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Theory of Impurity Induced Step Pinning and Recovery in Crystal Growth from Solutions

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We extend the terrace-step-kink model of crystal growth to impure solutions where the impurities act as barriers to step motion. The effects of supersaturation, step curvature, step repulsions and impurities on step motion are treated in a unified free energy framework. The model reproduces several features seen in experiments on growth of KDP crystals, wherein a dead zone at low supersaturations, and a recovery of crystal growth by motion of large coherent step bunches at larger supersaturations are observed. We identify a key feature of solution growth that leads to these effects.

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Crystal growth at low temperatures is characterized by the attachment and detachment of adatoms at the edges of steps. Under ideal conditions growth on a vicinal surface proceeds by step flow, with steady motion of a uniform train of steps. However the addition of small concentrations of impurities can greatly change the properties, morphology, and kinetics of the growing crystal, with important consequences in both biological and materials applications [1–4]. In a recent series of experiments, De Yoreo and coworkers [5–7] studied the effect of metallic ion impurities that locally inhibit step motion on potassium dihydrogen phosphate (KDP) crystals grown from a stirred solution. Using AFM imaging, they found that at low supersaturation the impurities induced the formation of v-shaped bunches of closely spaced steps as the crystal growth slowed down and essentially stopped. However, at larger supersaturation, they observed a recovery of growth to a rate approaching that of an impurity free solution. Surprisingly, the growth was dominated by the motion of large step bunches, whereas isolated steps still seemed immobile.

The initial step bunching at small driving force is qualitatively consistent with the classic Frank impurity model [8], originally developed to describe vapor growth and extended to two dimensions (2D) by Kandel and Weeks (KW) [9]. Impurities are assumed to adsorb on the crystal surface at random times and positions. An impurity immediately in front of a step impedes its motion, but once the step moves beyond it, the impurity is assumed to be desorbed or incorporated into the crystal and does not affect the motion of other steps. This interaction between steps and impurities causes a uniform step train to become unstable and form step bunches [8, 9].

Here we adapt these ideas to stirred solution growth, where the driving force for adatom attachment is essentially constant and independent of the configuration and spacing of neighboring steps. Fig. 1 schematically shows a top view of a typical surface configuration with both steps and impurities present. Steps on the vicinal crys-

tal surface are described by the terrace-step-kink (TSK) model, which has been widely used to describe impurity-free step motion in both vapor and solution growth [10]. In this coarse-grained model individual atomic positions in the bulk crystal or solution are formally integrated out and we focus only on configurations of vertical step segments, pictured here as heavy lines that lie along the links of a 2D square lattice. Step segments move right (left) as adatoms attach to (detach from) the step and this process defines the fastest relevant time scale in the model. The energy of a specific configuration of step segments in the absence of impurities is given by an effective TSK Hamiltonian as described below. As in the classic Langmuir model [11] impurities are treated as finite-sized particles that deposit or desorb randomly at prescribed rates on the centers of the cells of the 2D lattice. We assume these rates for isolated impurities are much slower than the basic hopping rate for step segment fluctuations. At most one impurity can occupy a site and for simplicity they do not diffuse.

Our generalized Frank model effectively couples the TSK and Langmuir models together with important consequences for crystal growth. Frank and KW originally suggested a dynamical removal of impurities by moving steps, but we find that most effects can be captured in a simple energetic model that adds an extra repulsive (positive) energy E_I to the step Hamiltonian whenever a step segment is next to an impurity. This interaction slows down crystal growth by inhibiting the approach of a nearby step to an adsorbed impurity. However, when a step segment successfully moves next to an impurity we assume that the impurity desorbs at a much larger rate than that of an isolated impurity.

As suggested by Fig. 1, n_S steps, each consisting of L_y vertical segments reside on the links of a 2D square lattice with periodic boundary conditions in both directions. In general the impurity size in the single occupancy Langmuir model set both the scale of the lattice spacing and the size of the effective step segments in the TSK model.

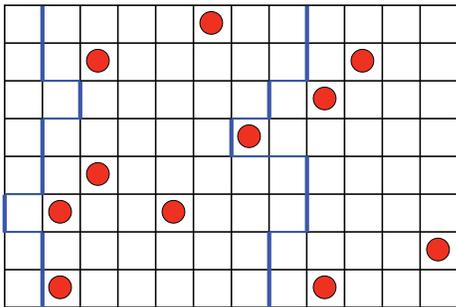


FIG. 1: Top view of a vicinal surface with steps and impurities. A step contains L_y discrete vertical segments that are placed on the links of a lattice of total width L_x . The surface height decreases when crossing a step segment in the positive X direction. The figure above shows many such segments joined together to form an array of steps. Impurities are represented above by colored circles that singly occupy centers of lattice sites.

The position of the y th vertical segment of the m th step on the lattice is given by $X_m(y)$. There are $N = L_y \times L_x$ cells in the lattice, and $w = L_x/n_S$ is the terrace width in an ideal vicinal surface with equally-spaced steps. We use occupation numbers $[abc]$ to specify the state of a particular lattice cell, where $a = 1$ ($c = 1$) if the left (right) link in the cell is occupied by a step segment and zero if it is vacant, and similarly $b = 1$ if the cell center is occupied by an adsorbed impurity.

We use this cell description to specify a discrete time kinetic Monte Carlo model for impure crystal growth. The basic process consists of choosing a cell at random and trying to make changes in its occupation numbers $[abc]$ using rules reflecting the desired physics. Distances are measured in units of the lattice spacing and time in units of a surface sweep, where the cell selection process is repeated N times. Thus on average in a sweep each step segment is chosen twice, once with a possibility to move left and once to move right.

The model is defined by specifying the transition probabilities $p([a'b'c']|[abc])$ in a given surface configuration from an initial cell state $[abc]$ for all permitted choices of final cell state $[a'b'c']$. Here we assume

$$p([a'b'c']|[abc]) = p_S^*([a'c']|[ac])p_I^*(b'|b) \quad (1)$$

where $p_S^*([a'c']|[ac])$ denotes a transition of the local step configuration in the cell. The * superscript indicates that this transition is modified by the initial impurity state. Similarly, $p_I^*(b'|b)$ describes impurity transitions as modified by neighboring step segments.

We use the standard Metropolis criterion for the step transitions, where we determine the total energy change ΔE_{tot}^* associated with a possible local segment move. The trial move is always accepted if $\Delta E_{tot}^* < 0$ and it is accepted with probability $\exp(-\Delta E_{tot}^*/k_B T)$ for positive ΔE_{tot}^* , where k_B is Boltzmann's constant and T is

the temperature.

In the absence of impurities $p_S^*([a'c']|[ac])$ reduces to $p_S([a'c']|[ac])$, which describes possible step transitions in a pure TSK model, and we discuss this case first. Consider for concreteness $p_S([01]||[10])$ where a segment at $X_n(y)$ moves to the right, reflecting adatom attachment. The total energy change ΔE_{tot} has two components. The first is the equilibrium energy change ΔE_S from the local segment move as determined from the TSK step Hamiltonian. In this case it takes the standard form [10]

$$\Delta E_S = 2G [1/(W_n(y))^3 - 1/(W_{n-1}(y))^3] + \gamma [X_n(y+1) + X_n(y-1) - 2X_n(y)], \quad (2)$$

where $W_n(y) = X_{n+1}(y) - X_n(y)$ is the local terrace width, the parameter G takes into account the strength of the repulsions and γ plays the role of a line tension.

Atoms in a supersaturated solution have a higher free energy ΔE_{sol} than at a kink site of an isolated step (taken as the energy zero) and this nonequilibrium exchange energy or driving force as the adatom joins the step should be accounted for in ΔE_{tot} as well. Thus for $p_S([01]||[10])$ we have $\Delta E_{tot} = \Delta E_S - \Delta E_{sol}$. In a backwards move $p_S([10]||[01])$ reflecting adatom transfer from the step to solution, ΔE_{sol} enters with the opposite sign. This biases the acceptance probabilities and leads to crystal growth with a net motion of steps to the right.

In the simple impurity model discussed above we add an energy E_I if a step segment is next to an impurity. The relevant transition probability $p_S^*([a'c']|[ac])$ in Eq. (1) now involves the total energy change in the presence of impurities, $\Delta E_{tot}^* = \Delta E_{tot} + \Delta E_I$, where ΔE_I is the change in the step-impurity energy resulting from the step move. Note that this involves impurities on adjacent sites as well as the site where the step move takes place.

Impurity transitions in Eq. (1) can be easily modified to incorporate step-induced desorption. Here we assume impurity deposition is unaffected by steps so $p_I^*(1|0) = p_I(1|0) = F_{on} \ll 1$ but if an impurity is next to a step its removal rate $p_I^*(0|1) = F_{off}^*$ is much greater than F_{off} , the rate in the absence of the step.

We choose model parameters (with energies given in units of $k_B T$) describing strong impurity blocking, $E_I = 6$, and slow intrinsic impurity adsorption/desorption $F_{on} = F_{off} = 0.00002$ but with very efficient step-induced desorption $F_{off}^* = 1$. Changing the line tension and the repulsion parameter G did not qualitatively affect results so we present data only for $\gamma = 1.0$ and $G = 0.0$ over a wide range of driving forces. Entropic repulsion [10] is always present since two step segments can never occupy the same lattice link.

The main effects of the step-induced removal of impurities on crystal growth can be seen from a model with only a single step with periodic boundary conditions. This describes the motion of a uniform step train with terrace width $w = L_x$ where step bunching is not possible. Figure 2 gives simulation results for the stable steady state

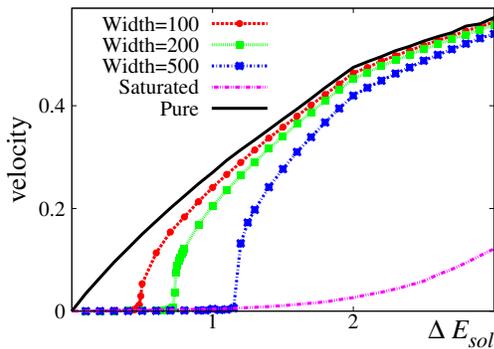


FIG. 2: (color online) The steady state velocity for uniform step trains as a function of the driving force ΔE_{sol} for different widths. Comparison to the impurity free surface and the surface with a saturated impurity field are also shown. Lines through data points are guides to the eye.

velocities as a function of driving force ΔE_{sol} and terrace width w . There are two limiting cases. The impurity-free crystal has the maximum possible growth rate. This is independent of terrace width, linear in ΔE_{sol} at small driving force, and will reach a finite limit at very large driving force. With impurities present, the smallest possible growth rate at fixed ΔE_{sol} occurs in the limit $w \rightarrow \infty$ where the step train moves in the saturated impurity field seen on a flat surface. At small driving force the high concentration of impurities creates a “dead zone”, usually described by an impurity fence model controlled by line tension [12], where crystal growth is strongly suppressed.

Steady states at smaller w can have a much higher velocity because impurities are continually removed as the steps advance, reducing the density seen by the next step. At small driving forces a dead zone is still seen but beyond a threshold that increases with w the velocity rapidly increases and approaches that of the impurity free crystal, reminiscent of the experimental results.

This dependence on terrace width can be easily understood from results for the Langmuir model on an infinite terrace. Here the average impurity density $n \leq 1$ at a site satisfies the equation $dn/dt = F_{on}(1-n) - F_{off}n$, whose solution starting from an impurity free surface is

$$n(t) = n_{\infty}[1 - e^{-t/\tau_{fill}}] \quad (3)$$

The “filling time” $\tau_{fill} \equiv (F_{on} + F_{off})^{-1}$ sets the time scale for the newly deposited impurities to reach a significant fraction of the saturated equilibrium density $n_{\infty} \equiv F_{on}/(F_{on} + F_{off})$.

Consider now a uniform 1D step train with terrace width w moving at a steady state velocity v_{ss} , where a step is at $x = 0$ at time t_0 . We assume perfect Frank impurity removal, with impurity concentration zero just behind the leading step at $x = w$. Using Eq. (3) the density of new impurities at any intermediate position $0 < x < w$ at t_0 is simply determined by the ratio of the

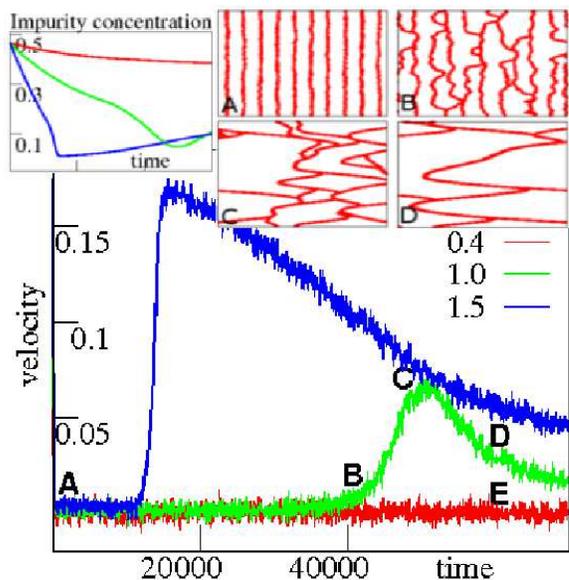


FIG. 3: (color online) The average step velocity as a function of time for different values of ΔE_{sol} . The top left panel shows the average impurity concentration over the same time interval. Snapshots of a 1000×1000 part of the system corresponding to points A, B, C and D are also shown.

“exposure time” $t_{ex}(x) \equiv (w - x)/v_{ss}$ since the step at w passed x to the filling time:

$$n_{ss}(x) = n_{\infty}[1 - e^{-t_{ex}(x)/\tau_{fill}}]. \quad (4)$$

With periodic extensions to other terraces, Eq. (4) also gives the steady state profiles in a frame where x moves with the steps. This kinematic relation between the impurity density and w holds for any possible v_{ss} in this model. The actual steady state velocity generated by a fixed set of other parameters is an increasing function of the driving force and a decreasing function of the impurity density n_{ss}^+ just in front of the step. n_{ss}^+ increases at larger w because of the larger exposure time. Thus a smaller driving force is needed to achieve a particular steady state velocity when w is smaller, as illustrated in Fig. (2). Earlier qualitative analysis of experimental data had recognized the importance of considering characteristic adsorption times for impurities relative to the terrace lifetime (exposure time) [5, 7].

We now discuss time-dependent results for the full model with many steps, where the impurities also induce step bunching and 2D step patterns. We carried out simulations for a range of driving forces with special initial conditions where a uniform step train with $w = 100$, $L_y = 1000$, and $n_s = 15$ initially encounters the maximum impurity density n_{∞} everywhere. As shown in Fig. 3, for $\Delta E_{sol} = 0.4$ the system is essentially in a dead zone where the growth velocity remains very small and there is little change in the impurity density with time. In particular the step pattern at point E is essentially

unchanged from the initial pattern shown panel A.

Very different behavior is seen for $\Delta E_{sol} = 1.0$, which is in the breakout region of the 1D steady state model in Fig. 2. Initially each step moves with a very small velocity in the saturated impurity field ahead, while leaving a greatly reduced density just behind it. If the next step can reach this depleted zone before many new impurities deposit, it can move much faster. This establishes a threshold driving force above which much more rapid growth is possible. Fig. 3 illustrates both the large increase in the average velocity when steps first reach the depleted zones and the initial rapid decrease in impurity density induced by the slowly moving steps (top left panel). The average velocity continues to increase for some time and can approach that of the idealized 1D steady states seen in Fig. 2.

Moreover, an ideal straight step bunch can move even faster than a single straight step in a given impurity field [13] in our model because repulsive step-step interactions suppress backwards moves in the bunch. But a moving step bunch is no more efficient than a single step in removing impurities in our model, so the speedup depends only weakly on bunch size, with a maximum observed speedup of about a factor of two under ideal conditions. However, experiments find that particular step bunches (supersteps and macrosteps) do move significantly faster than individual steps in the breakout region [5–7]. A more complex and nonlocal interaction between steps and impurities is probably needed in our model to reproduce this result. Since the impurities are often charged, this seems physically plausible as well, but detailed modeling seems quite difficult.

At longer times the simulations show that the average velocity reaches a maximum and then slowly declines. Panels A-D in Fig. 3 show snapshots of the emerging 2D step bunch patterns for $\Delta E_{sol} = 1.0$ at the indicated times [13]. The behavior is similar for $\Delta E_{sol} = 1.5$, but the maximum velocity is larger and is attained faster.

This indicates that the uniform steady state solutions shown in Fig. 2 are unstable. Driven by the basic Frank instability, segments of adjacent steps initially pair together (panel B). V-shaped patterns with high impurity density in front of the points begin to form (panels C and D) as additional steps join the bunch [9]. Formation of larger bunches increases the average terrace width and the associated exposure time, eventually leading to slower growth at long times, as seen in point D. It would be interesting to see if the experimental systems would experience a similar decrease in growth velocity at longer times.

In conclusion, even in its simplest form, our model captures many experimental results. It has steady states with fast growth rates that strongly resemble experimental data. A key assumption in the model is that in a well-stirred solution the driving force for step motion is

independent of the width of the terrace in front of the step. Under appropriate conditions, this permits the formation of large mobile step bunches, and much faster crystal growth for a small range of supersaturation just above the dead zone.

This model presents a general framework for describing impurity effects in crystal growth. By allowing a dependence of the driving force on terrace width, the model can describe vapor growth as well, and the kink poisoning mechanism proposed to explain the behavior of calcium oxalate crystals in the presence of citrate impurities [14] is related to the behavior at large line tension in our model. There also may be connections to ongoing work on collective and local pinning effects induced by (usually quenched) disorder in a wide variety of driven condensed matter systems [15]. Further analysis, generalizations and comparisons to related models will be the subject of a longer article.

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