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Growth mechanisms on stepped surfaces, from atomistic to step-flow models

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Abstract

Molecular beam epitaxy (MBE) serves as a prototype example for growth far from equilibrium. A variety of approaches to the modeling and simulation of epitaxial growth have been applied. They range from detailed treatments of microscopic processes in ab initio molecular dynamics to coarse-grained descriptions in terms of partial differential equations. A connection between these models is mainly missing. We will formally derive from solid-on-solid models via a diffuse interface approximation the well known Burton–Cabrera–Frank equations for step flow.

Keywords: A1. Computer simulation; A1. Crystal morphology

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1. Introduction

Various mathematical models and numerical algorithms are proposed for describing epitaxial growth processes. For a review on theoretical approaches see Refs. [1–3]. Due to the underlying multiscale phenomena, which range from the interaction of single atoms up to an engineering scale, on which the transport of material to the surface in the growth chamber needs to be described, the models can be distinguished by the relevant length and time scales they are living on:

(a) *molecular dynamics*: Real-space trajectories of atoms are determined by numerical integration of Newton’s equation of motion. All of the physics is contained in the interatomic potentials for the atoms in the system;
(b) *kinetic Monte Carlo* (KMC): Individual atoms are the basic degrees of freedom and single hoppings to neighboring lattice sites are performed according to a specified probability for these hops to occur;
(c) *step-flow models*: The atomic distance in the growth direction is discrete, but the atomic

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distance in the lateral direction is coarse-grained. The steps are assumed to be smooth curves and serve as free boundaries for an adatom diffusion equation on terraces;

(d) *continuous models*: The atomistic processes at steps are neglected, the overall surface is assumed to be smooth and is described by evolution laws for the height of the growing film.

The first approach, considered ab initio or classical, is today not feasible to perform realistic growth simulations. Due to the limitations in the time scales of these methods macroscopic growth cannot be reached even on high-performance computers. First-principle calculations can provide detailed information on the energies of specific atomic configurations and thereby are well suited to determine pathways and diffusion barriers [4] and molecular dynamics are suitable to provide energy barriers for particular kinetic processes. But in principle these methods suffer from the fact, that the system spends most of its time vibrating around local equilibrium states, with occasional sudden hops to neighboring sites. By regarding these vibration cycles as an attempt to perform a hop to a neighboring lattice site the pathway to KMC simulations is drawn, for a review see Ref. [5]. In these simulations the number of attempts necessary to perform the hop is represented by a probability. These methods are successfully applied to growth phenomena in epitaxy but still suffer from the discrete description of single atoms if length scales of several micrometers need to be reached. Attempts to combine KMC methods with step-flow methods to overcome this limitation have recently been described in Refs. [6,7]. Step-flow models can describe growth processes on larger scales by incorporating kinetic effects at step edges [8]. But a rigorous derivation of these models from atomistic models is still missing. Furthermore efficient numerical approaches for these models are only recently developed [9–11] and have until now not been shown to be applicable to realistic growth processes. In Ref. [12] a first step in this direction is performed by linking a one-dimensional step-flow model to macroscopic heat and mass transfer to model liquid-phase epitaxy. Combining step-flow models with continuum models for the height of the growing film is considered in Ref. [13]. This approach allows to reach macroscopic growth but also is until now only applied in one-dimensional settings. All available continuum models are phenomenological models in which kinetic effects are introduced in a heuristic way, for an overview see Ref. [14].

The main challenge in modeling epitaxial growth is to bridge the gap between these different models and to describe a growth process on a continuous scale by incorporating atomic effects. Even if there are many open questions regarding the coupling of each of these models, the main cut occurs between atomistic models and discrete–continuum models. In this article, we will concentrate on step-flow models and describe an idea how they can be derived from discrete atomistic models.

2. Discrete atomistic models

Descriptions of atomic mechanisms of epitaxial growth are based on surface models, which include

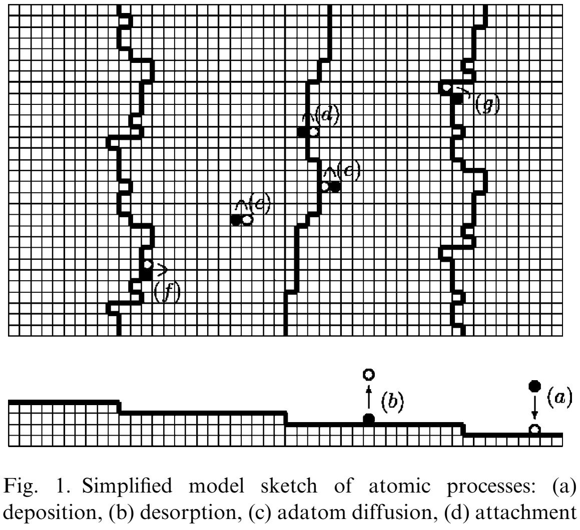

Fig. 1. Simplified model sketch of atomic processes: (a) deposition, (b) desorption, (c) adatom diffusion, (d) attachment of adatom to step edge from upper terrace, (e) attachment of adatom to step edge from lower terrace, (f) diffusion of edge adatom along step edge, (g) diffusion of step adatom into a kink position.

terraces, step edges and kinks, as well as several elemental entities such as adatoms and edge adatoms. See Fig. 1 for some basic events which can occur on such surfaces. The level of understanding of this phenomena has been driven by the information that can be obtained from available experimental techniques. Scanning tunneling microscopy (STM) today allows a direct visualization of the atomic structures and can be used to determine quantitatively kinetic and thermodynamic properties of the surface.

In addition to the experimental observations first-principle methods and molecular dynamics can be used to identify further kinetic processes. For each identified event transition state theory can be applied to calculate activation energies. As illustrated in Fig. 2 the total activation barrier E_a of a process is the sum of the energy difference E_if between the initial state i and the final state f and the kinetic barrier E_kb.

Together with the Arrhenius law, from this energy barriers rates for KMC simulations can be calculated for each single hop: $K(T) = K_0 \exp(-E_\mathrm{a}/k_\mathrm{B}T)$, where K_0 is a probability per attempt to perform the hop, k_B is the Boltzmann constant and T is the temperature. These processes are treated as probabilistic and random numbers are used within the KMC approach to decide which event occurs. Even if today length scales up to 1 μm and time scales of several seconds can be reached with KMC methods, technologically important phenomena on length scale of electronic devices can still not be simulated with such an approach.

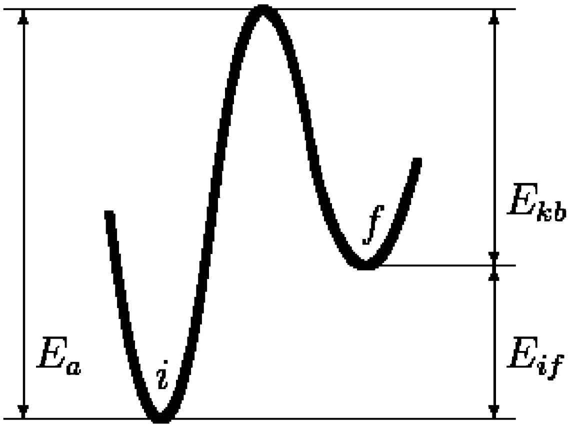

Fig. 2. Potential energy diagram for a diffusion process between neighboring sites.

3. Toward a continuum description

We introduce a continuous diffuse interface approximation for the shape of the stepped surface and the adatoms on it. Thereby, we treat the microscopically sharp step edges as a diffuse region were two terraces of different height coexist, see Fig. 3.

The phase-field variable ϕ smoothly varies from one discrete monolayer height to the other and can be seen as a continuous height function. All relevant atomic effects at the steps will thereby be incorporated into the continuous model through the diffuse interface region. Phase-field models for epitaxial growth which account for kinetic effects at the steps have recently been introduced [15–17]. The asymmetry in the attachment of adatoms to the steps from the upper and lower terrace (Ehrlich–Schwoebel effect) is thereby

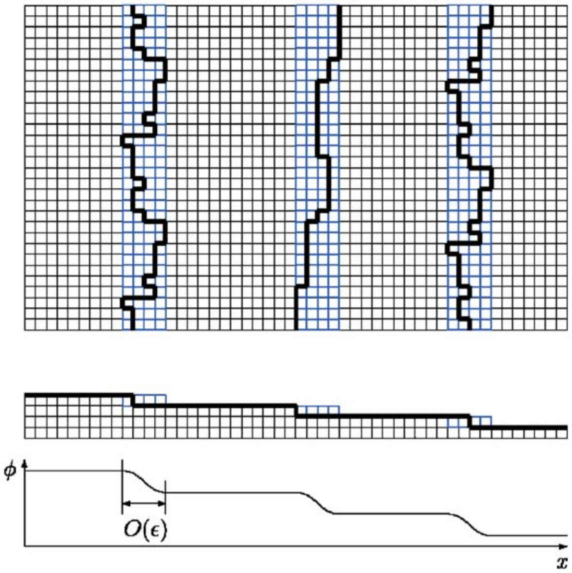

Fig. 3. Diffuse interface approximation of rough step edges. Smeared out interface region and phase-field variable.

introduced through a degenerate mobility function within the adatom diffusion equation inside the diffuse interface region. The diffusion of edge-adatoms along the steps (edge-diffusion) is modeled through an enhanced mobility [18] in that region. Even if these mobilities are mathematically introduced in order to recover the underlying phenomena in the discrete–continuum step-flow model, an analogy to the atomistic potential energy diagram can be drawn. If we translate this diagram into a mobility function an energy barrier corresponds to a low mobility whereas a energy sink results in an enhanced mobility, see Fig. 4.

The phase-field model reads

$$\partial_t \rho = \nabla \cdot (M(\phi)\nabla\rho) + F - \tau^{-1}\rho - \partial_t\phi,$$
$$\alpha\varepsilon^2\partial_t\phi = \varepsilon^2\Delta\phi - \frac{\partial G(\phi)}{\partial\phi} + \frac{\varepsilon}{\mu\rho^*}(\rho - \rho^*) \qquad (1)$$

with $\varepsilon \ll 1$ corresponding to the interfacial thickness, $\rho = \rho(x, y, t; \varepsilon)$ denotes the adatom density, $\phi = \phi(x, y, t; \varepsilon)$ the phase-field variable, F the deposition flux, τ^{-1} the desorption rate, μ the step stiffness and ρ^* an equilibrium adatom density for straight steps. α is a constant parameter and $G(\phi)$ a multiwell potential, where each minimum corresponds to a phase (terrace height) of the system. The potential can be chosen as $G(\phi) = c(\phi - i)^2(i + 1 - \phi)^2$, $\phi \in [i, i+1]$, $i = 0, \ldots, N-1$ counting the atomic monolayers. The mobility function $M(\phi)$ is chosen in a way as described in Fig. 4. The parameter α and the mobility function M contain all the kinetic information from the underlying discrete model.

4. Sharp interface limit

Matched asymptotic analysis has been performed in order to derive a sharp interface limit for vanishing interfacial thickness $\varepsilon \to 0$, see Fig. 5.

In Ref. [16] the Burton–Cabrera–Frank model in the attachment limited case is recovered:

$$\partial_t\rho_i - D\Delta\rho_i = F - \tau^{-1}\rho_i \quad \text{in } \Omega_i(t),$$
$$-D\nabla\rho_i \cdot \vec{n}_i = k_+(\rho_i - \rho^*(1 + \mu\kappa_i)) \quad \text{on } \Gamma_i(t),$$
$$D\nabla\rho_{i-1} \cdot \vec{n}_i = k_-(\rho_{i-1} - \rho^*(1 + \mu\kappa_i)) \quad \text{on } \Gamma_i(t),$$
$$v_i = -D\nabla\rho_i \cdot \vec{n}_i + D\nabla\rho_{i-1} \cdot \vec{n}_i \quad \text{on } \Gamma_i(t)$$

with $\rho_i = \rho_i(x, y)$ the adatom density on terrace $\Omega_i(t)$, $\Gamma_i(t)$ the smooth step of zero thickness between $\Omega_i(t)$ and $\Omega_{i-1}(t)$, attachment coefficients k_+ and k_- which depend on the used mobility function in the phase-field model and κ_i the curvature of the step. In Ref. [17] the Burton–Cabrera–Frank model in the diffusion limited case

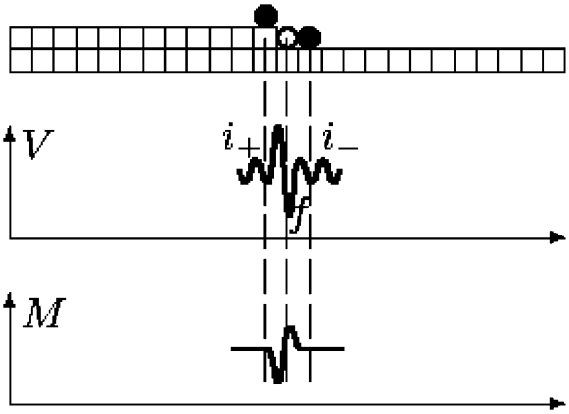

Fig. 4. Potential energy diagram for attachment of adatoms to a step edge (f) from upper terrace (i_+) and lower terrace (i_-) and corresponding mobility function.

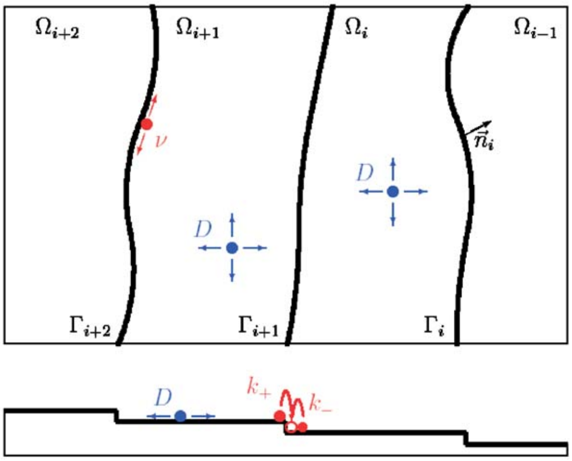

Fig. 5. Sharp interface limit with smooth step-edges of zero thickness, adatom diffusion on terraces, attachment of adatoms to step-edges from upper and lower terraces, step-edge diffusion.

with edge-diffusion is obtained:

$$\begin{aligned}
&\partial_t \rho_i - D\Delta\rho_i = F - \tau^{-1}\rho_i \quad \text{in } \Omega_i(t),\\
&\rho_i = \rho_{i-1} = \rho^*(1+\mu\kappa_i) \quad \text{on } \Gamma_i(t),\\
&v_i = -D\nabla\rho_i \cdot \vec{n}_i + D\nabla\rho_{i-1}\cdot\vec{n}_i\\
&\qquad + \nu\partial_{ss}\kappa_i \quad \text{on } \Gamma_i(t)
\end{aligned}$$

with ν a mobility function for step-edge diffusion again depending on the used mobility function in the phase-field model and ∂_s denotes derivative with respect to the arc length. Combining both phase-field models in an appropriate way and extending it to the anisotropic situation yields an approximation of the Burton–Cabrera–Frank model in the attachment limited case with edge-diffusion:

$$\begin{aligned}
&\partial_t \rho_i - D\Delta\rho_i = F - \tau^{-1}\rho_i \quad \text{in } \Omega_i(t),\\
&-D\nabla\rho_i \cdot \vec{n}_i = k_+(\rho_i - \rho^*(1+\mu\kappa_i)) \quad \text{on } \Gamma_i(t),\\
&D\nabla\rho_{i-1} \cdot \vec{n}_i = k_-(\rho_{i-1} - \rho^*(1+\mu\kappa_i)) \quad \text{on } \Gamma_i(t),\\
&v_i = -D\nabla\rho_i \cdot \vec{n}_i + D\nabla\rho_{i-1}\cdot\vec{n}_i\\
&\qquad + \partial_s(\nu\partial_s(\mu\kappa_i)) \quad \text{on } \Gamma_i(t)
\end{aligned}$$

In this model the kinetic coefficients k_+ and k_- as well as the edge adatom mobility ν are derived via the mobility function M and the parameter α, which can be related to the underlying microscopic potential energy surface.

5. Conclusions

The diffuse interface model serves in the described context as a connection between atomistic and discrete continuum step-flow models. The introduced mobility function in the phase-field model, thereby, translates in the limit of vanishing interfacial thickness the microscopic potential energy surface into the kinetic coefficient in the step-flow model.

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