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Process of irreversible nucleation in multilayer growth. I. Failure of the mean-field approach

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The formation of stable dimers on top of terraces during epitaxial growth is investigated in detail. In this paper we focus on mean-field theory, the standard approach to study nucleation. Such theory is shown to be unsuitable for the present problem, because it is equivalent to considering adatoms as independent diffusing particles. This leads to an overestimate of the correct nucleation rate by a factor $\mathcal{N}$, which has a direct physical meaning: on average, a visited lattice site is visited $\mathcal{N}$ times by a diffusing adatom. The dependence of $\mathcal{N}$ on the size of the terrace and on the strength of step-edge barriers is derived from well-known results for random walks. The spatial distribution of nucleation events is shown to be different from the mean-field prediction, for the same physical reason. In the following paper we develop an exact treatment of the problem.

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I. INTRODUCTION

A crystal can be produced artificially with different techniques: we can pull it from the melt, grow it from a solution or obtain it via deposition from a gas or vapor phase onto a suitable substrate. One of the key mechanisms of the growth process is the formation of supercritical nuclei, that is the nucleation—via diffusion and aggregation—of crystalline clusters whose growth rate exceeds the decay rate.

In this paper we devote our attention to epitaxial growth by atomic or molecular beams [1]: particles travel ballistically towards the growing surface where they undergo a thermally activated diffusion process. The size i^* of the critical nucleus is typically a few units and its actual value depends on several factors: the substrate and the type of adatoms deposited determine the activation barriers for the different atomistic processes, while the temperature and the flux determine what processes are really relevant on the time scale of the experiment. Here we consider the simplest case: nucleation is irreversible $(i^*=1)$, i.e., once two adatoms meet they form a stable dimer. After nucleation, the stable nucleus grows by capturing other adatoms.

We start by explaining in general terms the role of nucleation in the different stages of epitaxial growth and by discussing how rate equations and mean-field theory deal with it. The focus of the rest of the paper will be on nucleation on top of terraces bound by descending steps (often called second layer nucleation).

In the submonolayer regime diffusion takes place on the substrate: adatoms are deposited randomly and they diffuse until they meet another wandering adatom or a growing cluster.

Rate equations [2] are widely used to describe the processes of adatom capture and adatom detachment from clusters of j atoms (j clusters, $j \geqslant 2$). If only adatoms are mobile, the spatial density ρ_j of j clusters varies in time according to the relation [3] $\partial_t \rho_j = U_{j-1} - U_j$, where U_j is the net rate of the process (j cluster)$\Rightarrow$($j+1$ cluster). U_j is the sum of a "growth term" and a "decay term": the growth term represents the aggregation of an atom into a j cluster and it has the form $\sigma_j D \rho \rho_j$, where ρ is the adatom density, D the adatom diffusion constant, and σ_j is an adimensional capture number; the decay term represents the thermal detachment of an atom from a $(j+1)$ cluster and it has the form $-(4D/a_0^2)\rho_{j+1}\exp(-\Delta E/T)$, where a_0 is the lattice constant and ΔE is the energy difference between a j cluster (plus a free adatom) and a $j+1$ cluster. If $i^*=1$ such term is absent, because all j clusters are stable and the nucleation rate is $\omega_{\mathrm{RE}} = \sigma_1 D \rho^2$ (the subscript standing for "rate equations").

The capture factor σ_j is defined through the flux Φ_j of adatoms attaching to the j cluster: $\Phi_j \equiv D\sigma_j \rho$, and it accounts for the different adatom densities surrounding islands of different size. In a mean-field (MF) approach such density is taken as a constant, $\sigma = 2d$ [4] and the nucleation rate *per* lattice site reads $\omega_{\mathrm{MF}} = 2dD\overline{\rho}^2$.

By monitoring the adatom density $\overline{\rho}$ and the total density of islands $\overline{\rho}_{\mathrm{TOT}} = \Sigma_{j \geqslant 2} \overline{\rho_j}$ one realizes the existence of a regime characterized by $\overline{\rho}_{\mathrm{TOT}}$ almost constant in time, prior to the coalescence regime [5]. The average distance ℓ_{D} between islands can therefore be defined as $\ell_{\mathrm{D}}^d = 1/\overline{\rho}_{\mathrm{TOT}}$, d being the dimensionality of the substrate: usually $d=2$, but in the following we will consider $d=1$ as well. ℓ_{D} is called the diffusion length and it also gives the typical linear distance traveled by an adatom before being incorporated in an island.

During the time $1/F$, necessary for the deposition of a monolayer, there is on average a nucleation event per area ℓ_{D}^d [6]. Therefore, according to mean-field theory, $\omega_{\mathrm{MF}} \ell_{\mathrm{D}}^d / F \sim 1$, i.e., $D\overline{\rho^2}\ell_{\mathrm{D}}^d/F \sim 1$ with (see Appendix A1) $\overline{\rho} \sim (F/D)\ell_{\mathrm{D}}^2$. So we obtain the result $\ell_{\mathrm{D}} \sim (D/F)^\gamma$, with $\gamma = \frac{1}{5}$ in $d=1$ and $\gamma = \frac{1}{6}$ in $d=2$. This relation is wrong in one dimension, but essentially correct in two dimensions [6,7]. In Sec. IV A it will become clear that mean-field theory (MFT) gives the correct result for γ in $d=2$ because step-edge barriers at island edges play no role in the submonolayer regime.

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If adatoms freshly attached to a growing nucleus are immobile the resulting island is normally fractal, but if they can diffuse along the step-edge the island gets compact. Compact islands are therefore obtained at not too low temperatures (so that thermally activated edge diffusion actually occurs) whilst nucleation is irreversible at not too high temperatures (so that a dimer is thermally stable). In some experimental systems both conditions are fulfilled in a given temperature range: Pt(111)/Pt in the range 350–430 K [8], Ag(100)/Ag in the interval 200–300 K [9], and Fe(100)/Fe between 300 and 500 K [10] are some examples.

Once island coalescence has set off, most nucleation events take place on top terraces. The obvious reason is that even for layer-by-layer growth a new atomic layer starts to form before the completion of the previous one and consequently the growing surface is made up of a certain number of exposed layers. Terraces can be classified as top (T), vicinal (V), and bottom (B) terraces according to the type of steps surrounding them: in general only top terraces attain a size large enough to have a considerable probability of nucleating a new island. Since this probability grows abruptly from zero to one with increasing terrace size [11], it is possible to introduce a critical nucleation length $\ell_{\rm nuc}$ [12]. In the presence of step-edge barriers [13], hindering interlayer transport, such length differs for the three types of terraces: $\ell_{\rm nuc}^{\rm T}$ goes to zero with increasing barriers while $\ell_{\rm nuc}^{\rm V}$ and $\ell_{\rm nuc}^{\rm B}$ remain finite in such limit [12,14]. Nucleations generally occur on top terraces because the size of the vicinal and bottom terraces hardly reaches the nucleation length. However, nucleation is a stochastic phenomenon and therefore dimer formation may also occur on vicinal terraces every now and then, while on bottom terraces it is an exceedingly rare event. These occasional "vicinal nucleations" are an important stabilizing mechanism of the surface, even if their relative weight decreases as barriers increase [15,16].

The mean-field approach to evaluate the nucleation rate for (reversible and irreversible) nucleation on top terraces has been worked out by Tersoff, van der Gon, and Tromp in Ref. [11] and since then their results have been widely used to analyze experimental data and extract the values of step-edge barriers. The mean-field approximation can also be used in "mesoscopic" models of growth [17] for implementing the rule for the spatial distribution $P(x)$ of nucleation events, via the relation $P(x)\propto\rho^2(x)$.

Recently, several authors [18–20] have started to review critically the MF approach. In Refs. [18,20] authors are mainly interested in the validity of MFT for different values of the critical size i^*: this check has been done through scaling analysis and kinetic Monte Carlo simulations. A deeper investigation of the irreversible case $(i^*=1)$ is done in Ref. [19] in the limit of strong step-edge barriers, through a quantitative approach based on the different time scales involved in the nucleation process.

The inaccuracy of MF theory in dealing with the problem of second layer nucleation has therefore already been pointed out in the literature. In this work we analyze thoroughly the validity of the MF theory for irreversible second layer nucleation, we rigorously prove its inadequacy both for the nucleation rate ω and the spatial distribution $P(x)$ of nucleation sites and understand the physical origin of its failure. In the following paper [21] we compute exactly ω and $P(x)$, providing the correct expressions that must be used in place of the MF approximations.

We have organized this paper as follows. The three relevant time scales for the nucleation process and the associated regimes are introduced and discussed in the following section. In Sec. III we explain how we can get rid of the stochastic nature of the deposition process (Sec. III A) and we introduce the quantities of interest in the paper, the spatial distribution of nucleation events (Sec. III B), and the nucleation rate (Sec. III C). In Sec. IV we show the equivalence of MF theory with a model of noninteracting particles, both for the nucleation rate (Sec. IV A) and for the spatial distribution (Sec. IV B). The final section contains a critical summary of the results.

A short report of this work has been published in Ref. [22].

II. TIME SCALES

We consider a top terrace of fixed linear size L, subject to a flux F of particles. Once on the terrace, each particle moves with a diffusion constant D until it meets another particle or it leaves the terrace. At step edges an additional energy barrier, usually called Ehrlich-Schwoebel (ES) barrier [13], reduces the rate D' of interlayer transport and the ES length

$$\ell_{\rm ES}=\left(\frac{D}{D'}-1\right)a_0 \tag{1}$$

measures the asymmetry between D and D'. In the following the lattice constant a_0 will be taken as unit length $(a_0=1)$.

In general, throughout the paper we will consider discrete space and time, i.e., particles moving on a lattice (a square lattice in $d=2$), at fixed time steps. However, we will sometimes use a continuum notation as well. The matching between discrete and continuum is straightforward: if t_c is a continuous time and t_d its discrete counterpart (number of time steps), then $t_c=t_d\Delta t$, where $\Delta t=1/(2dD)$ is the time an atom remains on each lattice site.

Let us now discuss the three time scales involved in the problem [19].

(1) The traversal time (τ_{tr}) is the average time needed by a diffusing particle to reach the terrace boundaries. In the large L limit

$$\tau_{tr}=\beta L^2/D, \tag{2}$$

where β is a numerical prefactor depending on the dimension d and the shape of the terrace. Its value is discussed after Eq. (4).

(2) The residence time (τ_{res}) is the average time a particle spends on the terrace. It is related to the average density $\overline{\rho}$ of adatoms via the relation [19] $\overline{\rho}=F\tau_{res}$, where the density ρ (and therefore its average value $\overline{\rho}$) can be determined (see Appendix A1) by solving the stationary diffusion equation in the presence of a constant flux F,

$$D\nabla^2\rho+F=0. \tag{3}$$

Boundary conditions depend on the strength of the ES barrier at descending steps. If the equilibrium adatom density—due to thermal detachment from steps—is neglected, the boundary condition for ρ is $\partial_\perp\rho|_{\mathrm{step}}=\frac{\rho}{\ell_{\mathrm{ES}}}|_{\mathrm{step}}$, where $\partial_\perp$ is the local derivative in the direction perpendicular to the step (directed inward the terrace). In a discrete picture (for example in $d=1$) if $n=1$ is a lattice site at the edge of the terrace and $n=0$ is its fictitious neighbor outside the terrace, we have $\rho(1)-\rho(0)=\rho(0)/\ell_{\mathrm{ES}}$, i.e., $\rho(0)=\ell_{\mathrm{ES}}/(1+\ell_{\mathrm{ES}})\rho(1)\equiv a\rho(1)$.

The solution of Eq. (3) (see Appendix A1) gives the following result, valid both in one and two dimensions: $\bar{\rho}=(F/D)(\beta L+\alpha\ell_{\mathrm{ES}})L$, where α is another numerical factor depending on the dimension d and on the shape of the terrace. We can finally write

$$\tau_{res}=(\beta L+\alpha\ell_{\mathrm{ES}})L/D. \tag{4}$$

In the absence of ES barriers ($\ell_{\mathrm{ES}}=0$) τ_{res} and τ_{tr} are equal. From Eqs. (A7), (A8), (A18), and (A50) we infer that in $d=1$, $\beta=1/12$ and $\alpha=1/2$. In $d=2$, for a circular terrace of radius L, $\beta=1/8$ and $\alpha=1/2$, while for a square terrace, $\beta\simeq 32/\pi^6$ and $\alpha=1/4$.

In the discrete picture τ_{res} is clearly equal to the total number of sites (N_{all}) visited by an atom during its diffusional motion on the terrace. Since the adatom stays on a lattice site a time $1/(2dD)$ we have $\tau_{res}=N_{\mathrm{all}}/(2dD)$. Hence, the residence time τ_{res}, the average density $\bar{\rho}$ and the number N_{all} of all sites visited by the adatom carry the same piece of physical information, once F and D are set. The quantity N_{all} should not be confused with the number of *distinct* sites (N_{dis}) visited by an adatom: a given lattice site, visited k times, contributes for 1 to N_{dis} and for k to N_{all}.

(3) The deposition time (τ_{dep}) is the average time between a deposition event and the next one. For a terrace of area $\mathcal{A}=L^d$,

$$\tau_{dep}=\frac{1}{F\mathcal{A}}=\frac{1}{FL^d}. \tag{5}$$

Physically sensible values for F, L and D imply that $\tau_{tr}\ll\tau_{dep}$. This relation indeed is $L^2/D\ll 1/FL^d$, i.e., $D/F\gg L^{d+2}$: we can now recall the diffusion length [23] introduced in Sec. I, $\ell_{\mathrm{D}}\sim(D/F)^\gamma$ and measuring the "maximal" size of a terrace *in the absence* of step-edge barriers. For irreversible nucleation the exponent γ is equal to [23] $1/2(d+1)$ so that we obtain the condition $\ell_{\mathrm{D}}^{2(d+1)/(d+2)}\gg L$, i.e., $\ell_{\mathrm{D}}^{4/3}\gg L$ in $d=1$ and $\ell_{\mathrm{D}}^{3/2}\gg L$ in $d=2$. Smooth growth requires that $\ell_{\mathrm{D}}\gg 1$; furthermore L is at most of order ℓ_{D} if $\ell_{\mathrm{ES}}=0$, but for finite barriers it is (much) smaller. We conclude that the above conditions are fulfilled and that we can safely suppose that $\tau_{tr}\ll\tau_{dep}$.

This inequality has a consequence of primary importance: processes involving more than two adatoms at a time can be fully neglected. Once two adatoms are simultaneously on the terrace, they meet—if they do—on the time scale of the traversal time τ_{tr}. This fact is intuitively clear and it is proven in Ref. [21]. The probability that a third atom lands in the meanwhile is τ_{tr}/τ_{dep}, negligibly small. Irreversible nucleation is therefore the result of two-adatoms processes only.

Depending on the relative size of τ_{res} with respect to the other two time scales, three different regimes may occur:

$$\tau_{tr}\simeq\tau_{res}\ll\tau_{dep}\qquad \text{zero or weak barriers [regime (i)]}, \tag{6}$$

$$\tau_{tr}\ll\tau_{res}\ll\tau_{dep}\qquad \text{strong barriers [regime (ii)]}, \tag{7}$$

$$\tau_{tr}\ll\tau_{dep}\ll\tau_{res}\qquad \text{infinite barriers [regime (iii)]}. \tag{8}$$

The difference between the three regimes is easily understood. A nucleation may occur only if a new adatom is deposited before the previous one leaves the terrace. If $\tau_{res}\ll\tau_{dep}$ [regimes (i) and (ii)] this is a rare event. When it happens, the second atom finds the first one with a spatial distribution that differs in cases (i) and (ii) (see Appendix B). If $\ell_{\mathrm{ES}}\ll L$ [regime (i)] when the adatom reaches the edge of the terrace, it gets off. Steps act as absorbing boundaries and the adatom density vanishes there: ρ has a parabolic shape with a maximum in the middle of the terrace (see Appendix A1). If $\ell_{\mathrm{ES}}\gg L$ [regime (ii)] the adatom is pushed back from the terrace edge several times before being able to descend. Steps act as (imperfect) reflecting walls and ρ is approximately uniform over the whole terrace. In regime (iii) when a new adatom is deposited it always finds the previous one still on the terrace, they both have a flat distribution and they will certainly meet.

III. GENERAL FORMALISM

In the present and in the following paper (Ref. [21]) we are going to use a discrete formulation for particle dynamics, both in space and in time. In this section, n indicates the whole set of d integer numbers specifying the position of a particle on the terrace. A nucleation event is assumed to occur when two adatoms are on the same lattice site, rather than on neighboring lattice sites: this definition avoids useless mathematical complications, but retains all the physics of the nucleation process.

A. Reduction to two particles deposited simultaneously

It is clear that the problem of dimer formation on a terrace involves the study of the diffusion of two particles deposited *at different times*: the spatial and temporal distributions of landing events play therefore a prominent role. The incoming flux of particles is supposed to be spatially and temporally uniform [24]: a particle arrives on each lattice site with uniform probability $p_n^U\equiv 1/L^d$ and the interarrival time τ between two deposition events decays exponentially [25],

$$P_{\mathrm{dep}}(\tau)=\exp(-\tau/\tau_{dep})/\tau_{dep}. \tag{9}$$

Let us now consider any "two-particle" quantity $\mathcal{O}$, i.e., any quantity depending on the initial distributions of particle 1 and 2 and on their interarrival time τ.

Let $p_n(0)=p_n^U=1/L^d$ be the initial uniform distribution of an atom and $p_n(\tau)$ its dynamical evolution at time τ (*in the absence* of other particles). If particle 1 is deposited at time zero and particle 2 a time τ later, we call $\mathcal{O}\{p_n^{(1)}(\tau),p_n^{(2)}(0)\}$ the resulting physical quantity. $\mathcal{O}$ might be, for example, the probability $p_{\rm nuc}$ that a deposited particle nucleates a dimer before getting off the terrace [see Eq. (19)]. Once $\mathcal{O}\{p_n^{(1)}(\tau),p_n^{(2)}(0)\}$ is known, one should evaluate its average over τ,

$$\hat{\mathcal{O}}=\sum_{\tau=0}^{\infty} P_{\rm dep}(\tau)\mathcal{O}\{p_n^{(1)}(\tau),p_n^{(2)}(0)\}. \tag{10}$$

The crucial point is that if $\mathcal{O}$ is *linear* in the initial distributions $p_n^{(1,2)}$ of the two atoms (as all quantities discussed in the paper are), the above equation can be rewritten as

$$\hat{\mathcal{O}}=\mathcal{O}\{p_n^{\rm eff},p_n^{(2)}(0)\} \tag{11}$$

in such a way that the average over τ is now included in an effective initial distribution

$$p_n^{\rm eff}=\sum_{\tau=0}^{\infty} P_{\rm dep}(\tau)p_n^{(1)}(\tau). \tag{12}$$

We can make more explicit the physical content of the above reasoning, which is based on the linearity with respect to the initial distribution of the two particles. Atom 2 is deposited with probability $P_{\rm dep}(\tau)$ a time τ after atom 1, which means that atom 2 has the probability $P_{\rm dep}(\tau)$ to find atom 1 distributed according to $p_n^{(1)}(\tau)$: on average—and it is now that linearity comes into play—atom 2 finds atom 1 with the effective distribution given in Eq. (12).

In this way we have reduced the problem of evaluating $\hat{\mathcal{O}}$ to the evaluation of $\mathcal{O}$ for two particles deposited simultaneously. Thus we can ignore the stochasticity of the deposition process and assume that atoms 1 and 2 land *at the same time*, but the actual initial distribution for atom 1 (the uniform distribution) is replaced by $p_n^{\rm eff}$.

The next task is then the determination of $p_n^{\rm eff}$. The function $p_n(\tau)$ (discussed in Appendix A2) is the distribution of the first adatom at time τ, i.e., the solution of the diffusion equation for a single particle with initial condition

$$p_n(\tau=0)=p_n^U=\frac{1}{L^d}. \tag{13}$$

The sum of $p_n(\tau)$ over all times τ is the solution of the stationary diffusion equation (3) (of its discretized version, actually, see Appendix A1), whose normalized form will be indicated with p_n^S (S standing for stationary). It has, in general, a parabolic form, and in particular in $d=1$, $p_n^S=[\ell_{\rm ES}L+(L+1)n-n^2]/[\ell_{\rm ES}L^2+\frac{1}{6}L(L+1)(L+2)]$.

In Appendix B it is shown that in all dimensions we can write

$$p_n^{\rm eff}=\frac{\tau_{res}}{\tau_{dep}+\tau_{res}}p_n^S. \tag{14}$$

The physical content of Eq. (14) is readily understood. For infinite barriers [regime (iii)] $p_n^{\rm eff}=p_n^S=1/L^d$: the first particle cannot escape from the terrace and its distribution is still uniform and normalized when the second one lands. For strong but finite barriers [regime (ii)] $p_n^{\rm eff}=(\tau_{res}/\tau_{dep})p_n^S=(\tau_{res}/\tau_{dep})(1/L^d)$: most of the particles that arrive on the terrace leave it before another particle lands, but the distribution of the first particle remains practically uniform because many attempts are needed to overcome the ES barrier. In the limit of zero or weak barriers [regime (i)] $p_n^{\rm eff}=(\tau_{res}/\tau_{dep})p_n^S$ and p_n^S vanishes on the edges, reflecting the presence of the absorbing boundaries.

B. The spatial distribution of nucleation events

In the preceding section we have explained how to transform the original problem into the new problem of two atoms deposited at the same time, with normalized distributions p_n^S (the first) and p_m^U (the second). We can now define the probability $R(n,t)$ that a nucleation event occurs on site n at time t and introduce the following quantities:

$$P(n)=\sum_t R(n,t), \tag{15}$$

$$W=\sum_n P(n). \tag{16}$$

$P(n)$ is the spatial distribution of nucleation events and W is the probability that two atoms, both on the terrace at time zero, meet before leaving the terrace. It is useful to consider the *normalized* spatial distribution $P^{(\rm N)}(n)=P(n)/W$ as well.

C. The nucleation rate

The nucleation rate ω is defined as the number of nucleation events per unit time on the *whole* terrace of size L, irrespective of the spatial location of the meeting point. This quantity is of great importance because it is related to the probability of second layer nucleation. In a classical experiment [26] a fraction of a monolayer is deposited on the substrate and the size of islands is made as uniform as possible through an annealing procedure. Starting from this template a second dose of atoms is deposited and nucleation on top of existing islands is monitored. $\omega(L)$ enters in the interpretation of this experiment because the probability $\mathcal{P}(t)$ that a nucleation event has occurred on a terrace by time t is $\mathcal{P}(t)=1-\exp\{-\int_0^t d\tau\omega[L(\tau)]\}$. The rate $\omega(L)$ is defined and evaluated for a constant terrace size L: in the experiment instead, L grows in time and the time dependence of L is "system-dependent." Hence, the growth law $L(\tau)$ of the terrace size must be supplied beyond $\omega(L)$, and it depends on the specific morphology of the surface and the experimental setup. In other words, the nucleation rate—on the one hand—has a very general and basic meaning, but—on the other hand—it can hardly be measured directly. This means that, despite our results for $\omega(L)$ being exact, the evaluation of $L(t)$ introduces some approximations in the interpretation of experimental results, whose accuracy depends on the detail of the system considered. In addition, some secondary effects, as steering and nonuniform barriers, may further complicate the problem.

We now connect ω to $P(n)$ and W. In Sec. II we explained that only processes involving two adatoms are relevant for studying irreversible nucleation, because $\tau_{tr} \ll \tau_{dep}$. If we define the nucleation probability per atom, $\hat{p}_{\rm nuc}$, we can write the nucleation rate as the number of atoms landing on the terrace per unit time ($FL^d = 1/\tau_{dep}$) times the nucleation probability per atom,

$$\omega = FL^d \hat{p}_{\rm nuc}. \tag{17}$$

The quantity $\hat{p}_{\rm nuc}$ is the probability that a deposited particle nucleates a dimer before getting off the terrace and it can be written as

$$\hat{p}_{\rm nuc} = \sum_{\tau=0}^{\infty} P_{\rm dep}(\tau) p_{\rm nuc}\{p_n^{(1)}(\tau), p_n^{(2)}(0)\}, \tag{18}$$

where the dependence on the initial distributions of atoms 1 and 2 has been made explicit. We stress that the dependence on the initial distributions occurs *via the full diffusion process*. For example, for independent particles in one dimension, the explicit form of $p_{\rm nuc}$ is

$$p_{\rm nuc}\{p_n^{(1)}(\tau), p_n^{(2)}(0)\} = \sum_{m=1}^{L} \sum_{t=0}^{\infty} p_{m,m}(t)\{p_n^{(1)}(\tau), p_n^{(2)}(0)\}, \tag{19}$$

where $p_{m,m}(t)$ is the solution of the diffusion equation *in two dimensions* with the initial condition given by the product $p^{(1)}(\tau)p^{(2)}(0)$ (see Ref. [21] for more details).

Because of the linearity of $p_{\rm nuc}$, we have

$$\hat{p}_{\rm nuc} = p_{\rm nuc}\{p_n^{\rm eff}, p_n^{(2)}(0)\}. \tag{20}$$

The nucleation probability per atom can be thought as the probability that atom 1 is still on the terrace when atom 2 is deposited, times the probability they meet before getting off the terrace. This is exactly what emerges from Eq. (20) once expression (14) for the effective distribution $p_n^{\rm eff}$ is inserted,

$$\hat{p}_{\rm nuc} = \frac{\tau_{res}}{\tau_{dep} + \tau_{res}} p_{\rm nuc}\{p_n^S, p_n^{(2)}(0)\}. \tag{21}$$

The normalization factor of $p_n^{\rm eff}$ is the probability that atom 1 is still on the terrace when the next one shows up; for infinite ES barriers ($\tau_{res} \gg \tau_{dep}$) such a probability is trivially 1, while for weak and strong barriers ($\tau_{res} \ll \tau_{dep}$) it is τ_{res}/τ_{dep}. The remaining quantity on the right-hand side ($p_{\rm nuc}\{p_n^S, p_n^{(2)}(0)\}$) is the probability that two atoms, *both on the terrace at time zero* [p_n^S and $p_n^{(2)}(0)$ are normalized], meet before descending. Therefore it coincides with W and we finally obtain

$$\omega = FL^d \frac{\tau_{res}}{\tau_{dep} + \tau_{res}} W. \tag{22}$$

D. Noninteracting particles

We are considering a system such that once adatoms come together an immobile dimer is formed irreversibly: adatoms stop diffusing and the dimer does not dissociate. It turns out to be of great help to consider also an artificial model, with adatoms treated as independently diffusing particles: even if they meet on the same lattice site they go on diffusing and therefore they can cross each other several times before leaving the terrace. We consider all these meetings as "fictitious nucleations," and define also for noninteracting particles the quantities mentioned above: the nucleation rate $\omega_{\rm NI}$, the spatial distribution $P_{\rm NI}(n)$, and the total number $W_{\rm NI}$ of nucleation events, the subscript NI standing for "noninteracting."

IV. EQUIVALENCE OF MEAN-FIELD THEORY AND NONINTERACTING PARTICLES MODEL

A. The nucleation rate

We have introduced the nucleation rate in Sec. III C and obtained Eq. (22). W is the nucleation probability between two atoms that are both on the terrace at time zero. For the model of noninteracting adatoms W should be replaced by $W_{\rm NI}$, the average number of meetings between the two independent particles. Of course $W_{\rm NI}$ can be larger than 1.

The simplest and less interesting case is the regime (iii) of infinite barriers. In such a case W is trivially 1 and $\omega = FL^d = 1/\tau_{dep}$, i.e., any particle deposited on a terrace does form a dimer. In a sense, this limit is unphysical for mean-field theory because $\overline{\rho}$ and $\omega_{\rm MF} = 2dDL^d\overline{\rho^2}$ diverge when $\ell_{\rm ES} \to \infty$.

In the other two regimes (weak and strong barriers), Eq. (22) becomes

$$\omega = FL^d \frac{\tau_{res}}{\tau_{dep}} W = FL^{2d}\overline{\rho}W, \tag{23}$$

where we have used the relations $\tau_{dep} = (FL^d)^{-1}$ and $F\tau_{res} = \overline{\rho}$. We can repeat the same procedure for noninteracting particles and obtain

$$\omega_{\rm NI} = FL^d \frac{\tau_{res}}{\tau_{dep}} W_{\rm NI} = FL^{2d}\overline{\rho}W_{\rm NI}. \tag{24}$$

It is possible to relate W and $W_{\rm NI}$ to single-particle quantities, $N_{\rm dis}$ and $N_{\rm all}$ (see Sec. II). They are the number of distinct ($N_{\rm dis}$) and all ($N_{\rm all}$) sites visited by a single walker diffusing on the terrace [27]. Let us assume one of the two adatoms fixed on site s. $w(s)$ is the probability that the diffusing adatom visits site s before getting off the terrace. W is then the average value of $w(s)$, $W \simeq \Sigma_s w(s)/L^d$. The quantity $\Sigma_s w(s)$ is nothing but the total number of distinct sites

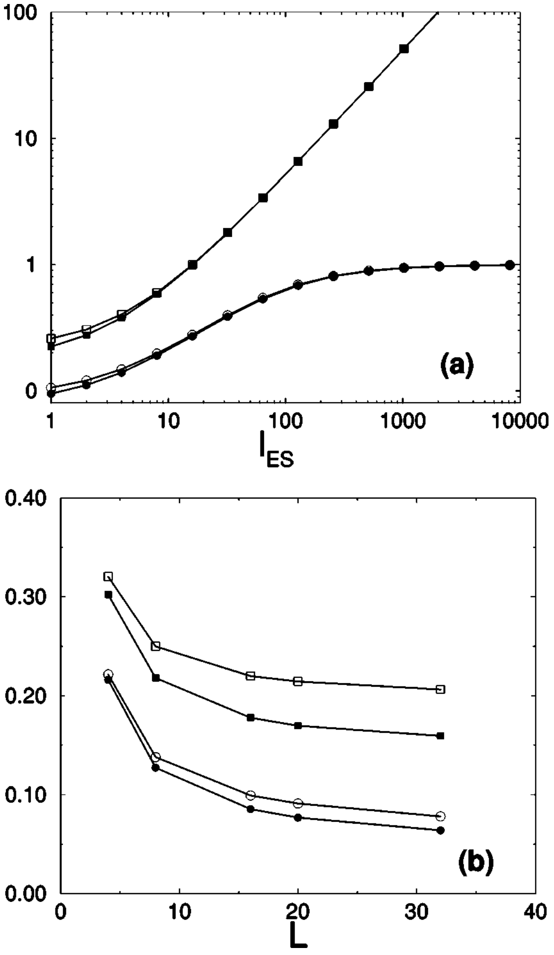

FIG. 1. (a) Log-log plot of W (empty circles), N_{dis}/L^2 (full circles), W_{NI} (empty squares), N_{all}/L^2 (full squares) versus ℓ_{ES} for $d=2$ and $L=20$. (b) The same quantities plotted versus L for $d=2$ and $\ell_{\mathrm{ES}}=0$.

N_{dis} visited by the diffusing adatom, so that $W \simeq N_{\mathrm{dis}}/L^d$. The same argument for noninteracting particles gives $W_{\mathrm{NI}} \simeq N_{\mathrm{all}}/L^d$.

The relations

$$W \simeq \frac{N_{\mathrm{dis}}}{L^d} \quad \text{and} \quad W_{\mathrm{NI}} \simeq \frac{N_{\mathrm{all}}}{L^d} \tag{25}$$

have been derived under the assumption that one atom is immobile. In Fig. 1 we compare numerically the values of single-particles quantities $(N_{\mathrm{dis}}/L^d, N_{\mathrm{all}}/L^d)$ with two-particle quantities (W, W_{NI}). The former have been calculated via Monte Carlo simulations and the latter through the numerical solution of the discrete diffusion equation for two atoms on a terrace (discussed in detail in Ref. [21]): it comes out that relations (25) are well satisfied, so that assuming one atom as immobile is perfectly reasonable for the evaluation of W and W_{NI}.

If we insert the relations (25) into Eqs. (23) and (24) we obtain

$$\omega \simeq F L^d \overline{\rho} N_{\mathrm{dis}}, \tag{26}$$

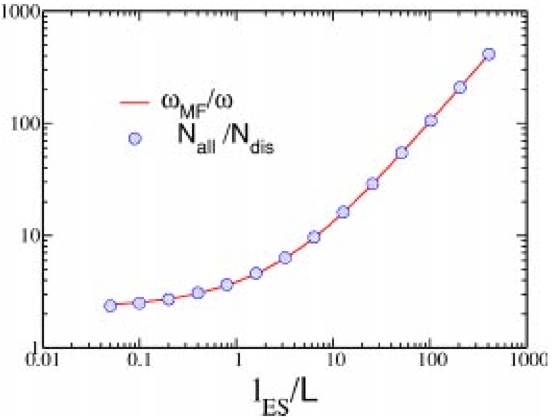

FIG. 2. Plot of the correction factor $\omega_{\mathrm{MF}}/\omega$ and of $\mathcal{N} \equiv N_{\mathrm{all}}/N_{\mathrm{dis}}$ versus ℓ_{ES}/L, for a square terrace of size $L=20$.

$$\omega_{\mathrm{NI}} \simeq F L^d \overline{\rho} N_{\mathrm{all}}. \tag{27}$$

Since N_{all} is related to the residence time by $\tau_{res} = N_{\mathrm{all}}/(2dD)$, we can write

$$\omega_{\mathrm{NI}} \simeq 2dFL^d \overline{\rho} D \tau_{res} = 2dDL^d \overline{\rho}^2 = \omega_{\mathrm{MF}}. \tag{28}$$

In this way we have shown that for the nucleation rate *the mean-field treatment is equivalent to considering particles as noninteracting*, i.e., counting also meeting events following the first one. For this reason the mean-field value is an overestimate of the correct nucleation rate. Furthermore we have proven that

$$\frac{\omega_{\mathrm{MF}}}{\omega} \simeq \frac{W_{\mathrm{NI}}}{W} \simeq \frac{N_{\mathrm{all}}}{N_{\mathrm{dis}}} \equiv \mathcal{N}. \tag{29}$$

In Fig. 2, the comparison of $\omega_{\mathrm{MF}}/\omega$, computed exactly in the companion paper [21] with $N_{\mathrm{all}}/N_{\mathrm{dis}}$, evaluated numerically, shows clearly that Eq. (29) is valid with great accuracy.

The correction factor $\mathcal{N}$ depends on well-known properties of single particles performing a random walk. The numerator N_{all} is just (see Sec. II): $N_{\mathrm{all}} = 2dL(\beta L + \alpha \ell_{\mathrm{ES}})$. The value of the denominator N_{dis} is well known [28] in the absence of step-edge barriers, being of order L in $d=1$ and of order $L^2/\ln L$ in $d=2$, and it is trivial in the limit of infinite barriers, being exactly equal to L^d. Hence in $d=1$ we obtain $\mathcal{N} \sim (L + \alpha \ell_{\mathrm{ES}})$, for all ℓ_{ES}.

In $d=2$ we have the limiting expressions $\mathcal{N} \sim \ln L$ for weak barriers and $\mathcal{N} \sim \ell_{\mathrm{ES}}/L$ for strong ones. For intermediate barriers it is possible to find a simple approximate expression for N_{dis} and therefore an interpolation between the two limits. The atom performs on average a number $N_{tr} = \tau_{res}/\tau_{tr}$ of traversals of the island. During a single traversal each site has a probability $p_1 \sim (1/\ln L)$ to be visited. After all N_{tr} traversals the probability p_s that a generic site has been visited at least once is given by $1 - p_s = (1 - p_1)^{N_{tr}}$. Hence we can estimate the number of distinct visited sites as

$$N_{\mathrm{dis}} = L^2 p_s = L^2 [1 - (1 - p_1)^{\tau_{res}/\tau_{tr}}]. \tag{30}$$

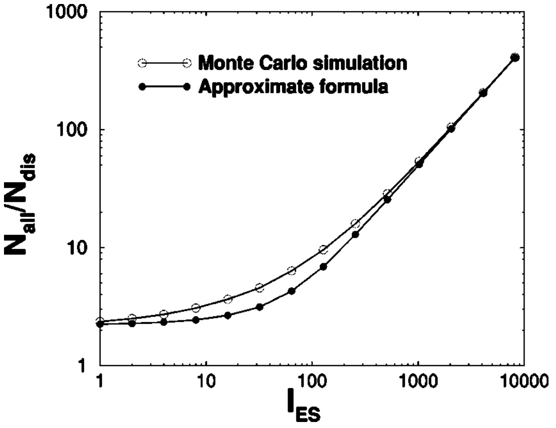

FIG. 3. Log-log plot of $N_{\mathrm{all}}/N_{\mathrm{dis}}$ versus ℓ_{ES} for $d=2$ and $L=20$.

This expression assumes all traversals to be independent, which is clearly not strictly correct. However, it gives the right values in the limits $\ell_{\mathrm{ES}}=0$ and $\ell_{\mathrm{ES}}=\infty$ and for intermediate barriers its accuracy can be tested numerically. In Fig. 3 we have plotted the ratio $N_{\mathrm{all}}/N_{\mathrm{dis}}$ as a function of ℓ_{ES}, for $L=20$. The picture shows a reasonable agreement between the analytical estimate and the numerical simulation.

B. The spatial distribution

In the preceding section we have shown that MF theory overestimates the nucleation rate by the quantity $\mathcal{N}$ because it counts all meetings between two noninteracting adatoms. We are now going to prove that the identification of the mean-field approach as a theory of noninteracting particles is valid for the spatial distribution of nucleation events as well. We adopt a continuum notation so that a single proof is sufficient to demonstrate that $P_{\mathrm{NI}}(x)$ and $\rho^2(x)$ are proportional in any dimension, for any value of the ES barrier and for any terrace shape. In the regimes of strong and infinite ES barrier this result is trivial because both $\rho^2(x)$ and $P_{\mathrm{NI}}(x)$ are constant.

We face the problem of determining the quantity $P_{\mathrm{NI}}(x)$ for a pair of adatoms, one with initial distribution $p^{(2)}(x,0)=p^U(x)$ and the other with the effective distribution $p^{(1)}(x,0)=p^{\mathrm{eff}}(x)=\Sigma_t p^{(2)}(x,t)=\rho(x)$.

We can consider the coordinates (x_1,x_2) of the two atoms ($x_{1,2}$ are vectors in a d-dimensional space) as defining the position $\mathbf{x}=(x_1,x_2)$ of a single particle in a space of dimensionality $d'=2d$. This particle moves according to the diffusion equation $\partial_t p=(D/2)\nabla^2 p$. The factor $\frac{1}{2}$ appears because of the different time step Δt employed in describing a single walker ($\Delta t=1/2dD$) or two walkers ($\Delta t=1/2d'D$) on a terrace.

Integrating in time and defining $P(\mathbf{x})=\int_0^\infty dt p(\mathbf{x},t)$ one finds

$$\frac{D}{2}\nabla^2 P(\mathbf{x})=-p(\mathbf{x},0). \tag{31}$$

An interchange of the two particles $[p^{(1)}(x,0)=p^U(x)$ and $p^{(2)}(x,0)=\rho(x)]$ is equally legitimate and it is useful to use a symmetrized form for $p(\mathbf{x},0)$:

$$p(\mathbf{x},0)=\frac{1}{2}[\rho(x_1)p^U(x_2)+p^U(x_1)\rho(x_2)]. \tag{32}$$

Notice that $\rho(x)$ is also the solution of the equation $D\nabla^2\rho(x)=-p^U(x)$. Therefore,

$$\frac{D}{2}\nabla^2 P(\mathbf{x})=\frac{D}{2}[\rho(x_1)\nabla_2^2\rho(x_2)+\rho(x_2)\nabla_1^2\rho(x_1)], \tag{33}$$

where ∇_i^2 acts on x_i only and $\nabla^2\equiv\nabla_1^2+\nabla_2^2$. Hence,

$$\nabla^2 P(\mathbf{x})=\nabla^2[\rho(x_1)\rho(x_2)], \tag{34}$$

i.e., the function $\chi(\mathbf{x})=P(\mathbf{x})-\rho(x_1)\rho(x_2)$ is harmonic. It is easy to show [29] that $\chi(\mathbf{x})$ must be identically zero. Hence,

$$P(\mathbf{x})=\rho(x_1)\rho(x_2). \tag{35}$$

If we set $x_1=x_2=x$, the left-hand side is just the nucleation probability $P_{\mathrm{NI}}(x)$ at point x between two noninteracting adatoms, and the right-hand side is the mean-field prediction. Notice that we have not used the explicit form of $p^U(x)$. Hence, the proof holds for *any* initial spatial distribution $p^U(x)$, so that the equivalence between MF theory and the noninteracting particles model is true even if atoms are not deposited uniformly.

So far we have rigorously shown that the MF result for $P(n)$ is not exact. However, one may wonder whether the error introduced by taking into account all meeting events following the first one is expected to be large or negligible. We address this issue by evaluating the relative weight of successive encounters for noninteracting particles.

Let us consider noninteracting particles and define μ_j as the fraction of times the jth meeting event actually occurs. Clearly $\mu_0=1$ and $\mu_j\geqslant\mu_{j+1}$. Let us also define the *normalized* distribution for the jth nucleation event $P_j^{\mathrm{NI}}(n)$. Notice that $P_1^{\mathrm{NI}}(n)=P^{(N)}(n)$, the distribution for interacting particles.

The total distribution of nucleation sites is simply

$$P_{\mathrm{NI}}(n)=\sum_{j=1}^{\infty}\mu_j P_j^{\mathrm{NI}}(n), \tag{36}$$

and the quantities W and W_{NI} are given by

$$W=\mu_1, \tag{37}$$

$$W_{\mathrm{NI}}=\sum_n P_{\mathrm{NI}}(n)=\sum_{j=1}^{\infty}\mu_j. \tag{38}$$

If we now introduce the normalized distribution of all fictitious nucleations following the first one,

$$\hat{P}^{\mathrm{NI}}(n)=\frac{\sum_{j=2}^{\infty}\mu_j P_j^{\mathrm{NI}}(n)}{\sum_{j=2}^{\infty}\mu_j}, \tag{39}$$

we can write

$$P_{\mathrm{NI}}(n)=\mu_1 P_1^{\mathrm{NI}}(n)+\sum_{j=2}^{\infty}\mu_j P_j^{\mathrm{NI}}(n)=WP^{(N)}(n)+\hat{P}^{\mathrm{NI}}(n)\times(W_{\mathrm{NI}}-W). \tag{40}$$

For weak barriers, in $d=1$, the weight W of the first term is constant, while the second one diverges as L. As a consequence, for large L the distribution $P_{\mathrm{NI}}(n)$ is dominated by the contribution of the fictitious successive nucleations. In $d=2$ the first term goes as $1/\ln L$ while the second is constant. Again, for large L, the contribution of first nucleation events becomes negligible. For strong and infinite barriers, $W=1$ while W_{NI} is infinite, so $P_{\mathrm{NI}}(n)$ coincides with $P_{\infty}^{\mathrm{NI}}(n)$.

In all cases the MF expression for the spatial distribution of nucleation sites $[P_{\mathrm{NI}}(n)]$ is dominated for large L by the contribution of the fictitious nucleations following the first one. *A priori* there is no reason for supposing that the distribution of the jth nucleation event is equal to the distribution of the first one, so we expect that the difference between the MF spatial distribution and the exact result persists for all values of L. This will be checked and confirmed in the following paper [21].

V. CONCLUSIONS

This paper has been devoted to an accurate investigation of the mean-field approach to the problem of irreversible nucleation. The main outcome is the proof that MFT is equivalent to a model where particles do not interact and all their meetings are counted as fictitious nucleations.

In the regime of infinite ES barriers, MFT simply breaks down because it predicts a diverging nucleation rate, in contrast to the correct value $\omega=FL^d$. In the other, physically more interesting, regimes the equivalence of MFT with the model of noninteracting particles implies that ω_{MF} overestimates the correct nucleation rate by the factor $\mathcal{N}=N_{\mathrm{all}}/N_{\mathrm{dis}}$. This ratio has a clear meaning: a diffusing adatom passes $\mathcal{N}$ times on a visited site. It depends on single-particle quantities $(N_{\mathrm{all}},N_{\mathrm{dis}})$ whose expressions are well known from the theory of random walks.

In Table I we summarize the value of the correction factor $\mathcal{N}$ in regimes (i) and (ii) and we report the approximate expressions for the nucleation rate ω. They are approximate in the sense that numerical prefactors are neglected, but they scale correctly with L,D,D',a_0. The lattice constant a_0 has been reintroduced in order to give dimensionally correct espressions. Also, we have made explicit the dependence of ℓ_{ES} on D and D', so that only basic quantities appear.

The expression $\omega\sim F^2L^5a_0/D'$, valid in two dimensions for strong step-edge barriers has already been given in Ref. [19]. It is worth repeating that the nucleation rate in this limit does not depend on the diffusion constant D so that the nucleation rate cannot be promoted by using surfactants.

TABLE I. We report the nucleation rate ω and the correction factor $\mathcal{N}$ in the two regimes of weak (i) and strong (ii) step-edge barriers and in one and two dimensions. The conditions defining regimes (i) $(\tau_{res}\simeq\tau_{tr})$ and (ii) $(\tau_{tr}\ll\tau_{res}\ll\tau_{dep})$ are written in terms of the basic quantities L,D,D',a_0.

	(i)		(ii)	
	$\frac{D-D'}{D'}\ll\frac{L}{a_0}$		$\frac{D}{D'}\gg\frac{L}{a_0}$	$D'\gg FL^{d+1}a_0$
	ω	$\mathcal{N}$	ω	$\mathcal{N}$
$d=1$	$\frac{F^2L^4}{D}$	$\frac{L}{a_0}$	$\frac{F^2L^3a_0}{D'}$	$\frac{D}{D'}$
$d=2$	$\frac{F^2L^6}{D\ln(L/a_0)}$	$\ln(L/a_0)$	$\frac{F^2L^5a_0}{D'}$	$\frac{Da_0}{D'L}$

Application of MFT is acceptable only in the regime of vanishing barriers in two dimensions, because in this case the correction factor $[\mathcal{N}=\ln(L/a_0)]$ is a small number, for realistic terrace sizes.

In order to obtain exact expressions for ω it is necessary to have an accurate estimate of W, or equivalently of N_{dis}. W is a function of the terrace size L and of the ES length ℓ_{ES}: for strong barriers $W=1$, while for weak barriers $W\sim 1$ in $d=1$ and $W\sim 1/\ln L$ in $d=2$. So, for realistic values of L, W depends on L and ℓ_{ES} much more weakly than the other quantities appearing in $\omega=FL^{2d}\overline{\rho}W$. However, its dependence is not fully negligible: Figs. 1(a) and 1(b) show that (in $d=2$) for $L=20$, W varies by a factor 10 by changing ℓ_{ES} from zero to infinity and for $\ell_{\mathrm{ES}}=0$, W varies by a factor 3 by changing the terrace size from $L=4$ to $L=32$ $(\ln 32/\ln 4=2.5)$. For comparison, the quantity $\overline{\rho}$, which appears along with W in the expression for ω, varies by a factor 50 by changing ℓ_{ES}/L from 0 to 6 and by a factor 64 by changing L from 4 to 32, for $\ell_{\mathrm{ES}}=0$. The problem of the exact determination of W will be tackled again in the following paper [21].

A last comment on rate equations and mean-field approximation is in order here. According to the former, the nucleation rate is written $\omega_{\mathrm{RE}}=\sigma_1 D\rho^2$ and the latter corresponds to taking σ_1 as a constant. In general, σ_1 is defined through the relation $\Phi_1=D\sigma_1\rho$, where Φ_1 is the flux of atoms attaching to an adatom. The resulting relation $\omega_{\mathrm{RE}}=\Phi_1\rho$ is *exact*, if Φ_1 is evaluated correctly; for example, we can solve the diffusion equation for a single walker on the terrace, where a second walker is taken as an absorbing sink. Since we have shown that the nucleation rate can be evaluated assuming an atom as immobile, such treatment is essentially correct. In other words, if the capture number is not taken as a constant, the expression $\omega_{\mathrm{RE}}=\sigma_1 D\rho^2$ may give correct results, but this method has nothing to do with the usual mean-field approach.

Finally, with regard to the spatial distribution, we have provided a very general demonstration of the equivalence between mean field and noninteracting particles. We have also shown that the difference between $P(n)$ and $P_{\mathrm{NI}}(n)$ is not an effect of the finite size of the terrace and it remains true for large L. The full computation of the spatial distribution of nucleation events requires the solution of the dynamical problem of two interacting atoms diffusing on a terrace. This problem will be solved analytically and/or numerically in the following paper [21].

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APPENDIX A: SINGLE PARTICLE ON A TERRACE

In this appendix we summarize the behavior of a single particle on a terrace for all values of the Ehrlich-Schwoebel length ℓ_{ES}.

1. The stationary adatom density

The discrete evolution equation for a particle in a cubic d-dimensional space is

$$p_n(t+1)=\frac{1}{2d}\sum_{\delta} p_{n+\delta}(t), \tag{A1}$$

where $n+\delta$ indicates a neighbor of the site n. If we sum over t and define the quantity $\rho_n=\Sigma_{t=0}^{\infty}p_n(t)$ we obtain

$$\left[\sum_{\delta}\rho_{n+\delta}-2d\rho_n\right]+2dp_n(0)=0. \tag{A2}$$

The terms in square brackets give the discrete Laplacian of ρ_n; therefore the sum $\rho_n=\Sigma_t p_n(t)$ is simply the solution of the stationary diffusion equation in the presence of the flux $2dp_n(0)$.

In $d=1$, for constant $p_n(0)$, it is possible to find the exact discrete solution for any value of ℓ_{ES}, once we remark that the general solution of the homogeneous equation is $\rho_n=c_0+c_1 n$ and a particular solution of the nonhomogeneous equation is $\rho_n=-c_2n^2$ [the factor c_2 depending on the constant term in Eq. (A2)].

Boundary conditions are $\rho_0=a\rho_1$ and $\rho_{L+1}=a\rho_L$, where $a=\ell_{\mathrm{ES}}/(1+\ell_{\mathrm{ES}})$ goes from 0 to 1 as the Ehrlich-Schwoebel length ℓ_{ES} varies from 0 to ∞.

The explicit expression of ρ_n is

$$\rho_n=\frac{1}{L}[\ell_{\mathrm{ES}}L+(L+1)n-n^2]. \tag{A3}$$

Its normalized version is

$$p_n^S\equiv\frac{\rho_n}{\sum_n \rho_n}=\frac{1}{\ell_{\mathrm{ES}}L^2+\dfrac{L(L+1)(L+2)}{6}}\times[\ell_{\mathrm{ES}}L+(L+1)n-n^2]. \tag{A4}$$

In a continuum formalism, the equation is $D\partial_x^2\rho+F=0$ and the solution in $d=1$ is

$$\rho(x)=\frac{F}{2D}[\ell_{\mathrm{ES}}L+Lx-x^2]. \tag{A5}$$

In $d=2$ the solution of the continuum equation is as easy as in $d=1$ if we specialize to a circular terrace. If L now denotes the radius, the solution for generic ℓ_{ES} is

$$\rho(r)=\frac{F}{4D}[L^2+2L\ell_{\mathrm{ES}}-r^2]. \tag{A6}$$

We finally evaluate the average density $\overline{\rho}$ on the terrace

$$\overline{\rho}=\frac{F}{12D}L(L+6\ell_{\mathrm{ES}})\quad d=1, \tag{A7}$$

$$\overline{\rho}=\frac{F}{8D}L(L+4\ell_{\mathrm{ES}})\quad d=2\ \text{[circular terrace]}. \tag{A8}$$

2. The dynamical problem in one dimension

We now summarize the dynamical behavior of a single particle on a one-dimensional terrace. The two-dimensional case is treated in the following section.

The discrete evolution equation for the particle is

$$p_n(t+1)=\tfrac{1}{2}[p_{n+1}(t)+p_{n-1}(t)], \tag{A9}$$

with the usual boundary conditions $p_0(t)=ap_1(t)$ and $p_{L+1}(t)=ap_L(t)$. The solution is found by separating the space and time variables, $p_n(t)=X(n)F(t)$,

$$\frac{F(t+1)}{F(t)}=\lambda=\frac{X(n+1)+X(n-1)}{2X(n)},\quad 0<\lambda<1. \tag{A10}$$

The temporal part is $F(t)=\lambda^tF(0)$. The spatial part has the general form

$$X(n)=A\sin(n\phi)+B\cos(n\phi), \tag{A11}$$

which gives $\lambda=\cos\phi$. The boundary conditions determine the values of A, B, and ϕ.

In particular, by imposing the boundary condition in $n=0$ one obtains $B=bA$ with $b=a\sin\phi/(1-a\cos\phi)$. Using this relation and imposing the other boundary condition in $n=L+1$ one obtains

$$\tan(L\phi)=\frac{(a^2-1)\sin\phi}{(1+a^2)\cos\phi-2a}. \tag{A12}$$

This equation has L solutions that we label as ϕ_k with $k=1,\dots,L$. Then the general solution is

$$p_n(t)=\sum_{k=1}^{L}\cos^t(\phi_k)X_k(n), \tag{A13}$$

with

$$X_k(n)=A_k\sin(\phi_k n)+B_k\cos(\phi_k n). \tag{A14}$$

Given $p_n(t)$ one can compute $S(t)$, the probability that an adatom is still on the terrace at time t after deposition (survival probability),

$$S(t)\equiv\sum_{n=1}^{L} p_n(t). \tag{A15}$$

Another important quantity is the residence time, defined as

$$\tau_{res}\equiv\sum_{t=1}^{\infty} t[S(t-1)-S(t)] \tag{A16}$$

because $S(t-1)-S(t)$ is the probability that the particle stays on the terrace exactly a time t. It is easy to check that

$$\tau_{res}=\sum_{t=0}^{\infty} S(t)=\sum_{n=1}^{L}\left[\sum_{t=0}^{\infty} p_n(t)\right]=\sum_{n=1}^{L}\rho_n. \tag{A17}$$

Recalling Appendix A1, for the initial distribution $p_n(0)=p_n^U=1/L$ we have, for any value of the ES barrier,

$$\tau_{res}=\frac{(L+1)(L+2)}{6}+\ell_{\mathrm{ES}}L. \tag{A18}$$

In order to pass to a continuous time we have to multiply it by $\Delta t=1/2D$. For large L, $\tau_{res}=L/D(L/12+\ell_{\mathrm{ES}}/2)$. This result agrees with the relation $\bar{\rho}=F\tau_{res}$ [see Eq. (A7)].

Unfortunately it is not possible to solve explicitly Eq. (A12) for generic values of a: we now discuss the two limit cases where an explicit solution is possible.

a. Zero barriers

For $\ell_{\mathrm{ES}}=0$ $(a=0)$, the allowed values of ϕ_k are

$$\phi_k=\frac{k\pi}{L+1}\quad(k=1,\ldots,L) \tag{A19}$$

and the general solution is

$$p_n(t)=\sum_{k=1}^{L} A_k\cos^t\left(\frac{k\pi}{L+1}\right)\sin\left(\frac{nk\pi}{L+1}\right) \tag{A20}$$

with

$$A_k=\frac{2}{L+1}\sum_{n=1}^{L} p_n(0)\sin\left(\frac{nk\pi}{L+1}\right). \tag{A21}$$

In particular, two forms of $p_n(0)$ are most interesting to us. For a uniform distribution $p_n(0)=p_n^U=1/L$ the coefficients are

$$A_k\equiv A_k^U=\frac{2}{L(L+1)}\sin\left(\frac{L}{2}\,\frac{k\pi}{L+1}\right)\sin\left(\frac{k\pi}{2}\right)\mathrm{cosec}\left(\frac{1}{2}\,\frac{k\pi}{L+1}\right). \tag{A22}$$

For the distribution $p_n(0)=p_n^S=6/[L(L+1)(L+2)]n(L+1-n)$ [see Eq. (A4)], the explicit solution is

$$A_k\equiv A_k^S=\frac{6}{L(L+1)^2(L+2)}\,\frac{\sin\left(\dfrac{k\pi}{2}\right)}{\sin^3\left[\dfrac{k\pi}{2(L+1)}\right]}\sin\left[\frac{Lk\pi}{2(L+1)}\right]. \tag{A23}$$

As shown in Appendix A1, p_n^S is the normalized version of $\rho_n=\Sigma_{\tau=0}^{\infty}p_n(\tau)$ where $p_n(\tau)$ is the solution of the diffusion equation with uniform initial condition p_n^U. Writing explicitly the sum we obtain

$$\sum_{\tau=0}^{\infty} p_n(\tau)=\sum_{\tau=0}^{\infty}\sum_{k=1}^{L} A_k^U\cos^{\tau}\left(\frac{k\pi}{L+1}\right)\sin\left(\frac{nk\pi}{L+1}\right) \tag{A24}$$

$$=\sum_{k=1}^{L}\frac{A_k^U}{1-\cos\left(\dfrac{k\pi}{L+1}\right)}\sin\left(\frac{nk\pi}{L+1}\right). \tag{A25}$$

Hence

$$A_k^S\propto\frac{A_k^U}{1-\cos\left(\dfrac{k\pi}{L+1}\right)}=\frac{A_k^U}{2\sin^2\left[\dfrac{k\pi}{2(L+1)}\right]}, \tag{A26}$$

as can be easily verified by comparing Eq. (A22) with Eq. (A23).

If we sum $p_n(t)$ over n [see Eq. (A20)] we obtain the survival probability

$$S(t)=\sum_{k=1}^{L} A_k\cos^t\left(\frac{k\pi}{L+1}\right)\sin\left(\frac{L}{2}\,\frac{k\pi}{L+1}\right)\sin\left(\frac{k\pi}{2}\right)\times\mathrm{cosec}\left(\frac{1}{2}\,\frac{k\pi}{L+1}\right). \tag{A27}$$

The distribution $p_n(t)$ is in general a sum of exponential decays

$$p_n(t)=\sum_{k=1}^{L} A_k\sin\left(\frac{nk\pi}{L+1}\right)\exp\left[t\ln\cos\left(\frac{k\pi}{L+1}\right)\right]. \tag{A28}$$

It can be considered as a single exponential when the second slowest decaying exponential is negligible. For $L\gg1$ this means

$$\exp\left[-\left(\frac{2\pi}{L}\right)^2\frac{t}{2}\right]\ll1\quad\Rightarrow\quad t\gg\frac{L^2}{2\pi^2}\simeq\tau_{tr}. \tag{A29}$$

Hence, for $t\gg\tau_{tr}$,

$$p_n(t)\simeq A_1\sin\left(\frac{n\pi}{L+1}\right)\exp\left[-\left(\frac{\pi}{L}\right)^2\frac{t}{2}\right]$$

$$\simeq A_1\sin\left(\frac{n\pi}{L+1}\right)\exp\left(-\frac{t}{\tau_{res}}\right). \tag{A30}$$

For the same reason, for $t \gg \tau_{tr}$,

$$S(t) \simeq A_1 \frac{2(L+1)}{\pi} \exp\left(-\frac{t}{\tau_{res}}\right). \tag{A31}$$

b. Infinite barriers

For $\ell_{\mathrm{ES}} = \infty$ $(a=1)$ the allowed values of ϕ_k are

$$\phi_k = \frac{k\pi}{L} \quad (k=0,\dots,L-1) \tag{A32}$$

and $A_k = B_k \tan(k\pi/2L)$, so that the general solution is

$$p_n(t) = \sum_{k=0}^{L-1} A_k \cos^t\left(\frac{k\pi}{L}\right) X_k(n), \tag{A33}$$

where

$$X_k(n) = \left[\tan\left(\frac{k\pi}{2L}\right)\sin\left(\frac{nk\pi}{L}\right) + \cos\left(\frac{nk\pi}{L}\right)\right]. \tag{A34}$$

The coefficients A_k depend on the initial condition through the relation

$$A_k = \frac{1}{N_k} \sum_{n=1}^{L} p_n(0) X_k(n), \tag{A35}$$

where (δ_{k0} is the Kronecker symbol)

$$N_k = \frac{L}{2}\left[1 + \tan^2\left(\frac{k\pi}{2L}\right)\right](1+\delta_{k0}). \tag{A36}$$

$p_n(t)$ is the sum of a constant (the term for $k=0$) and exponentially decaying terms $(k>0)$. For $p_n(0) = 1/L$, the only nonvanishing coefficient is $A_0 = 1/L$ and this implies for all times

$$p_n(t) = \frac{1}{L}. \tag{A37}$$

In the general case of nonconstant $p_n(0)$, the exponential decays are negligible when $\exp[-(\pi/L)^2 t/2] \ll 1$, that is to say $t \gg (2/\pi^2)L^2 \simeq \tau_{tr}$.

c. Strong barriers

Let us consider now the case of finite but large ℓ_{ES} $(\ell_{\mathrm{ES}} \gg L)$. The solution of Eq. (A12), with $a \to 1$ and large but fixed L, yields, for the two smallest ϕ_k,

$$\phi_1 \simeq \sqrt{\frac{2(1-a)}{L}} = \sqrt{\frac{2}{L\ell_{\mathrm{ES}}}}, \tag{A38}$$

$$\phi_2 = \frac{\pi}{L} + O(1-a). \tag{A39}$$

The slowest decays in the general solution are therefore $\exp(-\phi_1^2 t/2)$ and $\exp(-\phi_2^2 t/2)$. For finite values of L we can neglect the second exponential for times such that

$$\exp[t \ln\cos(\phi_2)] \ll 1 \quad \Rightarrow \quad t \gg \frac{2}{\pi^2} L^2 \simeq \tau_{tr}. \tag{A40}$$

Hence for times larger than τ_{tr} one can write

$$\begin{aligned} p_n(t) &= B_1 \cos\left(n\sqrt{\frac{2}{L\ell_{\mathrm{ES}}}}\right)\cos^t\left(\sqrt{\frac{2}{L\ell_{\mathrm{ES}}}}\right) \\ &\simeq B_1 \exp\left(-\frac{t}{L\ell_{\mathrm{ES}}}\right), \end{aligned} \tag{A41}$$

where $B_1 \simeq 1/L$ and $\tau_{res} = L\ell_{\mathrm{ES}}$. This value of τ_{res}, multiplied by $\Delta t = 1/2D$ coincides with its continuum counterpart $\overline{\rho}/F = L\ell_{\mathrm{ES}}/(2D)$.

3. The dynamical problem in two dimensions

It is useful to summarize here some results for a single particle on a two-dimensional terrace. The general solution is

$$\begin{aligned} p_{m,n}(t) = \sum_{k,j=1}^{L} A_{kj} \frac{1}{2^t}\Bigg[&\cos\left(\frac{k\pi}{L+1}\right) \\ &+ \cos\left(\frac{j\pi}{L+1}\right)\Bigg]^t X_k(m) X_j(n), \end{aligned} \tag{A42}$$

where the coefficients A_{kj} are

$$A_{kj} = \frac{1}{N_k N_j} \sum_{m,n=1}^{L} p_{m,n}(0) X_k(m) X_j(n). \tag{A43}$$

For zero barriers $X_k(n) = \sin[nk\pi/(L+1)]$ and $N_k = (L+1)/2$. For a uniformly distributed adatom, $p_{m,n}^U = 1/L^2$ and the coefficients are

$$\begin{aligned} A_{kj}^U = A_k^U A_j^U = &\left[\frac{2}{L(L+1)}\right]^2 \sin\left(\frac{k\pi}{2}\right)\sin\left(\frac{j\pi}{2}\right)\sin\left[\frac{Lk\pi}{2(L+1)}\right] \\ &\times \sin\left[\frac{Lj\pi}{2(L+1)}\right]\csc\left[\frac{k\pi}{2(L+1)}\right]\csc\left[\frac{j\pi}{2(L+1)}\right]. \end{aligned} \tag{A44}$$

We indicate as $p_{m,n}^S$ the normalized solution of the stationary diffusion equation in the presence of a constant flux. Differently from what occurs in the one-dimensional case, the explicit form of $p_{m,n}^S$ is not known exactly for a square terrace. However, the expression of its coefficients A_{kj}^S can be obtained by exploiting the property (see Appendix A 1) that $p_{m,n}^S = N\Sigma_{\tau=0}^{\infty} p_{m,n}(\tau)$ where $p_{m,n}(\tau)$ is the solution of the diffusion equation with uniform initial condition $p_{m,n}^U = 1/L^2$ and $N = 1/\tau_{res}$ is a normalization factor

$$\begin{aligned}\sum_{\tau=0}^{\infty} p_{m,n}(\tau) &= \sum_{\tau=0}^{\infty} \sum_{k,j=1}^{L} A_{kj} \frac{1}{2^{\tau}} \left[\cos\left(\frac{k\pi}{L+1}\right) + \cos\left(\frac{j\pi}{L+1}\right) \right]^{\tau} \sin\left(\frac{mk\pi}{L+1}\right) \sin\left(\frac{nj\pi}{L+1}\right) \\ &= \sum_{k,j=1}^{L} \frac{A_{kj}}{1-\frac{1}{2}\left[\cos\left(\frac{k\pi}{L+1}\right)+\cos\left(\frac{j\pi}{L+1}\right)\right]} \sin\left(\frac{mk\pi}{L+1}\right) \sin\left(\frac{nj\pi}{L+1}\right). \end{aligned} \tag{A45}$$

Hence

$$A_{kj}^{S} = N \frac{A_{kj}^{U}}{1-\frac{1}{2}\left[\cos\left(\frac{k\pi}{L+1}\right)+\cos\left(\frac{j\pi}{L+1}\right)\right]}. \tag{A46}$$

The numerical prefactor N can be determined by imposing that the sum over m and n of $p_{m,n}^{S}$ is 1, that is

$$\sum_{m,n} \sum_{k,j} A_{kj}^{S} \sin\left(\frac{mk\pi}{L+1}\right) \sin\left(\frac{nj\pi}{L+1}\right) = 1, \tag{A47}$$

which implies

$$\frac{1}{N} = \left[\frac{L(L+1)}{2}\right]^{2} \sum_{k,j} \frac{(A_{kj}^{U})^{2}}{1-\frac{1}{2}\left[\cos\left(\frac{k\pi}{L+1}\right)+\cos\left(\frac{j\pi}{L+1}\right)\right]}. \tag{A48}$$

In the limit of large L,

$$\tau_{res} = \frac{1}{N} \simeq \left[\frac{L(L+1)}{2}\right]^{2} \frac{(A_{11}^{U})^{2}}{1-\cos\left(\frac{\pi}{L+1}\right)} \simeq \frac{2^{7}}{\pi^{6}} L^{2}. \tag{A49}$$

Hence in the continuum $\tau_{res} \simeq (32/\pi^{6}) L^{2}/D$ and

$$\beta \simeq \frac{32}{\pi^{6}}. \tag{A50}$$

In the limit of strong but finite barriers one finds $\tau_{res} = L\ell_{\mathrm{ES}}/(4D)$, so that $\alpha = 1/4$.

APPENDIX B: THE EFFECTIVE DISTRIBUTION

We want to evaluate the effective distribution

$$p_{n}^{\mathrm{eff}} \equiv \sum_{\tau=0}^{\infty} P_{\mathrm{dep}}(\tau) p_{n}(\tau) \tag{B1}$$

introduced in Sec. III A. Since $p_{n}(\tau)$ decays to zero after a time of order τ_{res}, for regimes (i) and (ii) (where $\tau_{res} \ll \tau_{dep}$) $P_{\mathrm{dep}}(\tau)$ can be taken as a constant. Hence

$$p_{n}^{\mathrm{eff}} = \frac{1}{\tau_{dep}} \sum_{\tau=0}^{\infty} p_{n}(\tau) \quad \text{[(i) and (ii)]}. \tag{B2}$$

The sum $\Sigma_{\tau} p_{n}(\tau)$ has been shown in Appendix A1 to be equal to the solution ρ_{n} of the stationary diffusion equation, which always has a parabolic shape. Its normalized version p_{n}^{S} is

$$p_{n}^{S} = \frac{\rho_{n}}{\sum_{n=1}^{L} \rho_{n}} = \frac{\rho_{n}}{\tau_{res}}, \tag{B3}$$

so that

$$p_{n}^{\mathrm{eff}} = \frac{\tau_{res}}{\tau_{dep}} p_{n}^{S} \quad \text{[(i) and (ii)]}. \tag{B4}$$

This equation corresponds to Eq. (14) in the limit $\tau_{res} \ll \tau_{dep}$.

For strong and infinite barriers [regimes (ii) and (iii)], the contribution of times shorter than τ_{tr} is smaller than τ_{tr}/τ_{dep} and therefore negligible. Accordingly, we can evaluate the sum (B1) using the expression for $p_{n}(\tau)$ that is valid in the limit $\tau \gg \tau_{tr}$ [see Eq. (A41), in $d=2$ the generalization is trivial], $p_{n}(\tau) = (1/L^{d}) \exp(-\tau/\tau_{res})$ and obtain

$$p_{n}^{\mathrm{eff}} = \frac{1}{L^{d} \tau_{dep}} \sum_{\tau=0}^{\infty} \exp\left[-\tau\left(\frac{1}{\tau_{dep}} + \frac{1}{\tau_{res}}\right)\right]. \tag{B5}$$

Converting the sum over discrete times into an integral, we have

$$p_{n}^{\mathrm{eff}} = \frac{\tau_{res}}{\tau_{res}+\tau_{dep}} \frac{1}{L^{d}} = \frac{\tau_{res}}{\tau_{res}+\tau_{dep}} p_{n}^{S}, \tag{B6}$$

where—as usual—p_{n}^{S} is the normalized solution of the stationary diffusion equation. Thus, formula (14),

$$p_{n}^{\mathrm{eff}} = \frac{\tau_{res}}{\tau_{res}+\tau_{dep}} p_{n}^{S} \tag{B7}$$

can be used in all the different regimes.

In the continuum it is possible to work out a more rigorous approach and determine p_{n}^{eff} as the solution of a differential equation, which is the generalization of the stationary diffusion equation (3). We start with the diffusion equation for $p(x,t)$, $\partial_{t} p = D \nabla^{2} p$, where x is a d-dimensional vector. If we multiply both sides by $P_{\mathrm{dep}}(t)$ and integrate in time, we obtain

$$\int_0^\infty dt P_{\rm dep}(t)\partial_t p(x,t) = D\nabla^2 \int_0^\infty dt P_{\rm dep}(t) p(x,t). \qquad \text{(B8)}$$

The right-hand side is just $D\nabla^2 p^{\rm eff}(x)$ while the left-hand side is

$$\begin{aligned}\int_0^\infty dt P_{\rm dep}(t)\partial_t p(x,t) &= P_{\rm dep}(t)p(x,t)\big|_0^\infty \\ &\quad - \int_0^\infty dt[\partial_t P_{\rm dep}(t)]p(x,t) \\ &= -\frac{1}{\tau_{dep}}\frac{1}{\mathcal{A}} + \frac{1}{\tau_{dep}}\int_0^\infty dt P_{\rm dep}(t)p(x,t)\end{aligned} \qquad \text{(B9)}$$

and Eq. (B8) becomes

$$D\nabla^2 p^{\rm eff}(x) - \frac{1}{\tau_{dep}} p^{\rm eff}(x) + F = 0. \qquad \text{(B10)}$$

It differs from the stationary diffusion equation $D\nabla^2\rho + F = 0$ because of the presence of a "desorption" term $[-p^{\rm eff}(x)/\tau_{dep}]$ that is the responsible of the saturation of $p^{\rm eff}(x)$ at large $\ell_{\rm ES}$. As a matter of fact, in the limit $\ell_{\rm ES}\to\infty$, ρ is known to diverge as $(F/D)L\ell_{\rm ES}$ [see Eqs. (A7) and (A8)] while the above equation clearly shows that $p^{\rm eff}(x)$ goes to the constant $F\tau_{dep}=1/\mathcal{A}$.

The exact solution of Eq. (B10) can be found both in $d=1$ and in $d=2$ for a circular terrace and the proof that $p^{\rm eff}(x)=\tau_{res}/(\tau_{res}+\tau_{dep})p^S(x)$ works much in the same way in the two cases. We give here some more details for the bidimensional case. The solution of Eq. (B10) with the usual boundary condition $\partial_r p^{\rm eff}(r) = -p^{\rm eff}(r)/\ell_{\rm ES}$ evaluated for $r=L$ (the radius of the circular terrace) is

$$p^{\rm eff}(r) = \frac{1}{\pi L^2}\left[1 - \frac{I_0\left(\frac{r}{\sqrt{D\tau_{dep}}}\right)}{I_0\left(\frac{L}{\sqrt{D\tau_{dep}}}\right) + \frac{\ell_{\rm ES}}{\sqrt{D\tau_{dep}}} I_1\left(\frac{L}{\sqrt{D\tau_{dep}}}\right)}\right], \qquad \text{(B11)}$$

where I_0 and I_1 are the modified Bessel functions of order zero and one, respectively. The arguments of the Bessel functions are at most equal to $L/\sqrt{D\tau_{dep}} = \sqrt{8\tau_{tr}/\tau_{dep}}$, a small quantity. An expansion of the Bessel functions gives

$$p^{\rm eff}(r) = \frac{1}{\pi L^2}\frac{L^2 + 2\ell_{\rm ES}L - r^2}{4D\tau_{dep} + L(L+2\ell_{\rm ES})}. \qquad \text{(B12)}$$

By using the results (A6) and (A8), after some algebra we obtain the final expression

$$p^{\rm eff}(r) = \frac{\tau_{res}}{\tau_{dep} + \frac{L}{D}\left(\frac{L}{4} + \frac{\ell_{\rm ES}}{2}\right)} p^S(r), \quad d=2. \qquad \text{(B13)}$$

The calculation in $d=1$ leads to the result

$$p^{\rm eff}(x) = \frac{\tau_{res}}{\tau_{dep} + \frac{L}{D}\left(\frac{L}{8} + \frac{\ell_{\rm ES}}{2}\right)} p^S(x), \quad d=1. \qquad \text{(B14)}$$

The quantity $L/D(\cdots)$ appearing on the right-hand side in the denominator does not coincide with τ_{res} because the term L^2/D has a prefactor $\frac{1}{4}$ instead that $\frac{1}{8}$ in $d=2$ and a prefactor $\frac{1}{8}$ instead that $\frac{1}{12}$ in $d=1$. Nonetheless such quantity differs from τ_{res} for a quantity of order τ_{tr} which can be safely neglected with respect to τ_{dep} (always appearing in the denominator) so that, in the limit $\tau_{tr}\ll\tau_{dep}$ (a limit applied throughout the paper) we can conclude that the relation

$$p^{\rm eff}(x) = \frac{\tau_{res}}{\tau_{dep}+\tau_{res}} p^S(x) \qquad \text{(B15)}$$

is always valid.

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