Mean field approach for describing thin film morphology: 2. Adatom life time

# Mean field approach for describing thin film morphology: 2. Adatom life time

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**Abstract**
By means of the analytical expression of the decay of the number of rigid discs as a function of the fraction of covered surface, we are able to evaluate averages of stochastic variables related to the distribution of impenetrable discs. In particular, we consider the edge–edge mean distance between discs, $\lambda_p$, and the distance from the edge disc of a point chosen at random, $\delta$. The second moment of $\delta$ and its connection to the adatom life time in thin film growth is highlighted and discussed on the basis of the comparison with Monte Carlo results. We also demonstrate numerically that the adatom life time in mean field coalescence is the same as that calculated in genuine coalescence.

In a couple of recent articles [1, 2] two of us have shown a possible way to treat the process of coalescence which takes place during thin film growth both for two and three dimensional islands. In particular, we have approached the issue making use of a kind of mean field approximation: after any coalescence event, which, it is worth remembering, implies a redistribution of mass in such a way that the mass and the shape of the islands are conserved, the size of all the islands is renormalized to be the same. This average allows one to use results of the statistical mechanics of rigid discs to determine the kinetic behaviour of some quantities, namely: the fraction of surface coverage, the evolution of the number of islands and the film perimeter. In the past, the same quantities have been determined for a film growth where the morphology of the film is ruled by impingement (see figure 1). In this case, a collision between two clusters is not followed by the redistribution of their mass, i.e. each cluster maintains its individuality (figure 1). The comparison between the above-quoted kinetic quantities for the two extreme collision processes is shown and discussed in [1, 2]. As far as the distribution of non-overlapping identical islands is concerned, it is of a certain interest to evaluate the moments of the probability density function (pdf), $P(\delta)$, which gives the probability that a generic point of the surface lies between $\delta$ and $\delta + \mathrm{d}\delta$ from the edge of some island. In effect, by resorting to the quasi-static approximation [3], the second moment can be related

Collision event between two clusters

Coalescence                    Impingement
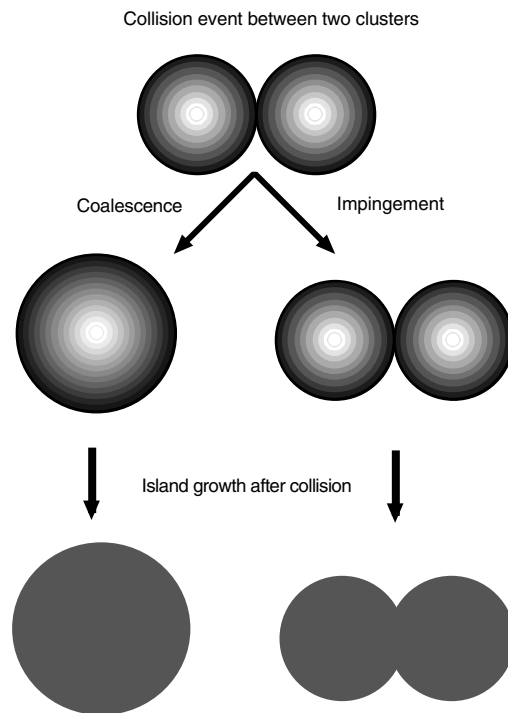
Island growth after collision

**Figure 1.** When two clusters meet, two extreme events can follow: coalescence and impingement. The former consists in the conservation of shape and the island centre locates at the mass centre of the two clusters. The latter does not entail any redistribution of mass and each cluster maintains its individuality. In this case, as the growth proceeds, discs (representing clusters) overlap.

to the monomer lifetime [4, 5] (random walk theory) during the stage of growth, i.e. when the nucleation rate is exhausted. To this is devoted the last part of the present article, where we will discuss the strength and weaknesses of this conjecture comparing the analytical results with Monte Carlo (MC) simulations. The first part is dedicated to the definition of the quantities and to the calculation of the moments.

The pdf $P(\delta)$ has been described in detail by Torquato in his book [6] and here we will make use of the same notation as Torquato. To begin with, let us define the pdf at issue; it is

$$P(\delta) = \frac{H_v(\delta + \sigma/2)}{1 - \Theta} \tag{1}$$

where $H_v(r) = -\frac{\partial E_v(r)}{\partial r}$ and $E_v(r)$ is the probability of finding a region of area $\pi r^2$ around some arbitrary point, empty of island centres. The expression of the exclusion probability $E_v(r)$, for a system of dots (centres of the islands) obeying any degree of spatial correlation, has been derived in [7] and [8]. $\Theta$ is the fraction of surface covered by discs.

Let us suppose to have a random distribution of $N_0$ non-overlapping discs of diameter $\sigma$; in this case from [6] we get

$$H_v(r) = \frac{8\Theta}{\sigma}\left(a_0\frac{r}{\sigma} + a_1\right)E_v(r) \tag{2}$$

and

$$\frac{E_v(r)}{1 - \Theta} = \exp\left\{-\Theta\left[4a_0\left(\frac{r}{\sigma}\right)^2 + 8a_1\frac{r}{\sigma} + a_2\right]\right\}, \tag{3}$$
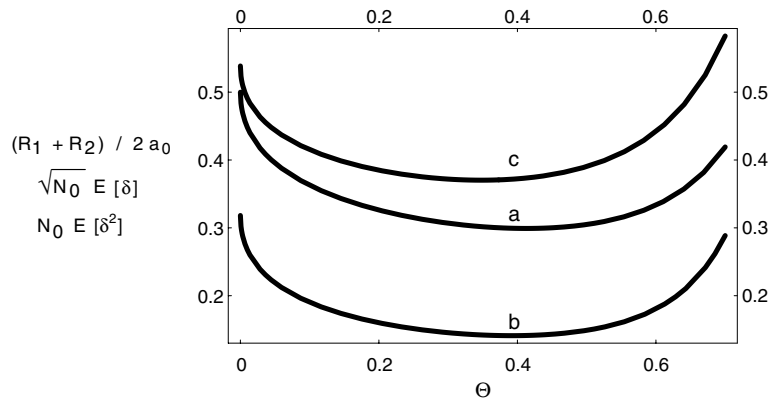
**Figure 2.** Mean field coalescence approximation. The curves (a) and (b) represent the first and second moments of the probability density function that a generic point of the surface lies between $\delta$ and $\delta + \mathrm{d}\delta$ from the edge of some island, equations (8), (9). $N_0$ is the number density of nuclei. The minimum of these curves, a peculiarity of coalescence process, can be understood through the simple model pictured in figure 5 (see also the text). In this model two representative distances, $R_1$ and $R_2$, are used to describe the space available for growth at a given coverage. Their average is shown by curve (c).

where $a_0 = \frac{1+0.128\Theta}{(1-\Theta)^2}$, $a_1 = \frac{-0.564\Theta}{(1-\Theta)^2}$, and $a_2 = -(a_0 + 4a_1)$. Nonetheless, simpler relations can be used paying a small tribute to the exactness of the result after Helfand *et al* [9]; they are $a_0 = \frac{1}{(1-\Theta)^2}$, and $a_1 = \frac{-\Theta}{2(1-\Theta)^2}$. We will make use of these in what follows. In the mean field approximation [1] it is possible to determine the evolution of the number of islands as a function of coverage, obtaining

$$n(\Theta) = \frac{N(\Theta)}{N_0} = (1 - \Theta)\mathrm{e}^{-\frac{\Theta}{1-\Theta}}, \tag{4}$$

where $N_0$ is the number of dots or islands (or discs) at $\Theta = 0$. It is quite clear that the following expression holds:

$$\frac{\Theta}{n(\Theta)} = N_0 \frac{\pi \sigma^2}{4}. \tag{5}$$

Thanks to equations (1)–(5) it is possible to calculate the first two moments of $P(\delta)$,

$$\mathbb{E}[\delta] = \frac{(4\Theta)^{\frac{3}{2}}}{\sqrt{\pi N_0 n(\Theta)}} \int_{\frac{1}{2}}^{\infty} (2\xi - 1)(a_0\xi + a_1)\mathrm{e}^{-\Theta(4a_0\xi^2 + 8a_1\xi + a_2)} \, \mathrm{d}\xi \tag{6}$$

$$\mathbb{E}[\delta^2] = \frac{8\Theta^2}{\pi N_0 n(\Theta)} \int_{\frac{1}{2}}^{\infty} (2\xi - 1)^2(a_0\xi + a_1)\mathrm{e}^{-\Theta(4a_0\xi^2 + 8a_1\xi + a_2)} \, \mathrm{d}\xi \tag{7}$$

which, respectively, lead to the following formulae:

$$\mathbb{E}[\delta] = \sqrt{\frac{1 - \Theta}{4N_0}} \mathrm{e}^{\frac{\Theta(3-2\Theta)}{2(1-\Theta)}} \mathrm{Erfc}(\sqrt{\Theta}) \tag{8}$$

$$\mathbb{E}[\delta^2] = \frac{(1 - \Theta)}{\pi N_0} \mathrm{e}^{\frac{\Theta}{1-\Theta}} \left[ 1 - \sqrt{\pi \Theta}\mathrm{e}^{\Theta}\mathrm{Erfc}(\sqrt{\Theta}) \right]. \tag{9}$$

The plots of the first two moments as a function of coverage are reported in figure 2. Both display a minimum at $\Theta \approx 0.4$.
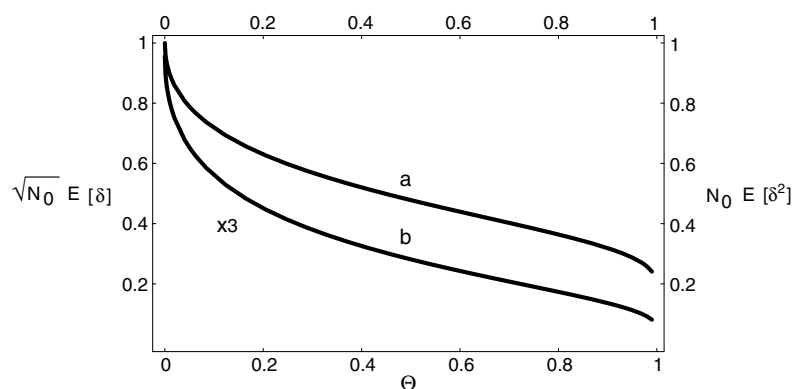
**Figure 3.** Impingement growth mode. Curve (a) (left scale) and curve (b) (right scale) represent the first and the second moments of the probability density function that a generic point of the surface lies between $\delta$ and $\delta + \mathrm{d}\delta$ from the edge of some island, equations (10), (11). $N_0$ is the number density of nuclei.

In figure 3 the first two moments have been reported as a function of coverage in the case of growth governed by impingement where the nucleation of the $N_0$ centres is simultaneous and their distribution is random throughout the whole surface. They have been obtained following the same procedure as for equations (8), (9) but now $E_v(r) = \mathrm{e}^{-N_0\pi r^2}$. The respective analytic expressions are

$$\mathbb{E}[\delta] = \frac{1}{1-\Theta}\frac{1}{\sqrt{\pi N_0}}\int_{\sqrt{-\ln(1-\Theta)}}^{\infty}\mathrm{e}^{-x^2}\,\mathrm{d}x$$

$$= \frac{1}{\sqrt{N_0}}\frac{1}{1-\Theta}\mathrm{Erfc}\left(\sqrt{-\ln(1-\Theta)}\right) \tag{10}$$

$$\mathbb{E}[\delta^2] = \frac{2}{\pi N_0}\frac{1}{1-\Theta}\int_{\sqrt{-\ln(1-\Theta)}}^{\infty}\left(x - \sqrt{-\ln(1-\Theta)}\right)\mathrm{e}^{-x^2}\,\mathrm{d}x$$

$$= \frac{1}{\pi N_0}\left\{1 - \frac{\sqrt{-\pi\ln(1-\Theta)}}{1-\Theta}\mathrm{Erfc}[\sqrt{-\ln(1-\Theta)}]\right\}. \tag{11}$$

In this case the moments go to zero monotonically as $\Theta$ goes to one.

It is also possible to evaluate the average distance between the edges of two islands by exploiting the function $H_p(r) = -\frac{\partial E_p(r)}{\partial r}$ [6], $E_p(r)$ being the probability that no dots fall within the circle of area $\pi r^2$ whose centre coincides with another dot chosen at random. In the case of non-overlapped hard discs

$$E_p(r) = \exp\left\{-\Theta\left[4a_0\left(\left(\frac{r}{\sigma}\right)^2 - 1\right) + 8a_1\left(\frac{r}{\sigma} - 1\right)\right]\right\}. \tag{12}$$

Insofar as the average distance among dots is

$$l_p = \int_{\sigma}^{\infty}H_p(r)r\,\mathrm{d}r, \tag{13}$$

integrating by parts, so as to evidence the average edge–edge island separation, equation (13) can be recast:

$$\lambda_p = l_p - \sigma = \int_{\sigma}^{\infty}E_p(r)\,\mathrm{d}r, \tag{14}$$
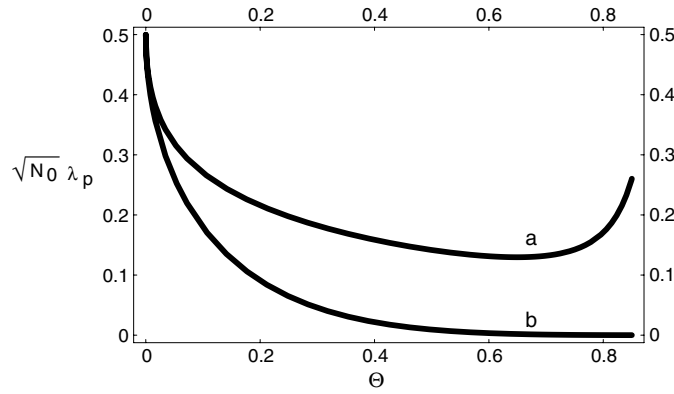
**Figure 4.** The average edge–edge distance among islands is reported for coalescence (curve (a)) and impingement (curve (b)) growth modes (equations (15), (16)). $N_0$ is the number density of nuclei.

and using equation (12), one ends up with

$$\lambda_p^{\text{coal}} = \frac{\sqrt{1 - \Theta}}{2\sqrt{N_0}} e^{\frac{\Theta(3 - \Theta)(3 - 2\Theta)}{2(1 - \Theta)^2}} \text{Erfc}\left[\frac{\sqrt{\Theta}(2 - \Theta)}{1 - \Theta}\right]. \tag{15}$$

The behaviour of $\lambda_p^{\text{coal}}$ as a function of coverage is displayed in figure 4. In the same figure $\lambda_p^{\text{imp}}$ in the case of impingement, whose analytic expression is

$$\lambda_p^{\text{imp}} = \frac{1}{2\sqrt{N_0}} \text{Erfc}[2\sqrt{-\ln(1 - \Theta)}], \tag{16}$$

is also displayed for comparison.

As for the first two moments of $P(\delta)$, also in this case while impingement gives a monotonic behaviour towards zero as $\Theta$ goes to one, coalescence discloses a minimum. It occurs at $\Theta = 0.649$, which is a value intriguingly close to the two dimensional (2D) percolation threshold in the case of random distribution of circular islands in the impingement mechanism (0.67) [10]. As a matter of fact, a similar calculation for the 1D case (not reported here), reveals a minimum at $\Theta = 1$, that is exactly at the percolation threshold. We conjecture that the minimum yields the percolation threshold and the small disagreement in the 2D case is ascribable to the approximated correlation function and, in turn, to the $n(\Theta)$ function.

From figures 2 and 3 it stems that the minimum of the moments of $P(\delta)$ is a peculiarity of the coalescence regime if the gaps created by the wiping action subsequently to a coalescence event are not filled by secondary nucleation [11]. In order to evidence the origin of the minimum the following rough but instructive calculation has been performed.

Let us consider, at any time during the growth with coalescence, islands to be arranged in a 2D hexagonal lattice. The lattice parameter is $a = \sqrt{\frac{4}{N\sqrt{3}}} = \frac{a(0)}{\sqrt{n}} = (\sigma + 2R_1)$, where $a(0) = \sqrt{\frac{4}{N_0\sqrt{3}}}$ is the value of $a$ at zero coverage and $2R_1$ is the distance between the edges of two neighbouring islands as shown in figure 5. Besides, we denote with $R_2$ the distance of the island edge from the centre of the equilateral triangle of side $a$ (see figure 5). The following relationship holds:

$$\Theta = \frac{\pi}{2\sqrt{3}}\left(\frac{\sigma}{a}\right)^2, \tag{17}$$
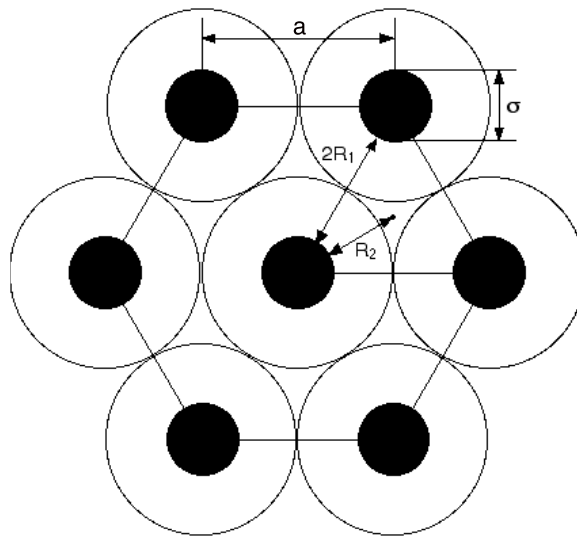
**Figure 5.** Drawing of the hexagonal lattice employed to explain the minima in the curves (a) and (b) of figure 1. The black discs are the islands. The variables used in the text are also defined.

which implies that

$$\frac{\sigma}{a} = \sqrt{2\frac{\sqrt{3}}{\pi}\Theta}. \tag{18}$$

Since $R_1 = \frac{a}{2}(1 - \frac{\sigma}{a})$ and $R_2 = \frac{a}{\sqrt{3}}(1 - \frac{\sqrt{3}\sigma}{2a})$, we end up with

$$\frac{R_1}{a(0)} = \frac{1}{2(1-\Theta)^{1/2}}\left[1 - \sqrt{\frac{2\Theta\sqrt{3}}{\pi}}\right]e^{\frac{\Theta}{2(1-\Theta)}} \tag{19}$$

and

$$\frac{R_2}{a(0)} = \frac{1}{\sqrt{3}(1-\Theta)^{1/2}}\left[1 - \sqrt{\frac{3\Theta\sqrt{3}}{2\pi}}\right]e^{\frac{\Theta}{2(1-\Theta)}}. \tag{20}$$

The average of these functions, displayed in figure 2, exhibits a minimum at $\Theta \approx 0.4$.

This simple calculation shows that the consumption of the free area during growth is overcompensated by the decrease of the number of the islands resulting in the minimum of the momenta.

It is worth noting that the mean field approach can also be used to evaluate the moments of $\delta$, and therefore, as we will show shortly, the adatom life time, in the case of spatially correlated nuclei according to the hard core interaction [8]. To this end equations (6), (7) can still be employed provided the $n(\Theta)$ function appropriate to the correlated case is used [1].

The second moment of $P(\delta)$ can be exploited for determining the characteristic time (hereafter capture time) that a monomer spends wending on the surface before being captured by an island, when all the islands have the same size and shape. This is the very condition described at the beginning of the paper which could be referred to as the average coalescence mechanism.

Although in a slight different manner, we have already used $P(\delta)$ to estimate the capture time for growth governed by impingement [12]. As a matter of fact, the area $\langle r^2 \rangle$ covered by a
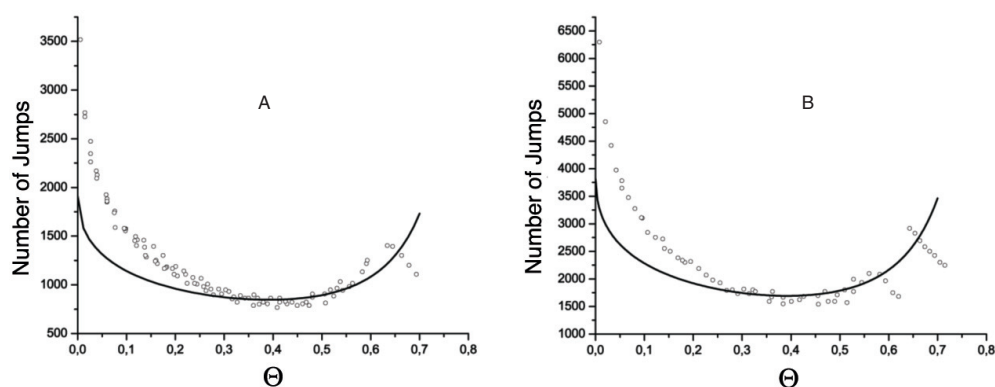
**Figure 6.** Behaviour of the normalized adatom life time ($DN_0\tau$) in the coalescence regime. The Monte Carlo simulations are compared to the analytical results reported in equation (9). To adapt the analytical result to the numerical output the former has been multiplied by the factor 15/4 (see the text for details). The number of nucleation centres per lattice point is $3.125 \times 10^{-4}$ (panel A); $6.25 \times 10^{-4}$ (panel B). The analytical and numerical results become comparable above $\Theta \approx 0.2$.

random walker, after a time $t$, is proportional to $t$, thus within the time of capture, $\tau \sim \langle \delta^2 \rangle$. In other words, apart from a constant, the function $\tau(\Theta)$ is the second moment of $P(\delta)$.

In order to check our hypothesis an MC simulation has been performed. The simulation takes place in a $400 \times 400$ square lattice on which 50 or 100 centres of nucleation are chosen at random. The growth law is deterministic and is modelled as $r(t) = ct^n$, $r$ being the radius of the island while $c$ and $n$ are constants. The growth law applies to all islands, thus they have always the same size. For any given coverage the number of islands is calculated by means of equation (4) and a correspondent morphology is generated. A random walker is generated at random onto the non-covered surface and is left free to diffuse with equal probability in the four directions. The walker can perform only one lattice unit jump at a time. When it encounters the edge of an island it is captured and the number of jumps is stored; the number of jumps is, in fact, the capture time. Its value is obtained by the following procedure. After having generated a new morphology, a mean capture time is evaluated by averaging over 10 000 random walks and then the final value is achieved by averaging ten mean values. The comparison between the simulation and equation (9) is reported in figure 6. In order to adapt the numerical output to equation (9), the latter has been multiplied by a factor 15/4 independently of the number of nucleation centres in order to best fit the analytical result to the high coverage region. This choice is suggested by the apparent limits of our model where the region swept by the random walker is substituted by a compact disc [12, 13]. The validity of this approximation has been discussed in some details in [12], where a suitable corrective factor has been inserted in the probability distribution function whose effect results in a multiplicative factor in the expression of the adatom life time. The approximation becomes better and better the larger the size of the islands and the larger the number of jumps before the capture, although the latter becomes less important as the islands go on growing. The effect of these two conditions is particularly dramatic at lower coverage $\Theta \lesssim 0.25$, as witnessed by figure 6. This explanation can be better appreciated if instead of the random walk of a point among a distribution of discs, one considers the dual, for all practical purposes, equivalent process, according to which a random walk is performed by a disc among points. In this case the discs are substituted by their own centres and the walker carries with it an area equal to that of one disc at given $\Theta$. On the basis of this argument the agreement between the analytical model and the simulation is expected to increase as the nucleation density decreases. This is supported by figure 6, too.
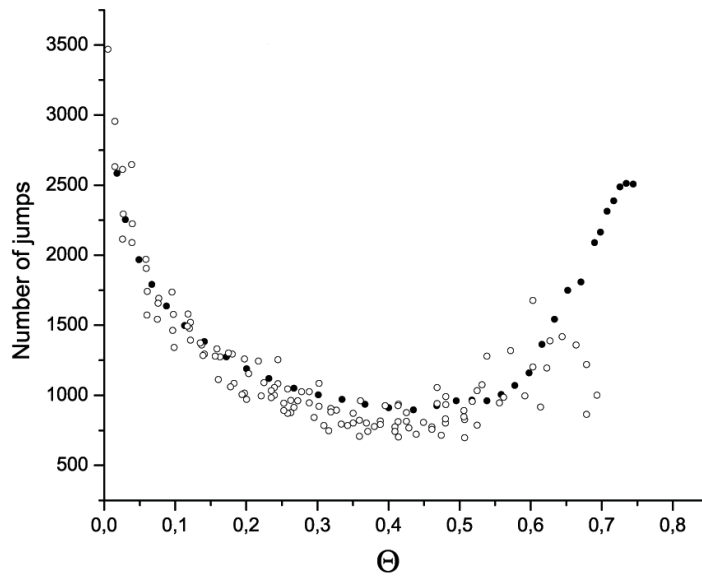
**Figure 7.** Comparison between the Monte Carlo simulations for mean field (open symbols) and genuine coalescence (full symbols). The number of nucleation centres per lattice point is $6.25 \times 10^{-4}$.

Here and in the previous article [2] we have adopted the mean field approach to treat the morphology of the film ruled by coalescence. In order to test the validity of the approximation we have performed an MC simulation for genuine coalescence, according to which the island forming after a collision (basically binary) conserves the shape and the area and is centred in the centre of mass of the parent islands [14]. Figure 7 shows the case of 100 initial nuclei growing in a $400 \times 400$ square lattice. The capture time, for each coverage, is obtained by averaging 30 mean values (i.e. 30 different morphologies) obtained from any single morphology over 6000 random walks. The comparison with the mean field output, displayed in the same figure, demonstrates that the two curves are hardly distinguishable in spite of the quite different morphologies (figure 8). The scattering of the open symbol points beyond $\Theta = 0.65$ is due to the fact that after that coverage value, on average, just one island remains. Obviously, under these circumstances, collision events no longer occur; as a consequence the life time can only decrease with coverage. In other words the comparison makes sense up to $\Theta = 0.65$.

The analytical modelling of the adatom life time can also be exploited for estimating a kinetic quantity that is a key ingredient in the rate equation approach to the film growth, namely the capture number, $\sigma_c$. It is worth emphasizing that this last quantity is, in general, a function of the island size [15]. By averaging over the island size distribution function, it can be reduced to a function of coverage which enters in the rate equation for adatom density [16, 17]. As anticipated, the adatom life time, $\tau$, is related to the second moment of the distribution according to $\mathbb{E}[\delta^2] = 4D\tau$, where $D$ is the diffusion coefficient of the adatoms. On the other hand, in the mean field rate equations the consumption of adatoms by the growing islands is usually written as $n_1 N D \sigma_c$, where $n_1$ is the number density of the adatoms. Furthermore, since this last expression is also equal to $n_1/\tau$, one ends up with the coverage dependent capture factor

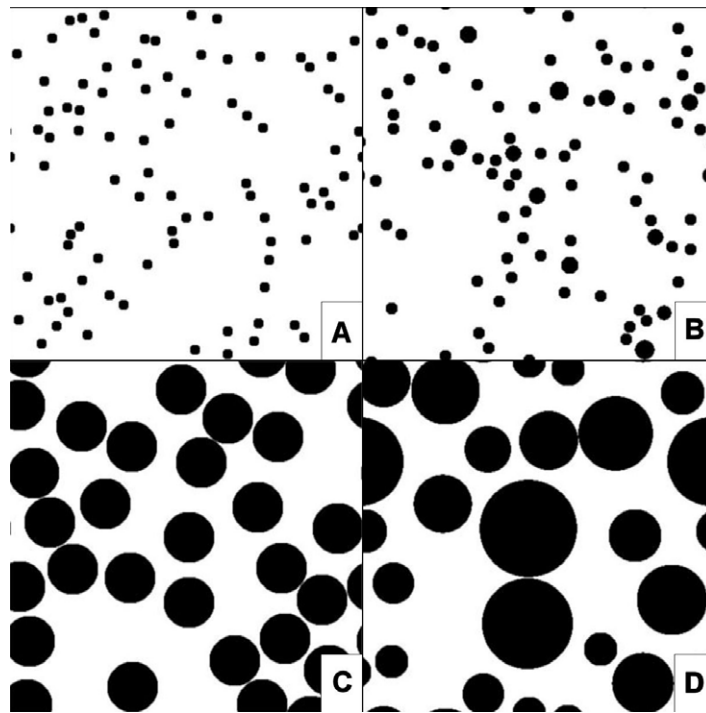$$\sigma_c = \frac{4}{N_0 \mathbb{E}[\delta^2] n}. \tag{21}$$

**Figure 8.** Comparison between the morphologies for mean field (panels (A), (C)) and genuine (panels (B), (D)) coalescence. Panels (A) and (B) $\Theta = 0.06$; panels (C) and (D) $\Theta = 0.43$.
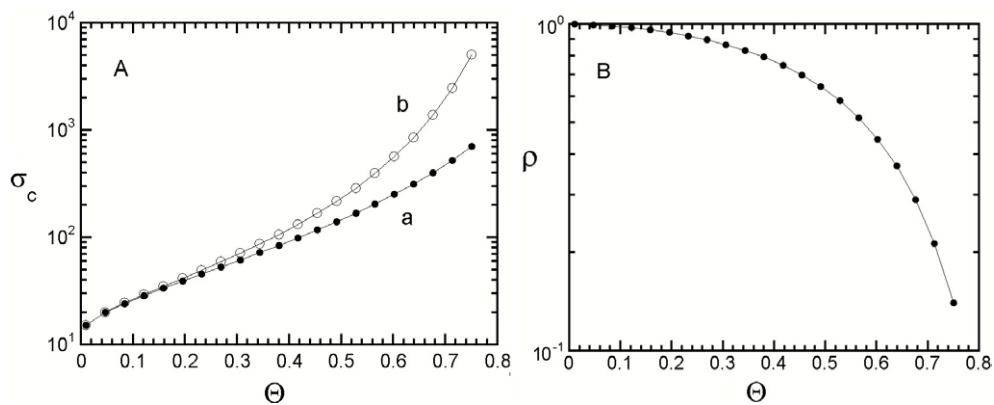


**Figure 9.** Panel (A) Analytical estimation of the island capture factor for coalescence (curve (a)) and impingement (curve (b)) growth modes. Panel (B) Ratio between the capture factors of panel (A).

Although equation (21) has been derived in the specific case of simultaneous nucleation, its validity is more general. In fact, as discussed in [18], in the framework of the rate equation approach (mean field) it can be used for describing non-simultaneous nucleation as well. The capture factors for growth ruled by both coalescence and impingement mechanisms have been shown in figure 9 (panel (A)) as a function of coverage. In panel (B) the ratio between the

two functions, $\rho = \frac{\sigma_{\mathrm{c}}^{(\mathrm{imp})}}{\sigma_{\mathrm{c}}^{(\mathrm{coal})}}$ is also displayed. It is worth noting that in the low coverage regime ($\Theta < 0.15$) the capture factors are nearly equal. This means that the kinetics of the film growth, as described by microscopic rate equations, should not be sensitive to the growth mechanism up to $\Theta = 0.15$.

In summary, on the basis of the mean field approach the statistical mechanics of rigid discs can be exploited for computing the adatom life time in thin film growth ruled by the coalescence mechanism. Moreover, we proved by numerical simulation that the adatom life time in the mean field coalescence is, in fact, equivalent to that obtained in the genuine coalescence case.

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