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Terrace sizes in molecular beam epitaxy

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Abstract . — The order of magnitude of the typical distance ℓ between steps in MBE-grown crystal surfaces is calculated from simple scaling assumptions in the absence of evaporation. This distance is measurable by diffraction methods and yields access to the surface diffusion constant D . At the lowest non trivial temperatures the characteristic distance is of order $(D/F)^{1/6}$ where F is the beam flux. At slightly higher temperature, ℓ is given by an algebraic formula which depends on the lifetime τ_2 of a bound pair of adatoms at the surface, as well as of the diffusion constant D_2 of these pairs. In certain ranges, ℓ varies as $F^{-1/4}$ or $F^{-1/5}$. At higher temperatures yet, ℓ is given by a formula which depends on a larger number of parameters. In special cases, our results are in agreement with the classical formulae of Stoyanov and Kashchiev, but disagree with certain recent works. ℓ is found to increase with temperature more rapidly than an Arrhenius exponential. Monte-Carlo simulations are reported and the discrepancy with certain other authors is clarified.

1. Introduction.

The theory of crystal growth involves three lengthscales: at microscopic lengthscales one has to worry about the chemical properties of the constituents, and this difficult task can only be numerical, and is different for different chemical species. At "macroscopic" scales, continuum theories are appropriate, the most popular of which is that of Kardar, Parisi and Zhang [1]. The present work is concerned with what may be called "mesoscopic" scales, i.e. the average size of terraces of atomic thickness which are growing until they coalesce. This size increases rapidly with temperature. The mechanism of crystal growth has been described a long time ago by Frenkel [2], and then by Zinnsmeister [3], who wrote the appropriate rate equations. These works have been reviewed by Venables *et al.* [4]. The rate equations can be used to

evaluate the typical radius ℓ of islands (or "terraces") on a growing surface, and the results are reported in detail by Stoyanov and Kashchiev [5]. More recently, the development of molecular beam epitaxy motivated new investigations, for example by Irisawa *et al.* [6] and De Miguel *et al.* [7] who found a dependence of ℓ on the beam flux F which is different from that obtained by Stoyanov and Kashchiev. On the other hand, Mo *et al.* [8] found the same result as Stoyanov and Kashchiev in the isotropic case, but also investigated growth on an anisotropic surface and found new results. The anisotropic case is of great interest since Si(001) is an example [8]. In the present work this problem is reinvestigated. Our results are in agreement with those of Stoyanov and Kashchiev [5] apart from weak corrections, but new formulae are obtained in certain cases which were not investigated by these authors. In the anisotropic case our results do not reproduce those of Mo *et al.*

Our model of MBE is the following : there is a constant flux of atoms hitting the surface and the sticking coefficient is 1 or, at least, independent of the local conditions (step or not step). The freshly landed atoms diffuse until they reach a step. In most of this paper it will be assumed, as is generally done [5] that terraces larger than some critical size (say with more than i^* atoms) do not release atoms and do not move. At low temperatures, i^* is expected to be equal to 1. In the terminology used here, a pair of adatoms is already a "terrace", although the words "cluster" or "island" will also be used for such small terraces.

The flux of atoms per adsorption site and unit time will be called F . The interesting case is when F is sufficiently small, so that surface diffusion is appreciable. However, volume diffusion will be neglected.

To simplify notations, all lengths will be measured in atomic distances, all velocities in atomic distances per time unit, and the diffusion constant D will be measured in squared atomic distances per unit time. The number of adsorption sites will be assumed to be equal to the number of surface atoms on the ideal surface (in Stoyanov's notations, $N_o = 1$). Evaporation will be neglected, as is correct if the temperature is not too high. The absorption probability of an adatom reaching a step will be taken equal to 1. Finally, the model is applicable to the surface of an element rather than a compound as GaAs.

2. The nucleation process and the characteristic length ℓ .

ℓ has been defined as the typical terrace size. It will be assumed to be also the typical distance between steps. And it will be assumed to be the same in the steady regime of RHEED oscillations and in the submonolayer regime, when about 1/4 of monolayer has been deposited on an initially flat substrate. In addition, it will be assumed not to fluctuate by a huge factor, so that the variance of the distance between steps is not much bigger than its average value. This is a reasonable assumption which is equivalent to the statement that nucleation should take place as soon as a terrace reaches a size of order ℓ .

The deposition of the first fraction (say, 1/4) of monolayer on the initially flat substrate occurs as described by figure 1. First (Fig. 1a) adatoms form "nuclei" (pairs if $i^* = 1$ as in figure 1). This occurs with probability $1/\tau_{\text{nuc}}$ in the unit time on each site. Then these nuclei grow by capture of adatoms (Fig. 1b). Thus they become "islands" or "terraces" and finally, after reaching a size of order ℓ , they merge into a unique set which, after filling the holes, will form the first deposited monolayer. This picture implies that terraces reach a size of order ℓ in a time of order $1/F$, the time necessary for monolayer completion. Therefore the average number $\ell^2/(F\tau_{\text{nuc}})$ of nucleation events in an area $\ell \times \ell$ during the time $1/F$ should be of order 1.

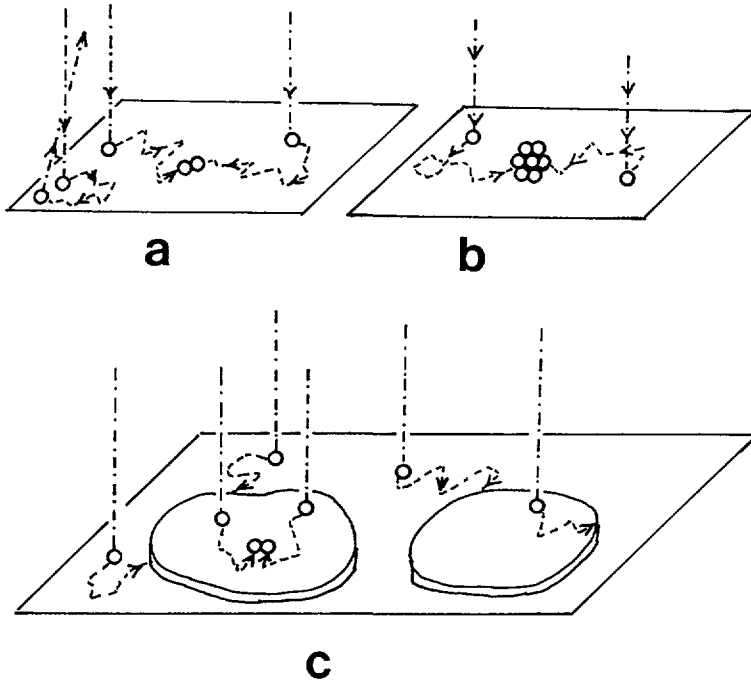


Fig. 1. — Phases of MBE growth. a) Two adatoms diffuse on the surface until they meet and form a stable nucleus (here a pair, $i^* = 1$) while a third one evaporates and is pumped by the vacuum apparatus. b) The nucleus grows by capture of adatoms and forms a terrace. c) two growing terraces (the atomic structure of which is not shown) have reach such a size that they are going to merge, while a new nucleus appears inside one of the terraces. The time between (a) and (c) is of order $1/F$ if evaporation is negligible.

Thus, the nucleation rate per site $1/\tau_{\text{nuc}}$ can be related to the typical length ℓ by the following relation valid in order of magnitude:

$$\boxed{1/\tau_{\text{nuc}} \approx \frac{F}{\ell^2}} \quad (1)$$

An important assumption in the derivation of this relation is that coalescence of islands occurs only near layer completion, i.e. when islands cease to be islands. The alternative method used by Venables *et al.* or Mo *et al.* is equivalent: they write that the density $N = 1/\ell^2$ of islands is changed only by nucleation, and not by coalescence.

In deriving (1), it has also been assumed that islands are compact rather than fractal. This is not true at very low temperature. This point is addressed in section 9. Also, the case of anisotropic diffusion is addressed in section 6.

The strategy is now to evaluate the nucleation time τ_{nuc} and then to use (1). When evaporation is important, formula (1) is not applicable.

3. The lifetime and density of adatoms.

A freshly landed adatom diffuses during a time τ_1 until it sticks to a step.

The density ρ_1 of adatoms is equal to the beam flux F multiplied by the "lifetime" τ_1 .

$$\rho_1 = F\tau_1. \quad (2)$$

In the absence of evaporation, the mean free path of an adatom is of the order of magnitude of the typical distance ℓ between steps. Therefore, its average lifetime is

$$\tau_1 \approx \ell^2/D \quad (3)$$

where D is the diffusion constant of adatoms on the surface.

According to (2) and (3) the adatom density is equal to

$$\rho_1 \approx \frac{F\ell^2}{D} \quad (4)$$

Even at equilibrium ($F = 0$) ρ_1 has a non-vanishing value, which is not negligible at high temperature. However, it will be neglected here for the sake of simplicity.

Relation (4) holds only as an average, since ρ_1 is by no means uniform. Its variation in space and time in the absence of clustering has been studied by Burton, Cabrera and Frank [9], whose results are consistent with (4). The symbol " \approx " means "of the order of magnitude of".

4. Collisions of adatoms with other adatoms or small adatom clusters.

In order to evaluate the nucleation time τ_{nuc} , which appears in (1), one needs the rate of formation of a critical nucleus, which may be a pair, a triplet, etc. A critical nucleus forms when an adatom hits a subcritical nucleus which is a single adatom or a pair, etc. Thus one has to calculate the number of collisions of an adatom with another adatom or a pair, etc.

The adatom diffuses during a time $t = \tau_1$. During the time t it moves by a distance $R(t)$ defined by $R^2(t) \simeq 4Dt$, where D is the surface diffusion coefficient. In two dimensions, the probability that $R = 0$ at time t is well known to be of order $1/Dt$. Thus the average number of times the adatom visits its landing point is of order $\ln(Dt)$. This should also be the order of magnitude of the number of times the atom visits all sites visited. Since the adatoms makes Dt jumps in the time t , the average number of sites visited in the time t is approximately $\nu(t) \approx Dt/(\ln Dt)$. This derivation is approximate because the average of the reciprocal number of visits is not the reciprocal of the average number of visits. However, the result turns out to be exact [10]. More precisely, the number of sites visited in a random walk of n steps is for large n

$$\nu(n) \simeq \frac{\pi n}{\ln(n)} \approx \frac{\pi \ell^2}{\ln(\ell^2)} \approx \frac{\pi Dt}{\ln(Dt)} \quad (5)$$

Replacing t by τ_1 , the probability that an adatom collides with a motionless species of low density ρ_n is seen to be

$$p_n \approx \frac{D\tau_1}{\ln(D\tau_1)} \rho_n \quad (6)$$

This formula yields the number of collisions of an adatom with a pair ($n = 2$) or a triplet, etc. Adatom-adatom collisions ($n = 1$) are given by an analogous formula (in principle with a slightly larger coefficient). Indeed it is possible to repeat the argument in the frame of reference in which one of the adatom is motionless.

5. Low temperatures : the case $i^* = 1$.

The temperatures considered in this section are such that i) there is no evaporation. ii) pairs are stable and immobile. This case has been considered by many authors [5,8] and their results will be re-established here as an exercise... and with a logarithmic correction.

If condition (ii) is satisfied, the nucleation rate is equal to the rate of adatom collisions. It is therefore the product of p_1 by the rate F of incoming atoms per sites. Using (6), (5), (3) and (4) one obtains

$$\frac{1}{\tau_{\text{nuc}}} \approx F p_1 \approx \frac{F D \tau_1}{\ln(D \tau_1)} \rho_1 \approx \frac{F^2 \ell^4}{D \ln(\ell^2)} \quad (7)$$

Insertion into (1) yields

$$\frac{\ell^6}{\ln(\ell^2)} \approx \frac{D}{F} \quad (8)$$

This formula has been obtained by several authors [5,8] apart from the logarithm. However the logarithmic correction is small in all cases of practical interest, and the usual formula

$$\ell \approx (D/F)^{1/6} \quad (9)$$

is in practice acceptable. For instance, if $F = 1$ Hz and $D = 10^{12}$ Hz (which is certainly a strong overestimation at low temperature), (9) yields $\ell = 100$ interatomic distance and $\ln(\ell^2) \simeq 9$. At low temperatures where pairs are stable and (7) applies, the diffusion coefficient is expected to satisfy $D < 10^6$ Hz, and the logarithmic correction in (8) is less than 3.

Note that a number of quantities of order of magnitude 1 have been omitted in (8), which are present in the formula of Stoyanov and Kashchiev.

Formula (9) disagrees with that of De Miguel *et al.* [7] and Irisawa *et al.* [6] who find an exponent 1/4 rather than 1/6. As discussed in section 9, this disagreement is probably due to the small size and short times used in simulations.

6. Anisotropic diffusion.

From now on, logarithmic corrections will be disregarded.

6.1 INFINITELY ANISOTROPIC DIFFUSION AND STICKING. — It is of interest to treat the case of an anisotropic substrate like Si [8]. Let the anisotropy be assumed first to be infinite. Each atomic row is disconnected from the others. The problem is now one-dimensional, but it is of interest to call d' the dimension of the space where diffusion takes place. In this subsection, $d' = 1$, while the previous sections correspond to $d' = 2$. Equations (2), (3) and (4) are correct for any value of d' . However, equation (1) has to be generalized as

$$1/\tau_{\text{nuc}} \approx \frac{F}{\ell^{d'}} \quad (10)$$

On the other hand, (5) is to be replaced for $d' \leq 2$ by

$$\nu(t) \approx (Dt)^{d'/2}$$

and (6) by

$$p_1 \approx \rho_1 (D \tau_1)^{d'/2}$$

Using (3) and (4) which are still correct, (7) becomes

$$\frac{1}{\tau_{\text{nuc}}} \approx F p_1 \approx F \rho_1 (D \tau_1)^{d'/2} \approx F \rho_1 \ell^{d'} \approx F^2 \ell^{2+d'} / D \quad (11a)$$

and insertion into (10) yields for $d' = 1$

$$\ell \approx (D/F)^{1/4} \quad (12)$$

This result is correct in the stationary regime. Mo *et al.* treated the growth of an initially flat surface and, for a coverage $\theta < 1/2$ they found $\ell \approx (D/F)^{2/7} \theta$. Our result (12) corresponds to $\theta \approx 1/4$, and therefore disagrees with the result of Mo *et al.* Indeed, these authors use an expression of the nucleation rate $1/\tau_{\text{nuc}}$ which would be correct in the absence of islands. Then, in a d' -dimensional space, an adatom visits $(Dt)^{d'/2}$ sites in a time t . The probability that an adatom meets another adatom in the time t is therefore $\rho_1 (Dt)^{d'/2}$. Mo *et al.* introduce a nucleation-limited lifetime τ_n corresponding to this probability being of order 1, hence

$$1/\tau_n \approx D \rho_1^{2/d'}$$

Then they write that the nucleation rate per site and unit time is

$$\rho_1/\tau_n = D \rho_1^{1+2/d'} \quad (11b)$$

This is correct when there are no islands yet. However, in the steady regime, the adatoms are mostly swallowed by steps before being able to form new nuclei, and the correct formula for the nucleation rate per site is (11a) and not (11b). Both formulae turn out to coincide in the isotropic case $d' = 2$ when (4) is applied. The computer simulations published by Mo *et al.* seem to be in good agreement with (12).

6.2 INFINITELY ANISOTROPIC DIFFUSION WITH ISOTROPIC STICKING. — Mo *et al.* noticed that anisotropic diffusion does not produce anisotropic islands. Anisotropic islands result from anisotropic sticking coefficients, when adatoms diffusing along a row do not stick to the island growing on the other row. It is of interest to treat the case of an infinitely anisotropic surface diffusion and an isotropic sticking. Then (11) is valid with $d' = 1$, but (10) should be applied with $d' = 2$. The result is

$$\ell \approx (D/F)^{1/5} \quad (13)$$

7. The case $i^* = 2$.

In this section, two effects neglected in the previous section will be taken into account:

i) When the temperature is increased, pairs are no longer stable. More precisely, their decay rate $1/\tau_2$ becomes too high to be neglected.

ii) The assumption that pairs do not move is not correct. The pair diffusion constant D_2 has to be introduced.

Let a rate equation be written for the density of pairs ρ_2 . Triplets will be assumed to be stable. The variation rate $\dot{\rho}_2$ is the sum of the following terms where logarithmic corrections are neglected:

i) The creation rate by adatom collisions. It should be equal to the rate of collision of adatoms per site and unit time, which is $p_1 F$ or, according to (6) and (2) and neglecting the logarithmic correction:

$$(\dot{\rho}_2)_1 = D\rho_1^2 \quad (14)$$

ii) The inverse process corresponds to a term

$$(\dot{\rho}_2)_2 = -\rho_2/\tau_2 \quad (15)$$

iii) The nucleation of stable triplets by adatom-pair collision is equal to minus the rate $p_2 F$ of adatom-pair collisions per unit time and per site, or according to (6) and (2) and neglecting the logarithmic correction

$$(\dot{\rho}_2)_3 = -D\rho_1\rho_2 \quad (16)$$

iv) The destruction of pairs by absorption by a bigger terrace yields a term

$$(\dot{\rho}_2)_4 = -\rho_2/\tau_2^{\text{dif}}$$

where τ_2^{dif} is the time necessary for a diffusing pair to reach a terrace. This time is just given by (3), where D has to be replaced by D_2 . Thus

$$(\dot{\rho}_2)_4 = -\rho_2 D_2/\ell^2 \quad (17)$$

v) There is a term analogous to (14), but with the opposite sign, due to coalescence of two diffusing pairs

$$(\dot{\rho}_2)_5 = -D_2\rho_2^2 \quad (18)$$

Addition of all terms yields

$$\dot{\rho}_2 = D\rho_1^2 - \rho_2/\tau_2 - D\rho_1\rho_2 - \rho_2 D_2/\ell^2 - D_2\rho_2^2 \quad (19)$$

One will now write that a steady regime has been reached, in which (19) vanishes. As stressed in section 5, the densities vary in space and time as testified by RHEED oscillations [11,12]. Therefore, only the average densities ρ_1 and ρ_2 may be assumed to satisfy the stationary form of (19), namely

$$D\rho_1^2 - \rho_2/\tau_2 - D\rho_1\rho_2 - \rho_2 D_2/\ell^2 - D_2\rho_2^2 = 0 \quad (20)$$

The nucleation rate is the sum of $-(\dot{\rho}_2)_3$ and $-(\dot{\rho}_2)_5$, namely

$$\frac{1}{\tau_{\text{nuc}}} \approx D\rho_1\rho_2 + D_2\rho_2^2$$

and, according to (1) :

$$D\rho_1\rho_2 + D_2\rho_2^2 = F/\ell^2 \quad (21)$$

The 3 quantities ρ_1 , ρ_2 and ℓ are given by the 3 equations (4), (20) and (21). Note that there is some ambiguity on the meaning of ℓ : is ℓ the average distance between terraces *including* pairs or not including pairs? This difference may be expected to be irrelevant because pairs are rapidly transformed into triplets which are transformed into bigger terraces, etc., so that there are much less pairs than bigger terraces. In other words

$$\rho_2\ell^2 \ll 1 \quad (22)$$

This relation will be proved a few lines below. A related problem is whether D is the diffusion constant of an adatom on the ideal, high symmetry surface, or should take into account the fact that an adatom can temporarily form a dimer before diffusing to a stable terrace, either after dissociation of the dimer, or inside the diffusing dimer. Again this question is irrelevant if (22) is satisfied, since most of adatoms reach a big terrace without forming a pair.

It will now be proved that the last term of (20), as well as the second term of the left hand side of (21), can be neglected in an order-of-magnitude calculation, provided $D_2 < D$. To prove this, it is sufficient to show that

$$D_2\rho_2/D\rho_1 < 1. \quad (23)$$

Actually, (20) implies

$$\rho_2 \approx \frac{D\rho_1^2}{1/\tau_2 + D\rho_1 + D_2/\ell^2 + D_2\rho_2} < \frac{D\rho_1^2}{D\rho_1} = \rho_1$$

This proves (23) provided $D_2 < D$. This inequality can reasonably be expected to hold in most cases. It may occur, however, that $D_2 > D$. Anyway, our treatment is an improvement on the usual theory in which D_2 is assumed to vanish.

Now, (23), (21) and (4) imply

$$\rho_2\ell^2 \approx \frac{F}{D\rho_1} \approx \frac{1}{\ell^2}$$

and this proves (22).

Using (23), elimination of ρ_2 between (20) and (21) yields

$$\frac{D^2\rho_1^3}{1/\tau_2 + D\rho_1 + D_2/\ell^2} = F/\ell^2$$

The equation for ℓ is now obtained by inserting (4)

$$\boxed{\frac{F^2\ell^8/D}{1/\tau_2 + F\ell^2 + D_2/\ell^2} \approx 1} \quad (24)$$

Various limiting cases may be distinguished.

i) If

$$F\ell^2 > 1/\tau_2 \text{ and } D_2/\ell^2 \quad (25)$$

relation (9) is recovered. Insertion into (25) yields

$$DF^2\tau_2^3 > 1 \quad (26a)$$

and

$$D^2F > D_2^3 \quad (26b)$$

This regime is reached if F is large enough. Remember, however, that F should be smaller than D , as noted in section 1.

ii) If

$$1/\tau_2 > F\ell^2 \text{ and } D_2/\ell^2 \quad (27)$$

relation (24) reads

$$\ell \approx \left(\frac{D}{F^2 \tau_2} \right)^{1/8} \quad (28)$$

Insertion into (27) yields the conditions

$$DF^2 \tau_2^3 < 1 \quad (29a)$$

and

$$F^2 D_2^4 \tau_2^5 < D \quad (29b)$$

These conditions are always fulfilled, in principle, if the beam intensity F is low enough.

iii) If

$$D_2/\ell^2 > 1/\tau_2 \text{ and } F\ell^2 \quad (30)$$

relation (24) reads

$$\ell \approx \left(\frac{DD_2}{F^2} \right)^{1/10} \quad (31)$$

Insertion into (30) yields

$$D^2 F < D_2^3 \quad (32a)$$

and

$$F^2 D_2^4 \tau_2^5 > D \quad (32b)$$

This is only possible if

$$D_2 \tau_2 > (D/D_2)^{3/5} \quad (33)$$

Relation (31) does not seem to be mentioned in the literature although condition (33) looks physically reasonable. Relation (28) has already been obtained by Stoyanov and Kashchiev [5]. These authors introduce a number of parameters which have been approximated by 1 here. In addition, they do not introduce directly D and τ_2 , but the activation energy for diffusion, E_d , and the binding energy of a pair, E_2 . E_d is defined by

$$D = D_o \exp(E_d/K_B T) \quad (34)$$

where D_o is a constant. The relation with our notations is easily established, but some care is necessary. In (20), the first two terms which correspond to pairing of adatoms and to the reverse process respectively should satisfy the detailed balance relation

$$D\tau_2 = (\rho_2/\rho_1^2)_{eq} = \exp(E_2/K_B T) \quad (35)$$

where the subscript "eq" denotes the equilibrium value and E_2 is positive. Note that (35) is the expression of $D\tau_2$, not of τ_2 .

The question naturally arises, whether the previous calculation can be extended to higher values of i^* . The answer is yes, as seen in the next section. As in the present section, certain approximations will be made. However, they will not be justified as precisely.

8. General rate equations.

In the previous sections it was assumed that trimers, tetramers, etc., were unable both to move and to dissociate. In the present section their motion and limited lifetime will be taken into account. The general rate equation for a n -mer (i.e. a terrace of n atoms) will be assumed to have the following form for $n \leq i^*$.

$$\dot{\rho}_n = D\rho_1\rho_{n-1} - (1/\tau_n)\rho_n - D\rho_1\rho_n + (1/\tau_{n+1})\rho_{n+1} - (D_n/\ell^2)\rho_n \quad (36)$$

The first and third terms correspond respectively to the creation of n -mers by collision of a $(n-1)$ -mer with an adatom and to the disappearance of a n -mer giving a $(n+1)$ -mer by a similar process. The last term represents coalescence of a diffusing n -mer with a bigger terrace. D_n is the diffusion constant of n -mers. The previous term corresponds to the dissociation of a $(n+1)$ -mer into an adatom and a n -mer. The second term corresponds to the decay of a n -mer with production of an adatom. The lifetime τ_n of a n -mer has no relation with the identical notation used in section 6 and taken from ref. 8. Detailed balance implies the following relation with the equilibrium densities ρ_n^0 :

$$1/\tau_n = D\rho_1^0\rho_{n-1}^0/\rho_n^0$$

Equation (36) implies a number of approximations which have been justified in the previous section in the special case ($D_n = 1/\tau_n = 0$ for $n > 2$). Their validity for the general case will not be justified in detail. For instance, the creation of a $(n+m)$ -mer by coalescence of a n -mer with a m -mer has indeed been omitted if n and m are both bigger than 1. Note that the equation (36) is to be applied only to smaller terraces, not to bigger terraces for which $1/\tau_n = D_n = 0$. The effect of those big terraces on small terraces is summarized by the last term in (36). Note that Venables *et al.* [4] give equivalent, but somewhat different-looking equations where big terraces are included in detail.

Averaging over the sample, the $\dot{\rho}_n$'s may be assumed to vanish. Replacing i^* by M for typographic reasons, the resulting equations are

$$\left\{ \begin{array}{l} D\rho_1^2 - (1/\tau_2)\rho_2 - D\rho_1\rho_2 + (1/\tau_3)\rho_3 - (D_2/\ell^2)\rho_2 = 0 \\ D\rho_1\rho_2 - (1/\tau_3)\rho_3 - D\rho_1\rho_3 + (1/\tau_4)\rho_4 - (D_3/\ell^2)\rho_3 = 0 \\ D\rho_1\rho_3 - (1/\tau_4)\rho_4 - D\rho_1\rho_4 + (1/\tau_5)\rho_5 - (D_4/\ell^2)\rho_4 = 0 \\ \dots \dots \dots \\ D\rho_1\rho_M - (1/\tau_M)\rho_M - D\rho_1\rho_M + (1/\tau_{M+1})\rho_{M+1} - (D_M/\ell^2)\rho_M = 0 \end{array} \right. \quad (37)$$

The additional equations are (1) and (4) and an equation which is to generalize (7). This equation is obtained by writing that the nucleation rate is equal to the rate of formation of $(M+1)$ -mers, since those and higher order terraces are stable. Therefore

$$\frac{1}{\tau_{\text{nuc}}} \approx D\rho_1\rho_M \quad (38)$$

Combining with (1), τ_{nuc} can be eliminated. Furthermore, ρ_1 may be replaced by its expression (4). One obtains

$$\left\{ \begin{array}{l} -(1/\tau_2)\rho_2 - F\ell^2\rho_2 + (1/\tau_3)\rho_3 - (D_2/\ell^2)\rho_2 = -F^2\ell^4/D \\ F\ell^2\rho_2 - (1/\tau_3)\rho_3 - F\ell^2\rho_3 + (1/\tau_4)\rho_4 - (D_3/\ell^2)\rho_3 = 0 \\ F\ell^2\rho_3 - (1/\tau_4)\rho_4 - F\ell^2\rho_4 + (1/\tau_5)\rho_5 - (D_4/\ell^2)\rho_4 = 0 \\ \dots \dots \dots \\ F\ell^2\rho_M - (1/\tau_M)\rho_M - F\ell^2\rho_M + (1/\tau_{M+1})\rho_{M+1} - (D_M/\ell^2)\rho_M = 0 \\ F\ell^2\rho_M = \frac{F}{\ell^2} \end{array} \right. \quad (39)$$

The last equation results from (38), (1) and (4). This system of M linear equations in the $(M - 1)$ densities $\rho_2, \rho_3, \rho_4, \dots, \rho_{M-1}, \rho_M$ has a solution if its determinant vanishes. This condition, which yields ℓ , is

$$\begin{vmatrix} -F\ell^2 - D_2\ell^{-2} - 1/\tau_2 & 1/\tau_3 & 0 & 0 & F^2\ell^4/D \\ F\ell^2 & -F\ell^2 - D_3\ell^{-2} - 1/\tau_3 & 1/\tau_4 & 0 & 0 \\ 0 & F\ell^2 & -F\ell^2 - D_4\ell^{-2} - 1/\tau_4 & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & -F\ell^2 - D_M\ell^{-2} - 1/\tau_M & 0 \\ 0 & 0 & 0 & F\ell^2 & -F/\ell^2 \end{vmatrix} \quad (40)$$

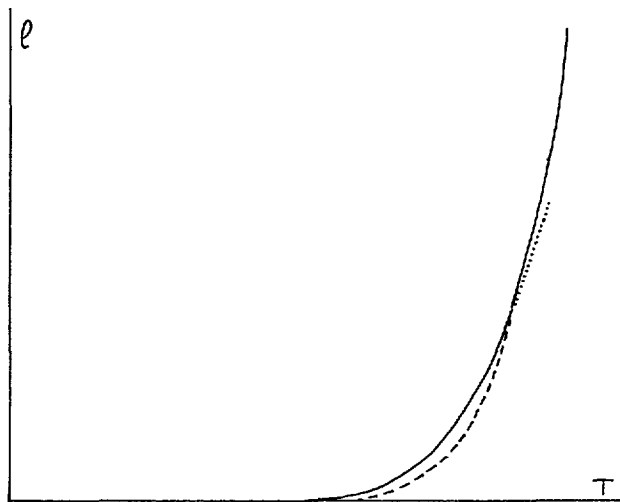


Fig. 2. — Full curve: Qualitative shape of the function $\ell(T)$ for fixed F , assuming it is given by (9) at very low temperature and by (28) at higher temperature. Dotted curve: the function (9) outside its range of validity. Dashed curve: the function (28) outside its range of validity.

The formulae of Stoyanov and Kashchiev [5] for $D_n = 0$ are easily recovered as a special case [13]. A qualitative feature of the function $\ell(T)$ at fixed flux F is the following: *it increases with T more rapidly than an Arrhenius exponential*. This property (already contained in Ref.5) can be seen in the simple case (Fig. 2) when ℓ is described by (8) at low temperatures and by (28) at higher temperatures. One can assume Arrhenius laws for D and τ_2 :

$$D = D_0 \exp(E_{sd}/K_B T), \quad \tau_2 = \tau_2^0 \exp(E_2/K_B T).$$

(29a) implies $3E_2 > E_{sd}$. Then the variation of ℓ is shown by figure 2 and has the above stated property. This is consistent with the experimental results (Fig. 2a) of Mo and Lagally [8].

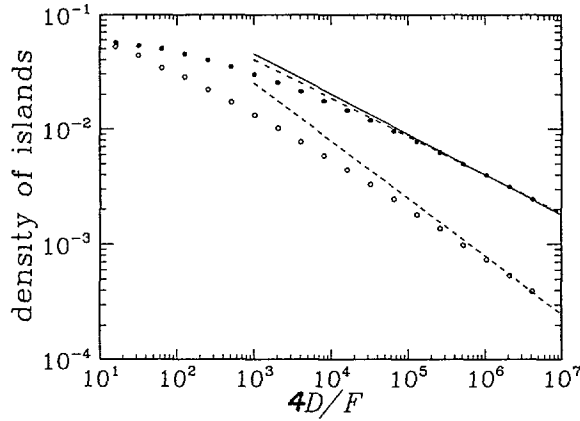


Fig. 3. — Black points: maximum island density determined by computer simulations. Empty circles: the density ℓ_1^{-2} defined in section 9. Only at very weak fluxes there is a good fit with (9) (dot-dashed line) or (42) (full line). A logarithmic correction as in (8) would give a comparable agreement. There is clearly no agreement with the formula $N_{max} \approx \sqrt{F/D}$ proposed in references 6 and 7 (dashed line).

9. Simulations for fractal terraces.

As mentioned in section 7, simulations with different results have been reported [6, 7, 8]. Therefore we performed our own computer experiments. Like other authors, we started with a perfectly smooth surface, a $L \times L$ square lattice with $L = 256$. Atoms are randomly created at a rate F . Each of them performs nearest neighbour hopping on a lattice with a waiting time satisfying the Poisson distribution. Any adatom of the first layer becomes immobile when it hits another adatom or the edge of an existing island. Adatoms created in the second layer diffuse in the same way as those in the first layer. They are incorporated into the film through collisions with atoms in the same layer or by falling over the edge of an island in the layer below.

This process corresponds to the case $i^* = 1$ addressed in section 5. However, since atoms incorporated to a terrace cannot move, small terraces have the fractal dimension $d_f = 1.7$ which corresponds to D.L.A. in two dimensions. If fractal terraces coalesce when they reach the diameter ℓ , this occurs after a time ℓ^{d_f-2}/F instead of $1/F$. Therefore (1) does not hold but should be replaced [13] by

$$1/\tau_{nuc} = F/\ell^{d_f} \quad (41)$$

Combination with (7) yields, neglecting the logarithm:

$$\ell \approx (D/F)^{1/(4+d_f)} \approx (D/F)^{1/5.7} \quad (42)$$

The quantity which has been extracted from simulations is the number $N(t)$ of terraces per unit area. This quantity has a maximum (corresponding to RHEED oscillations) which can be identified with ℓ^{-2} in order of magnitude. The numerical results are displayed in figure 3 for $4D/F = 2^n$, with $n = 10, 11, 12, \dots, 22$. The curve is clearly not in agreement with the claim $\ell \approx (D/F)^{1/4}$ of references [6-7]. There is a good fit with (41) for large ℓ , but it is impossible to discard (8). More precisely, for $D/F > 10000$, the following form of (42) is fitted within 1%:

$$\ell \approx 0.445(D/F)^{1/5.7} \quad (43)$$

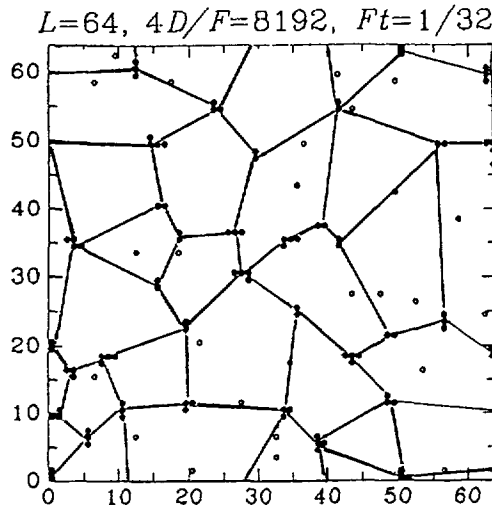


Fig. 4. — The network of small "terraces" or clusters obtained for $t \approx t_1$, when $N(t) \approx \rho_1(t)$. The figure corresponds to $4D/F = 2 \times 64^2$. Since the distance between clusters is small (of order $(D/F)^{1/4}$, here about 8 atomic distances) the process taking place for $t > t_1$ is subject to strong finite size effects.

However, for too high fluxes ($D/F < 10000$) there is a clear discrepancy between the computer results and the formulae (8), (9) and (41). In the following, we try to explain this.

At the beginning of the simulation, the density $N(t)$ of terraces (which are mostly pairs) is smaller than the density ρ_1 of adatoms, and most of adatoms die by pair formation rather than by absorption by terraces. In lowest order in t , $\rho_1(t)$ is equal to Ft . Thus (14) yields

$$N(t) \approx \rho_2(t) \approx DF^2t^3/3 \tag{44}$$

at third order. The third order expression for ρ_1 is

$$\rho_1(t) \simeq Ft - \rho_2(t)/2 \approx Ft - DF^2t^3/6. \tag{45}$$

This regime is very different from the steady regime, when $\rho_1 \ll N$. The transient regime ends when $\rho_1(t) \simeq N(t)$. The corresponding time, given by (45) and (44), is

$$t_1 \approx 1/\sqrt{FD}$$

and corresponds to

$$\rho_1(t_1) \approx N(t_1) \approx \ell^{-2}(t_1) \approx (F/D)^{1/2} \tag{46}$$

Thus, the formula $\ell \approx (D/F)^{1/4}$ of references [6-7] would be correct if the formation of new pairs were negligible after the time t_1 . As seen from figure 3, computer simulations tell us that indeed very few more pairs are formed if F/D is not very small, at least if only the first layer is considered. For $F/D > 0.05$ indeed, the maximum value of $N(t)$ does coincide with the value at the time t_1 at which $\rho_1 = N$. This is not very surprising since the adatoms deposited after time t_1 "see" a network (Fig. 4) of clusters at a distance given by (46), namely

$$\ell_1 \approx (D/F)^{1/4} \tag{47}$$

With respect to the cells of that network, finite size effects may be expected if ℓ_1 is smaller than 10, i.e. if $D/F < 10\,000$. Thus, the condition for the validity of (9) is that $(F/D)^{1/4}$ should be small, a stronger requirement than the smallness of F/D !

As seen from figure 3, our numerical results fit (47) with a coefficient near to 1 if F/D is smaller than 0.001. For larger values there are important corrections. No part of the log-log plot corresponds to ℓ being proportional to $(D/F)^{1/4}$. However, for $D/F < 1000$, ℓ is closer to $(D/F)^{1/4}$ than $(D/F)^{1/6}$. In that sense, our results may be considered in agreement with references [6-7].

Detailed reports on simulations will be presented elsewhere.

10. Conclusion.

Using the same conceptual framework as Stoyanov and Kashchiev [5], we have obtained several new results. The most important one is that cluster diffusion, and in particular pair diffusion, has been taken into account. The mechanism which gives rise to pair diffusion is the same as the one which allows clusters to rearrange and to take a compact, rather than fractal shape. Indeed in both cases atoms are able to move although they keep contact with other atoms of the same cluster. Thus, the usual derivation of the standard formula (9), which assumes both compact terraces and no diffusion of pairs, is not correct! Therefore, our formula (24) is of practical use, as well as its special case (31), which yields $\ell \sim F^{-1/5}$, and its generalisation (40). All those formulae are new.

Another important contribution of the present work is that the discrepancy between certain simulations and the theory of Stoyanov and Kashchiev has been clarified. We are indebted to Prof. Stoyanov for having suggested this explanation. His suggestion was of great help in the interpretation of our numerical data.

Our other new results are of lesser practical importance: the logarithmic correction in (8) does not modify the order of magnitude. The calculation of section 6, where a mistake of reference[8] has been corrected, has no experimental application in the present state of surface science: even if anisotropic diffusion does take place on semiconductor surfaces, many complications of semiconductors (such as the weak sticking coefficient of adatoms to terraces in certain directions) have not been taken into account in the present work.

It would be desirable to understand the disagreement of the theoretical formula (9) with experimental results in metals [17]. A complete discussion is beyond the scope of this article, but the assumption of immobile pairs is not necessarily correct for metals even at low temperature. If they are mobile, formula (9) should be replaced by (31) or the more complicated expression (40).

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