

## Mean-Field Nucleation Theory with Nonlocal Interactions

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Mean-field nucleation theory has for a long time been successfully used to extract microscopic parameters from island density data in growth experiments. However, it produces grossly incorrect results when used to analyze weakly corrugated systems, where adsorbate interactions cannot be neglected. Here, a mean-field theory that includes nonlocal adsorbate interactions is developed and successfully tested against kinetic Monte Carlo growth simulations for a realistic adsorbate system.

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Epitaxial growth in the submonolayer regime is a scientific field where experiment and theory have evolved substantially in recent years, allowing detailed comparisons between the two [1,2]. Mean-field nucleation theory (MFNT) has in this context emerged as a powerful method for extracting fundamental microscopic parameters such as diffusion barriers and adsorbate-adsorbate binding energies from island density data [3–7], and has become a popular tool among experimentalists for this very purpose. The theory is often used in epitaxial growth contexts, but can also be applied to other adsorbate-substrate systems.

Within MFNT, nucleation and growth processes are described in terms of rate equations for the density of clusters. The mean-field approximation is made by neglecting spatial correlations, i.e., assuming that the spatial dependence of the densities can be neglected. For epitaxial growth in the submonolayer regime, the rate equations under certain conditions read (cf. Ref. [3])

$$\begin{aligned} \frac{d\langle n_1 \rangle}{dt} &= F(1 - \Theta) - 2D\sigma_1\langle n_1 \rangle^2 \\ &\quad - D\langle n_1 \rangle \sum_{k=2}^{\infty} \sigma_k \langle n_k \rangle, \quad (1) \\ \frac{d\langle n_k \rangle}{dt} &= D\sigma_{k-1}\langle n_1 \rangle \langle n_{k-1} \rangle \\ &\quad - D\sigma_k \langle n_1 \rangle \langle n_k \rangle \quad k = 2, \dots, \infty. \quad (2) \end{aligned}$$

Here  $\langle n_k \rangle$  is the spatially averaged density of clusters of  $k$  atoms,  $D$  is the (tracer) diffusion constant,  $F$  the influx of particles,  $\Theta$  the surface coverage, and  $\sigma_k$  the so-called *capture numbers* for the attachment of monomers to clusters of size  $k$  [8]. All clusters are assumed to be stable, i.e., neither dissociating nor diffusing. If the capture numbers can be calculated, the island density can be predicted with  $D$  as the only internal parameter. Conversely,  $D$  and thereby the adatom diffusion barrier,  $E_d$ , can be extracted from experimental island-density data, which is to a great extent why MFNT has become so widely used within the experimental growth community.

By calculating the capture numbers  $\sigma_k$  from a diffusion model and solving Eqs. (1) and (2) self-consistently, Bales and Chrzan have shown that the theory correctly predicts the time evolution of the island density [9]. Other experi-

mental [1] and theoretical [7] studies have further demonstrated the predictive power of MFNT over a wide range of growth conditions.

However, MFNT in its present forms does not take into account adsorbate interactions (elastic and/or electronic), which are always present to some degree. These interactions modify the nucleation and growth process, especially in weakly corrugated systems where the perturbation to the no-interaction approximation becomes severe. In the language of the MFNT framework, it is the capture numbers, and thereby the island densities, that are affected. Recent combined density-functional theory and kinetic Monte Carlo (KMC) studies [10–12] have quantified such adsorbate interactions, rationalizing experimental observations of unexpectedly high island densities [13] and demonstrating how conventional MFNT analyses can yield grossly incorrect diffusion parameters [10–12].

In this Letter, a nonlocal mean-field nucleation theory (NL-MFNT) is developed to extend the utility of conventional MFNT to include adsorbate interactions. (“Nonlocal” refers to the fact that standard MFNT ignores all interactions except the nearest-neighbor chemical bond, which is responsible for the capture process.) A new set of equations for the determination of capture numbers is presented. The scheme is tested with a realistic potential for adsorbate interactions and compared with KMC simulations for the same potential. The proposed NL-MFNT is shown to very accurately reproduce the “exact” KMC-simulated island densities. The extended theory opens the doors for analyzing STM growth experiments with a mean-field approach also for weakly corrugated systems, and for gaining insight into the mechanisms governing such growth processes.

The capture number is defined as the probability per time and diffusivity unit for a random walker to be captured by a certain island. For a density of random walkers, monomers say, in the proximity of an island with  $k$  atoms  $n_1^k(\mathbf{r})$ , the capture number  $\sigma_k$  is given by the inward flux of this density at the island perimeter [5]:

$$\sigma_k = \frac{2\pi r_k}{\langle n_1 \rangle} \left( \frac{\partial n_1^k(\mathbf{r})}{\partial r} \right)_{r_k}, \quad (3)$$

where  $r$  is the distance from the center of the island,  $r_k$  its radius, and  $\langle n_1 \rangle$  the monomer density far away from the island. By mass conservation,  $n_1^k(\mathbf{r})$  must satisfy

$$\begin{aligned} \frac{\partial n_1^k(\mathbf{r})}{\partial t} &= R_{\text{ads}} - R_{\text{des}} \\ &+ \sum_{\mathbf{r}' \neq \mathbf{r}} [\nu_{\mathbf{r}' \rightarrow \mathbf{r}} n_1^k(\mathbf{r}') - \nu_{\mathbf{r} \rightarrow \mathbf{r}'} n_1^k(\mathbf{r})] \\ &- R_{\text{capt}} + R_{\text{release}}. \end{aligned} \quad (4)$$

Here the first two terms denote adsorption and desorption rates, respectively. The sum represents jumps to and from site  $\mathbf{r}$  with jump rates  $\nu_{\mathbf{r}' \rightarrow \mathbf{r}}$  and  $\nu_{\mathbf{r} \rightarrow \mathbf{r}'}$ , respectively. The last two terms account for the loss and gain of monomers to and from other islands, respectively. For simplicity, it is assumed that reevaporation is frozen, sticking is facile, and attachment to islands is irreversible, so that  $R_{\text{des}} = 0$ ,  $R_{\text{ads}} = F(1 - \Theta)$ , and  $R_{\text{release}} = 0$ . In the *uniform depletion approximation* [14], the loss to other islands is calculated as in Eq. (1), i.e.,

$$R_{\text{capt}} = 2D\sigma_1 \langle n_1 \rangle + D \sum_{s=2}^{\infty} \sigma_s \langle n_s \rangle =: D\xi^{-2}. \quad (5)$$

The challenge, then, is to calculate the sum ( $S$ ) in Eq. (4). For motion along one axis and jumps only between neighboring sites, the sum can be written

$$\begin{aligned} S &= \nu_{i+1 \rightarrow i} n_1^k(i+1) + \nu_{i-1 \rightarrow i} n_1^k(i-1) \\ &- (\nu_{i \rightarrow i+1} + \nu_{i \rightarrow i-1}) n_1^k(i) \end{aligned} \quad (6)$$

for the site with index  $i$ . For a system with interacting adsorbates the rates will depend not only on the diffusion barrier for isolated monomers  $E_d$  but also on the interaction potential  $V$ . Evaluating the rates according to transition-state theory yields the expression

$$\begin{aligned} S &= D[n_{i+1} e^{-\beta(E_{\text{TR}} - V_{i+1} - E_d)} + n_{i-1} e^{-\beta(E_{\text{TL}} - V_{i-1} - E_d)} \\ &- n_i e^{-\beta(E_{\text{TR}} - V_i - E_d)} \\ &- n_i e^{-\beta(E_{\text{TL}} - V_i - E_d)}], \end{aligned} \quad (7)$$

where  $V_i$  is the minimum energy at site  $i$ ,  $E_{\text{TR}}(E_{\text{TL}})$  the saddle-point energy between sites  $i$  and  $i+1$  ( $i-1$ ),  $n_i = n_1^k(i)$ , and  $\beta = 1/k_B T$ . Now, in order to relate the jump rates to the interaction potential  $V(r)$ , the approximation

$$E^{TS} = E_d + \frac{1}{2}(E_f - E_i) \quad (8)$$

is applied for the activation energy, where  $E_f$  and  $E_i$  are the energies of the final and initial states of the motion, respectively. This approximation, successfully used by Fichthorn and Scheffler [10], simply means that one half of the energy difference  $E_f - E_i$  between the sites has been gained or lost, when the transition state is traversed. The sum in Eq. (7) becomes

$$\begin{aligned} S &= D[e^{-\beta \frac{V_{i+1} + V_i}{2}} (n_{i+1} e^{\beta V_{i+1}} - n_i e^{\beta V_i}) \\ &- e^{-\beta \frac{V_i + V_{i-1}}{2}} (n_i e^{\beta V_i} - n_{i-1} e^{\beta V_{i-1}})]. \end{aligned}$$

In the continuum limit, i.e., when replacing central differences with derivatives, this expression simplifies to

$$S = D \left( \frac{d^2 n}{dx^2} + \frac{dn}{dx} \beta \frac{dV}{dx} + n \beta \frac{d^2 V}{dx^2} \right), \quad (9)$$

if the steps are of unit length. In two dimensions (on a square lattice), it generalizes to

$$S = D(\nabla^2 n_1^k + \nabla n_1^k \cdot (\beta \nabla V) + n \beta \nabla^2 V). \quad (10)$$

As pointed out in Ref. [9], Eq. (1) cannot be satisfied as  $r \rightarrow \infty$ , if the time derivative of  $n_1^k(\mathbf{r}, t)$  is neglected. Instead, Eq. (1) is subtracted from Eq. (4) and deviations of the time derivative from its average value are neglected [9]:

$$\begin{aligned} \frac{1}{D} \left( \frac{\partial n_1^k}{\partial t} - \frac{d\langle n_1 \rangle}{dt} \right) &= \nabla^2 n_1^k + \nabla n_1^k \cdot (\beta \nabla V) \\ &+ n_1^k \beta \nabla^2 V - \xi^{-2} (n_1^k - \langle n_1 \rangle) \approx 0. \end{aligned} \quad (11)$$

With  $u_k = n_1^k / (\xi^{-2} \langle n_1 \rangle)$  and  $V_k^\beta = \beta V$  (highlighting the  $k$  dependence of  $V$ ), one has

$$\nabla^2 u_k + \nabla V_k^\beta \cdot \nabla u_k + (\nabla^2 V_k^\beta - \xi^{-2}) u_k = -1, \quad (12)$$

which with the boundary conditions

$$\begin{aligned} n_1^k(r_k) &= 0, \\ \lim_{r \rightarrow \infty} \frac{\partial n_1^k}{\partial r} &= 0 \end{aligned}$$

can be used to determine  $\sigma_k$  from Eq. (3). The boundary condition at  $r_k$ , the capture radius, means that the interaction potential is assumed to be strongly attractive at short distances, so that the monomers are actually captured. Equation (12) differs from the corresponding equation in Ref. [9] only in that here  $\nabla^2 n_1^k$  is replaced by  $\nabla^2 n_1^k + \nabla n_1^k \cdot (\beta \nabla V) + n_1^k \beta \nabla^2 V$ .

In the case of no adsorbate interactions,  $V_k = 0$ , Eq. (12) reduces to the diffusion equation for  $n_1^k$  derived in Ref. [5]. The solution yields [5,14]

$$\sigma_k = 2\pi X_k \frac{K_1(X_k)}{K_0(X_k)}, \quad (13)$$

$$X_k = \sqrt{\sigma_x n_x r_k^2}, \quad (14)$$

$$\sigma_x n_x = \sum_k \sigma_k n_k, \quad (15)$$

where  $K_0$  and  $K_1$  are the modified Bessel functions. A simplifying approximation is to set  $\sigma_k = \sigma_x$  for  $r_k = r_x$

and  $\Theta = \pi n_x r_x^2$ , so that Eq. (14) can be solved self-consistently for each value of  $\Theta$  [5]. In the general case, however, Eq. (12) has to be solved numerically to yield a value of  $\sigma_k$  for every value of  $\xi$ .

In order to verify the ability of this theory to include interactions in MFNT, I calculate the island density with and without interactions according to Eqs. (1)–(3) and (12) for a realistic potential and compare with kinetic Monte Carlo [15] simulations for the same system.

The choice of potential is based on the following considerations. Reference [12] concludes that elastic adatom-adatom interactions are very important in the epitaxial growth of Al(111). The elastic repulsion falls off asymptotically as  $1/r^3$  [16]. However, at shorter separations, the interaction must decrease and change sign within the capture radius for systems where attachment to islands is irreversible. For an adsorbate-adsorbate interaction dominated by elastic contributions, I therefore employ the potential

$$V^\beta(r) = A \frac{r}{1 + Br^4}. \quad (16)$$

The interaction is assumed to be pairwise additive, which means that

$$V_k^\beta(r) = \int_S V^\beta(|r\hat{x}' - \mathbf{r}'|) dS', \quad (17)$$

where  $S$  is a surface of area  $k$ , which is assumed to be circular. Setting  $A/E_d = 0.4$  and  $B = 0.05$  yields a potential that resembles the recently calculated elastic interactions on Al/Al(111) and Cu/Cu(111) fairly well [11].

The capture radii  $r_k$  are assigned according to

$$r_k = \alpha k^{1/D_f}, \quad (18)$$

where  $D_f$  is the fractal dimension of the islands [9]. Since the boundary condition at  $r = r_k$  is not exact,  $\alpha$  is a free parameter of the theory, albeit arguably close to unity. Setting  $\alpha = 1.0$  for ramified islands (for which  $D_f \approx 1.7$  [9,17]), the KMC simulated island density is reproduced for a wide range of  $D/F$  values [9].

In the KMC simulations, atoms are deposited at random on an initially clean surface and allowed to diffuse on a close-packed lattice with periodic boundary conditions. The activation energy for adatom diffusion is subject to adjustments from interactions with nearby adatoms, as inferred from Eq. (16) using the barrier model in Eq. (8). For atomistic processes at kinks, corners, and edges of islands, the first-principles computed activation energies for Al/Al(111) reported in Ref. [18] are used, although at the relatively low temperatures considered here these processes are so rare that the ramified growth mode is preserved, and the island density is thus only marginally affected by them. The growth rate is set to 0.03 ML/s, while  $E_d/k_B T$  is varied within the range 6–19. A diffusion prefactor of  $6 \cdot 10^{12}$  Hz is used in all simulations.

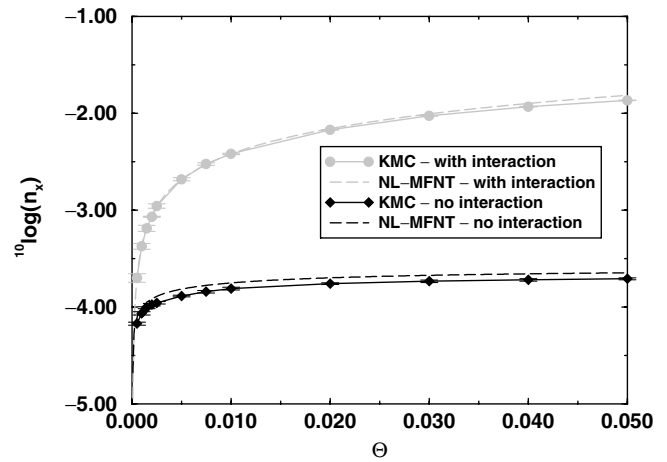


FIG. 1. Simulated island densities at  $k_B T = E_d/12$  and  $F = 0.03$  ML/s (so that  $D/F = 10^9$ , if the diffusion prefactor is  $6 \times 10^{12}$  Hz). The simulations are carried out with KMC and NL-MFNT with and without the interaction of Eq. (16).

In Fig. 1 the island densities for the cases of  $V = 0$  and  $V = V_k^\beta$ , both as simulated with KMC and calculated with NL-MFNT, are displayed as a function of the coverage  $\Theta$ . Evidently, the NL-MFNT reproduces the KMC results well, both with and without adsorbate interactions, even though the island density is augmented by more than 2 orders of magnitude by the interactions. Note that the same value of the parameter  $\alpha$  (1.0) is used in both cases [19].

The temperature dependence, too, is well reproduced by the NL-MFNT, as the diffusion parameter,  $D/F$ , is varied by 6 orders of magnitude (Fig. 2). The increasing discrepancies at high temperatures are related to a slight inconsistency in the calculations: the assumption of circular island geometry to calculate  $V_k^\beta$  from Eq. (17) is not perfectly

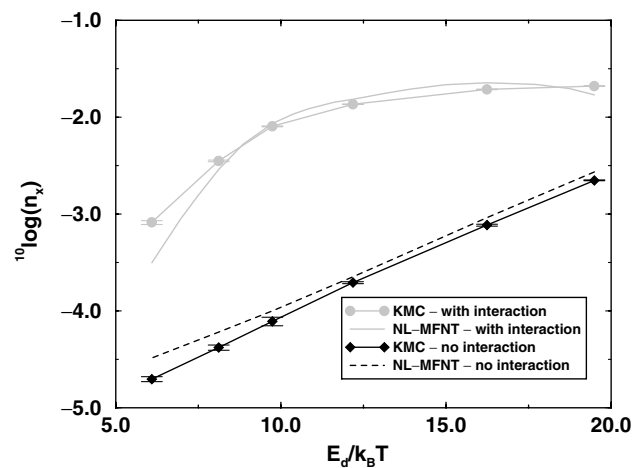


FIG. 2. Island density as a function of inverse temperature at  $\Theta = 5\%$  and  $F = 0.03$  ML/s (corresponding to  $D/F$  values in the range  $7 \times 10^5$  to  $5 \times 10^{11}$ ). The simulations are carried out with KMC and NL-MFNT with and without the interaction of Eq. (16).

valid and yields more appreciable errors, as the islands grow larger at higher temperatures.

In contrast, a traditional MFNT analysis for the island-density data presented in Fig. 2 would be very misleading: It assumes the island density to be related to the monomer diffusivity through a *scaling law* [5,20]

$$n_x = C \eta(\Theta, i) \left(\frac{D}{F}\right)^{-\chi} \exp\left[\frac{E_i}{(i+2)k_B T}\right]. \quad (19)$$

Here  $i$  denotes the *critical* cluster size, i.e., the number of atoms in the smallest stable nucleus minus one,  $E_i$  its binding energy,  $\chi = i/(i+2)$ ,  $\eta(\Theta, i)$  a universal function of the coverage  $\Theta$ , and  $C$  a geometry factor of order unity. At low temperatures, where dimers are stable,  $i = 1$  and  $E_i = 0$ , so that  $n_x$  obeys an Arrhenius law with the exponent  $1/3\beta E_d$ . At higher temperatures, the exponent is expected to change into  $\beta(1/2E_d + 1/4E_1)$ , as dimers begin to dissociate. In the standard MFNT analysis an apparent activation energy for monomer diffusion  $E_d^{\text{app}} \approx 0.4E_d$  would be deduced from the low-temperature data, and the drop of  $n_x$  at higher  $T$  would be interpreted as an effect of the dissociation of dimers with the binding energy  $E_1^{\text{app}} \approx 3E_d$ —both results being incorrect simply because standard MFNT neglects to include adsorbate interactions.

It should be pointed out that the NL-MFNT may not be applicable for extremely dense systems, where most mass transport does not take place where interactions are negligible. For such high densities, however, the very mean-field assumption is likely to break down anyway, with or without interactions.

To conclude, this study presents a generalization of standard mean-field nucleation theory that takes into account the effect of nonlocal adsorbate interactions. Without introducing any additional fitting parameters to conventional MFNT, the NL-MFNT is shown to successfully predict the island density, where MFNT fails to do so. By taking into account nonlocal adsorbate interactions, the new theory thus extends the realm of mean-field analyses to include also low-corrugated adsorbate-substrate systems. Given that the use of MFNT in other fields of research, e.g., catalysis, is often prevented by the neglect of adsorbate interactions, the proposed NL-MFNT should also facilitate a general extension of applicability of the theory.

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