arbitrary surface point. Strictly speaking this probability is exact in the case of impingement while the mean field assumption outlined in Sec. II A implies a sort of coalescence. However, according to the results of Ref. 8,  $n(\Theta)$  is, in effect, the same for both coalescence and impingement. This entitles us to use the  $E_v(x; \Theta^*)$  function; but, above all, the approach is corroborated by the results (see Fig. 2 below). The edge-to-edge average distance is

$$\bar{z}(R; \Theta^*) = \frac{2 \int_0^\infty E_v(z+R; \Theta^*) dz}{E_v(R; \Theta^*)} = \frac{2R \int_0^\infty E_v[R(1+\xi); \Theta^*] d\xi}{1 - \Theta(R; \Theta^*)}, \quad (12)$$

where in the last equation the identity  $E_v(R; \Theta^*) = 1 - \Theta(R; \Theta^*)$  has been exploited and  $\xi = z/R$ ; clearly  $R \neq 0$ . Therefore Eq. (12) reads

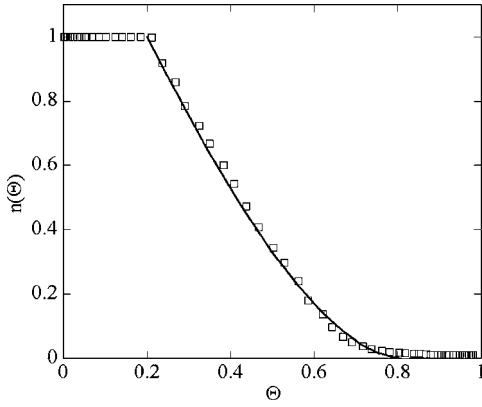


FIG. 2. Kinetics of island impingement as a function of surface coverage in the case of simultaneous nucleation of spatially correlated nuclei. Symbols are the Monte Carlo results for a correlated system according to the hard-core model for  $\Theta^* = 0.8$ . The semi-analytical result is shown as a full line [Eq. (18)].

$$\bar{z}(\Theta; \Theta^*) = \frac{2W_1(\Theta; \Theta^*)}{\sqrt{\pi N_0}}, \quad (13)$$

with

$$W_1(\Theta; \Theta^*) = \frac{\Theta_e^{1/2}}{1 - \Theta} \int_0^\infty E_v[R(1 + \xi); \Theta^*] d\xi. \quad (14)$$

The average diameter of the island when the fraction of covered surface is  $\Theta$  and  $N$  is the island density reads

$$D(\Theta, \Theta^*) = 2 \left( \frac{\Theta}{\pi N(\Theta, \Theta^*)} \right)^{1/2}, \quad (15)$$

while the distance between the centers of the islands can be written as

$$\bar{d}(\Theta, \Theta^*) = \frac{C}{\sqrt{\pi N(\Theta, \Theta^*)}}, \quad (16)$$

where  $C$  is a constant to be determined. Apparently,

$$\bar{d}(\Theta, \Theta^*) = D(\Theta, \Theta^*) + \bar{z}(\Theta, \Theta^*) \quad (17)$$

and, since for  $\Theta = \Theta^*/4$ ,  $N = N_0$ , from Eq. (17) the  $C$  constant is easily determined as  $C = 2W_1(\Theta^*/4; \Theta^*) + \sqrt{\Theta^*}$ . Using Eqs. (13) and (15)–(17) we end up with

$$n(\Theta, \Theta^*) = \left( \frac{C - \Theta^{1/2}}{W_1(\Theta, \Theta^*)} \right)^2, \quad (18)$$

which holds for  $\Theta \geq \Theta^*/4$ . As anticipated, we perform the computation of this kinetics by resorting to the exclusion probability of Ref. 22 which holds for the hard core

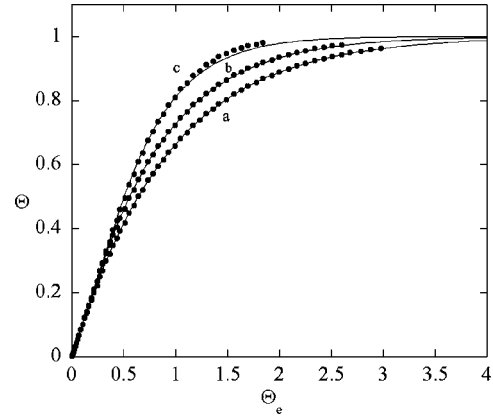


FIG. 3. Kinetics of surface coverage fraction as a function of the extended surface,  $\Theta_e$ , for simultaneous nucleation of correlated nuclei according to the hard-core model. The Monte Carlo simulations and the analytical results are shown as symbols and full lines, respectively. Curves *a*, *b*, and *c* refer to  $\Theta^* = 0.2$ ,  $\Theta^* = 0.7$ , and  $\Theta^* = 1.5$ , respectively.

correlation.<sup>26</sup> As far as this expression is concerned, it is given by

$$E_v(x; y) = (1 - yx^2)\chi_{[0, 1/2)}(x) + \left(1 - \frac{y}{4}\right) \exp\left[-\frac{y/4}{(1 - y/4)^2}\right] \\ \left(4x^2 - xy + \frac{y}{2} - 1\right) \chi_{[1/2, \infty)}(x), \quad (19)$$

where  $x = (\Theta_e/\Theta^*)^{1/2}(1 + \xi)$  and  $y = \Theta^*$ . Inserting Eq. (19) in Eq. (14), the numerical integration allows one to determine the decay of the islands as shown in Fig. 2 together with the MC simulation. The agreement is satisfactory.

Before concluding this paper, we take the occasion to apply the exclusion probability as derived in Ref. 20 to the determination of the kinetics of surface coverage in the case of Dirac delta spatially correlated nucleation. In our previous article<sup>23</sup> we evaluated the kinetics at hands by using Eq. (9) for three values of  $\Theta^*$ , namely 0.2, 0.7, and 1.5. Although those results were quite satisfactory, they can be improved by using the following exclusion probability,<sup>20</sup>

$$E_v(\Theta_e; \Theta^*) = (1 - \Theta_e)\chi_{[0, \Theta^*/4)} + \left(1 - \frac{\Theta^*}{4}\right) \exp\left[-\frac{\Theta^*}{4}\gamma(\Theta^*)\right] \\ \times \left(4\frac{\Theta_e}{\Theta^*} - \sqrt{\Theta^*\Theta_e} + \frac{\Theta^*}{2} - 1\right) \chi_{[\Theta^*/4, \infty)} \quad (20)$$

where  $\gamma(\Theta^*) = 1/(1 - \Theta^*/4)^2$ . The results are displayed in Fig. 3 together with the MC kinetics which have been described in Ref. 23.

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- <sup>24</sup>Clearly, the Monte Carlo simulation which gives the normalized number of islands is reproducible through an appropriate fit. It is worth noting that  $n(\Theta) = e^{-(2.2\Theta + 5.22\Theta^3)}$  perfectly fit to the MC simulation.
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