Mean-field theory of nucleation and growth on strained surfaces

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Over the past few years, it has become clear that capture of adparticles (atoms, molecules, and/or small clusters) on surfaces cannot always be treated in the diffusion-controlled limit and that adparticle interactions are often important in forming nanostructures. For example, repulsive interactions are thought to play an important role in the nucleation and growth of metal nanoclusters, hut clusters, and nanowires. Recent papers on the early stages of growth of metal nanoclusters, hut clusters, and nanowires. Forming nanostructures. For example, repulsive interactions limit and that adparticle interactions are often important in surfaces cannot always be treated in the diffusion-controlled approach and show that they are inapplicable to the case of strain fields. We then construct an extension of MFT which correctly describes nucleation and growth in the presence of strain fields and apply this theory to calculate island growth quantities of interest.

As mentioned by Ovesson,3 the challenge to deriving a continuum mean-field description from Eq. (1) stems from calculating the sum. Hence, we shall focus solely on this sum and ignore the other terms. According to transition-state theory, the hopping rate between two sites i and j take the general form,

\[ W_{i \rightarrow j} = W_{i \rightarrow j}^0 e^{-\beta E_{i \rightarrow j}} \]  

where \( E_{i \rightarrow j} \) is the energy barrier jump from site i to j and \( \beta = (k_B T)^{-1} \). In the absence of an external field, the diffusion barrier is given by \( E_{i \rightarrow j} = E_i - E_j \), where \( E_i \) and \( E_j \) are the adparticle energies at site i and at the saddle point between sites i and j, respectively. This energy difference is usually denoted as the diffusion energy \( E_d \). Here, we use \( E_d \) for the zero-strain value.

The application of an external field \( V \) changes the diffusion barrier to \( E_{i \rightarrow j} = E_i + V_i - E_j - V_j \). Assuming that the change of saddle-point energy in an external field equals the average changes at the binding sites, i.e., \( V_i = (V_i + V_j)/2 \), we get

\[ E_{i \rightarrow j} = E_d + \frac{V_i - V_j}{2}. \]

Note that this is exactly the expression used by Ovesson3 in the derivation of his nonlocal MFT. Thus, we stress that an implicit assumption is that the change of saddle-point energy in an external field equals the average changes at the binding sites. This assumption may perhaps work well in a particular
situation, e.g., Ref. 1; however, we show here that it is not
generally satisfied, for the important case of fields due to
strain. We illustrate this flaw using an analytic one-
dimensional (1D) model.

Consider a 1D substrate in which substrate atoms are
periodically placed with a lattice spacing \( a \). The interactions
between an adatom and substrate atoms and between the
substrate atoms themselves are via a Lennard-Jones (LJ) 6-12
potential: \( V(r) = 4\gamma \left[ (\sigma/r)^{12} - (\sigma/r)^{6} \right] \).

The equilibrium spacing between the substrate atoms is
\( a_0 = 2^{1/6} \sigma \), but since the spacing is kept fixed at a value \( a \), this implies that the surface
is under a strain given by \( \varepsilon = (a - a_0)/a_0 = 2^{-1/6} \sigma^{-1} a - 1 \). This
model was considered by Shu and Gong\(^7\) in the context of
carbon nanotubes, in which case, it was solved numerically.

We are interested in deriving explicit expressions for the
changes in potential energy at the binding sites and at the
saddle points as a function of strain; thus, we can assess
directly whether the assumption discussed in previous para-
graphs holds or not for the cases of compressive and tensile
strain fields. Note that the substrate is “frozen,” i.e., once the
spacing \( a \) (and thus the strain) is changed to a new value, the
substrate atoms are not allowed to relax back to the equilib-
rium spacing but remain in a stressed state with the new
spacing \( a \). Positive values of \( \varepsilon \) correspond to strain due to a
tensile stress and negative values to compressive strain.

The binding sites and the saddle points in this model natu-
really correspond to the hollow and the atop sites. To a first
approximation, the adatom will adopt a configuration such
that the distance to its nearest neighbors is equal to \( a_0 \) (see
Ref. 8 for a general discussion of this point). Then, it is
easily shown that the potential energy of the adatom includ-
ing interactions up to next-next nearest neighbors, at a bind-
ing site (\( V_1 \)) and at a saddle point (\( V_2 \)), is given by

\[
V_1 = 2 \gamma [4((\sigma r_1)^{12} - (\sigma r_1)^6) + 4((\sigma r_2)^{12} - (\sigma r_2)^6) - 1] \tag{4}
\]

\[
V_2 = \gamma [8((\sigma r_3)^{12} - (\sigma r_3)^6) + 8((\sigma r_4)^{12} - (\sigma r_4)^6) - 1] \tag{5}
\]

where distances are given by \( r_1^2 = a_0^2 + 2a^2 \), \( r_2^2 = a_0^2 + 6a^2 \), \( r_3^2 = a_0^2 + 4a^2 \), and \( r_4^2 = a_0^2 + 6a^2 \). Using the previously stated relation
between \( a especially one can Taylor expand these equations in
the strain to obtain

\[
V_1 = - \gamma (2.16 - 0.63 \varepsilon) + O(\varepsilon^2) \tag{6}
\]

\[
V_2 = - \gamma (1.50 - 1.47 \varepsilon) + O(\varepsilon^2) \tag{7}
\]

Using the notation introduced in the prelude to Eq. (3),
the changes in saddle-point energy and binding energy due to
the strain field are \( V'_s = 1.47 \varepsilon \gamma \) and \( V'_b = 0.63 \varepsilon \gamma \). This explicitly
shows that the assumption that the saddle-point energy is
an average of the neighboring binding site energies is incorrect
when a small strain field is applied to a given surface. Since
the barrier energy will vary with strain, then the local diffu-
sion coefficient \( D \) must also depend on the local magnitude of
the strain; this feature is missing from Ovesson’s extended
version of conventional MFT. These results can also be ob-
tained from a two-dimensional (2D) analog of our model; in
this more general case, the saddle-point and binding energies
(and hence values of \( D \)) at a site are linear combinations of
the local strain tensor components.

We note that the dependence of the diffusion barrier on
the strain is also known from first-principles calculations of
adatom diffusion on Si(001) surfaces.\(^9\) In line with the
predictions of these more detailed models, we find that \( D \)
generally increases with the application of compressive
strain (negative \( \varepsilon \) and decreases for tensile strain (positive \( \varepsilon \)).
First-principles calculations show that these effects are
still present when the substrate is allowed to relax due to the
adatom\(^9\) and that quantitative differences between this case
and the frozen substrate case are small,\(^8\) at least for the LJ
potential.

We now develop the continuum mean-field theory of ad-
particle dynamics on strained surfaces. Generally, the strain
at a given point on the surface will be due to nonlocal islands
or other nanostructures. The general case is that of an inho-
mogeneously strained surface such that the strain is given by
some function of space and time \( \varepsilon = \varepsilon(x, y, t) \). We will use the
results previously derived for homogenously strained sur-
faces locally; the use of the results for homogeneous fields to
understand the case of heterogeneous fields has been previ-
ously verified to yield qualitatively correct predictions using
microscopic simulations.\(^8\)

We shall assume that the adparticles move on a 2D square
lattice of substrate atoms. Let the strain at lattice site \( i \)
be \( \varepsilon_i \); then, the extra potential at binding site \( i \) due to
the application of a strain field is \( V_i = \alpha_i \varepsilon_i \). Similarly, the
change in the saddle-point potential \( V'_s = \alpha_s (\varepsilon_i + \varepsilon_j)/2 \). The values of these two parameters depend on the specific
type of adparticles, surfaces, and interactions under consid-
eration. Note that since \( \alpha_i, \alpha_s, \) and \( \varepsilon \) are generally tensors
(and functions of position), a summation convention is
implied in our equations for the potential energies, e.g.,
\( \alpha_i \varepsilon = \alpha_{1x} \varepsilon_{1x} + \alpha_{1y} \varepsilon_{1y} + \cdots \). In the spirit of mean-field approxi-
mation, we assume that the strain is slowly varying between
neighboring lattice points. Thus, the equation for the energy
barrier takes the form

\[
E_{i\rightarrow j} = E_d + V_s - V_i = E_d + \frac{\alpha_s}{2} (\varepsilon_i + \varepsilon_j - \alpha_i \varepsilon_i) \tag{8}
\]

which leads to transition rates of the form

\[
W_{i\rightarrow j} = W^0_{i\rightarrow j} e^{-\beta(E_d - (1/2)\alpha_s \varepsilon_i - \beta(1/2)\alpha_i \varepsilon_i)} \tag{9}
\]

The factor \( W^0_{i\rightarrow j} e^{-\beta E_d} \) has units of inverse time and so can be
expressed as \( D_1 / h^2 \), where \( D_1 \) is the diffusion coefficient
of the adparticles in the absence of external fields and \( h \) is the
lattice spacing. Hence, the previous expression can berewrite-
in the convenient form

\[
W_{i\rightarrow j} = f_j g_j / h^2 \tag{10}
\]

where

\[
f_j = \sqrt{D_1} e^{-(1/2)\alpha_s \varepsilon_i} \tag{11}
\]

\[
g_j = \sqrt{D_1} e^{-\beta(1/2)\alpha_i \varepsilon_j} \tag{12}
\]

In a separate but related development, Grima and
Newman\textsuperscript{11} showed that advection-diffusion equations of the general form
\begin{equation}
\frac{\partial c}{\partial t} = \nabla \cdot (D \nabla c) - \nabla \cdot (vc),
\end{equation}
where $D=fg$ and $v=g\nabla f - f \nabla g$ are the continuum limit of discrete master equations of the form
\begin{equation}
\frac{\partial c_j}{\partial t} = \sum_i [W_{i\rightarrow j} - W_{j\rightarrow i}],
\end{equation}
where the sum is over nearest neighbors of site $i$ and the transition rates are of the form of Eq. (10). Note that $f$ and $g$ are some functions of space and time and $f_j$ represents the value of the function $f$ at site $j$ on a regular lattice of step size $h$. This result is valid in all dimensions; it is useful in the context of this Brief Report in that it enables us to immediately construct the macroscopic dynamical equation from the underlying microscopic equations since our rate equations are exactly of the above form. Substituting the forms of $f$ and $g$ which we previously derived, Eqs. (11) and (12), into the expressions for the macroscopic diffusion and drift velocity following Eq. (13),
\begin{equation}
D(x,y) = D_1 e^{-\beta(\alpha_3-\alpha_1)e(x,y)},
\end{equation}
\begin{equation}
v(x,y) = -\beta D(x,y) \left( \frac{\partial (\alpha_1 e)}{\partial x} \hat{x} + \frac{\partial (\alpha_1 e)}{\partial y} \hat{y} \right).
\end{equation}
Hence, the continuum mean-field description of adparticle diffusion on homogeneously or inhomogeneously strained surfaces is given by Eq. (13) with Eqs. (15) and (16).

We now use these equations to investigate adatom kinetics near an island. This shall be done in two distinctive ways: first, by means of an analytical approach to distill the main features of adparticle movement in the neighborhood of an island and second, by direct numerical integration of the mean-field equations for the special case of Ge islands on Si(001).

The calculation of the strain field around an island is the subject of ongoing research. However, it is well known that for a relatively flat island in a one-dimensional space, an approximative expression is given by\textsuperscript{12,13}
\begin{equation}
e(x) = e_0 + 2e_0 \tan(\theta) \frac{1 + \nu}{\pi} \ln \left[ \frac{(x - H \cot(\theta) + L_2)(x + H \cot(\theta) - L_2)}{(x + L_2)(x - L_2)} \right],
\end{equation}
where $\theta$ is the angle of the island facets, $H$ is the height, $e_0$ is the misfit strain, $\nu$ is the Poisson ratio, and $L_2$ is half the base length $L$. Here, the edges are at $x=\pm L_2$. This approximation is valid for a relatively flat island satisfying $H/L \ll 1$; this has been verified by molecular dynamics simulations of Ge on Si(001).\textsuperscript{13} A two-dimensional ($1+1$) model of this type also captures the main features of the strain field close to a 2D island edge, though it neglects corner effects (see Zinovyev et al.\textsuperscript{14} and references therein).

Using the above expression and Eq. (15), one can easily get an expression for $D$ as a function of distance from the island. Close to the island, this expression reduces to $D(x) \approx (x-L_2)^{\omega}$ in the range $x > L_2$, where the proportionality constant is positive and $\omega=2\beta e_0 \tan(\theta)(\alpha_3-\alpha_1)/(1+\nu)/\pi$. Using Eq. (16), one can similarly calculate $v$ in the vicinity of the island, finding that the leading term is $v(x) \approx e_0 e(x-L_2)^{\omega-1}$. It is difficult to generalize beyond this point because the exact behavior depends on the signs of $\alpha_1$ and $\alpha_2-\alpha_1$. If we consider the case of Ge on Si, $\alpha_1$ and $\alpha_2-\alpha_1$ are known from Refs. 9 and 10 to be negative in the case of $\alpha_1$ and positive in the case of $\alpha_2-\alpha_1$. Since $e_0$ is also negative for this case,\textsuperscript{15} then it follows that the drift velocity is away from the island on each side. The diffusion coefficient increases monotonically as the island is approached from either side. Note that these predictions are different than those from Övesson’s theory;\textsuperscript{3} the latter corresponds to the special case $\omega=0$ in our theory which implies a constant diffusion coefficient and a drift velocity which decays artificially slowly with distance from the island.

Now, we consider the case of monolayer (ML) thick islands of Ge on Si(001), which we study by direct numerical integration of the mean-field equations. The case of anisotropic but spatially constant $D$ has already been studied.\textsuperscript{14} Here, we extend this by a brief study of the effect of strain on island growth, with a more detailed study to follow.\textsuperscript{15} The adparticle dynamics follows the continuum equation [Eq. (13)] with the diffusion coefficient and drift velocity given by Eqs. (15) and (16) and with the strain field given by Eq. (17). This equation is integrated using the master equation discretization approach;\textsuperscript{11} the stability analysis is given in Ref. 16.

We study the case of an island with $H=1$ in the $128 \times 1$ periodic simulation space, the facet angle $\theta=45^\circ$, and initial length $L=11$ units, at $T=450$ °C. We use $e_0=-0.042$, $\nu=0.26$, $\alpha_1=-1.75$ eV, and $(\alpha_2-\alpha_1)=0.75$ eV; all values are appropriate for Ge on Si.\textsuperscript{9,10,13} Illustrative results are given in Figs. 1 and 2.

Figure 1 shows the plots of diffusion coefficient, drift velocity, and strain as a function of distance from the island center. The deposited dose $Ft$ at $t=400$ is 0.4 ML in units of $H$; the initial adparticle concentration is 0.005 ML. The zero-strain values of $D_1=5$ and $\Delta t=0.03$ are chosen such that stability is assured for all strains encountered. The data are for the end of a run in which the island size and strain field are updated when the amount of material added to each side of the island has increased by one lattice constant. Time-lapse movies have been made to visualize the growth processes, as MATLAB movies (mov) and video clips (avi).\textsuperscript{14,15}

The diffusion constant $D$ and strain are both symmetric in position $x$, whereas the drift velocity $v$ is antisymmetric; the case of $\alpha_2-\alpha_1=0.75$ eV is highlighted, with the $\alpha_2=\alpha_1$ case shown by the dotted line for comparison. Note that strain causes a 60% increase in the diffusion constant far away from the island and a much larger enhancement close to the island edges.

Figure 2 shows the corresponding adparticle concentration profiles and final island sizes. We see directly that $\alpha_2=\alpha_1$, curve (a), leads to incorrect predictions of island growth rates. In our case [$e<0$ and $\alpha_2>\alpha_1$, curves (b) and
island. More cases are considered elsewhere. Strain-enhanced diffusion is able to overcome the general trend of drift away from the center. The dotted and dash-dotted lines are for \( \alpha_2 - \alpha_1 = -1.75 \) eV. The solid (red/gray, black, and green/light gray) lines are for \( \alpha_2 - \alpha_1 = 0.75 \) eV, with \( \alpha_1 = -1.75 \) eV.

To summarize, we have introduced a quantitative treatment of nucleation and growth on a lattice, in which the transport coefficients are directly deduced from the microscopic dynamics for the case of strain. For specific systems, such as Ge/Si(001), this may limit application to relatively low temperatures, where interdiffusion is unimportant. Epitaxial growth in such systems at high temperatures is complex and is specific to all the (nonlinear) processes, such as reconstruction and nucleation that need to be considered. Our general approach allows such processes to be added one at a time to study particular regimes in any specific system.

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17. The values of \( D_1 \) and time scale \( \tau \) given are for the simulation. They can be chosen to agree with experiment at a given temperature \( T \) by suitable choice of time units.