# Nonequilibrium capture of impurities that completely block kinks during crystal growth

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## ARTICLE INFO

## ABSTRACT

Some impurities cannot integrate into isolated kinks because they completely block the growth of the kinks to which they adsorb. For this class of impurity, we derive an equation for the amount that incorporates into a crystal during growth of the elementary step by assuming that such an impurity incorporates if and only if it gets captured between a kink and an antikink. We show that the impurity concentration in the crystal increases monotonically with the impurity concentration in the mother phase, but that it can vary non-monotonically with both the supersaturation of the mother phase and the kink density of the step. In contrast to other capture mechanisms, we find that weakly adsorbed impurities incorporate to an extent that is independent of the supersaturation when the supersaturation is high. Irrespective of the growth conditions, the amount of impurity that can incorporate into a crystal is limited by an upper bound determined by the kink density.

## 1. Introduction

Crystals can be tailored for their intended use by controlling their uptake of additives and unwanted impurities during growth [1–7]. Impurities generally get captured and buried by their host crystals before reaching equilibrium with the mother phase, and so the amount of impurity inside a crystal will depend on the surface processes responsible for its incorporation. Impurities that do not register with the crystal lattice will likely block kink growth. For example, organic impurities arrest the growth of inorganic crystals if the impurity concentration is high enough [8–10], indicating that these impurities completely block kink growth, and yet organic molecules generally incorporate into inorganic crystals, albeit in low amounts [11–14]. We propose that if an impurity completely blocks the growth of the kink to which it adsorbs, then the kink must collaborate with an antikink to capture the impurity by sandwiching it in place (Fig. 1a).

The existing models of nonequilibrium incorporation are not well-suited to describe this particular mechanism of capture. For example, some models suppose that an impurity is captured if the crystal grows a predefined distance at a uniform speed before the impurity desorbs [15,16]. While this criterion may be general enough to encompass the capturing of such a kink-blocking impurity, it has two drawbacks: (1) the capture event is not stochastic, and (2) without backward fluctuations of the crystal, the impurities have only one attempt at integrating into any given lattice site. Other models of incorporation are either concerned with integration into isolated kinks [17–21], where the impurity does not completely block the kink, or they are

not concerned with the capture mechanism at all, instead using a constant such as a partition coefficient to implicitly describe the surface processes [22–26].

In this paper, we derive an equation for the concentration of impurity that incorporates into a growing crystal for the special case of an impurity that completely blocks kink growth. The equation shows how crystal composition depends on the concentration and adsorption strength of the impurity, the supersaturation of the mother phase, and the kink density of the step. We demonstrate the accuracy of the equation by comparing its predictions to numerical simulation.

## 2. Theoretical model

The crystal belongs to a cubic lattice where each cube is either vacant (V), occupied by an impurity (Y), or occupied by a unit of the host crystal (C). The crystal grows by means of an infinite step with orientation (01). Because the crystal is growing, each vacant cube will eventually transition to either a crystal unit (V → C) or an impurity (V → Y), although there could be any number of intermediate steps before a cube permanently settles on either C or Y (e.g., V → C → V → Y). Our aim is to compute the probability that a cube settles permanently on Y, since this probability will equal the mole fraction of impurity inside the crystal, $\Theta$.

In the absence of impurities, the step moves at a speed $v_0 = a\rho(j^+ - j^-)$ where $a$ is the lattice constant, $\rho$ is the dimensionless kink density,

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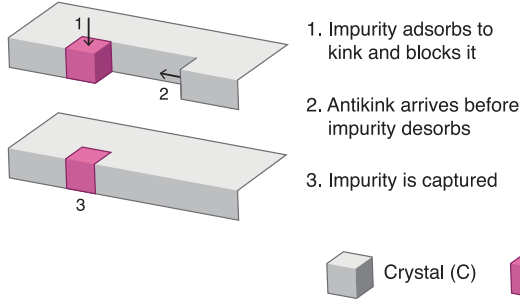  *E-mail address:* r.darkins@ucl.ac.uk (R. Darkins).

**a. Mechanism of capture of kink-blocking impurity**

**b. Markovian model of impurity capture**



1. Impurity adsorbs to kink and blocks it
2. Antikink arrives before impurity desorbs
3. Impurity is captured
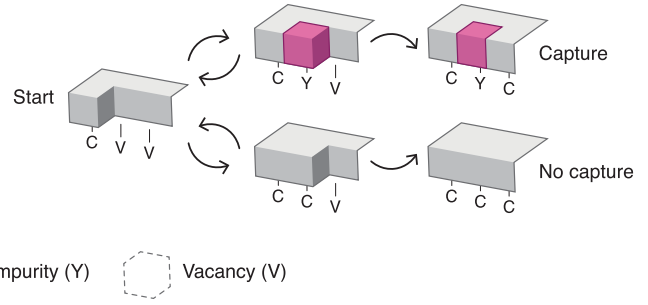
Crystal (C)    Impurity (Y)    Vacancy (V)

**Fig. 1.** (a) The impurity cannot incorporate into an isolated kink because it completely blocks kink growth. However, if the impurity gets sandwiched between a kink–antikink pair, then it can no longer desorb and it will incorporate. (b) Our analytical model treats impurity capture as a Markov process over the five states shown. Note that state CCC represents the kink having grown via a random walk and then annihilated with an antikink.

and $j^+$ ($j^-$) is the rate that crystal units attach (detach) at kinks. The mother phase supersaturation is $S = j^+/j^-$. In the presence of impurities, the steps are inhibited according to the Bliznakov model [27] and move at a reduced speed

$$v = v_0(1 - \theta) \tag{1}$$

where $\theta$ is the fractional occupancy of the kinks. Step pinning effects are ignored since impurities cannot integrate into a pinned step. This is equivalent to supposing that the impurities are easily overgrown under the prevailing growth conditions.

Impurities adsorb to kinks at a rate $k^+c$ where $k^+$ is the attachment rate coefficient and $c$ is the impurity concentration in the mother phase. They leave the kinks by either (1) desorbing at a rate $k^-$ or (2) being captured and buried by the crystal. An impurity adsorbed at a kink gets captured upon the arrival of an antikink which occurs at an approximate rate of $\frac{v}{2a}$ (generally, the step advances by a single row at a rate $\frac{v}{a}$, but this velocity is roughly halved because the adsorbed impurity has arrested a kink). Note that if an impurity adsorbs to a kink, and a second impurity adsorbs to the corresponding antikink, then growth suspends until one of the impurities dissolves. This temporary suspension is accounted for by the factor $(1 - \theta)$ that appears in $\frac{v}{2a} = \frac{v_0}{2a}(1 - \theta)$.

When the adsorption, desorption and capture events are in equilibrium, the kink occupancy satisfies

$$\theta = \frac{Kc}{Kc + 1 + \frac{v}{2ak^-}} \tag{2}$$

where $K = k^+/k^-$ is the equilibrium constant of adsorption. Note that $\theta$ reduces to the Langmuir isotherm when crystal growth is slow relative to the impurity kinetics ($v/a \ll k^-$). Note also that Eq. (2) is an implicit equation since $v$ is a function of $\theta$. It can be solved explicitly:

$$\theta = \frac{a}{v_0}\left[ k^+c + k^- + \frac{v_0}{2a} - \sqrt{\left(k^+c + k^- + \frac{v_0}{2a}\right)^2 - \frac{2v_0k^+c}{a}} \right]. \tag{3}$$

To determine the mole fraction of impurity inside the crystal, $\Theta$, we do not calculate the probability of $V \to \ldots \to Y$ over the space of every cube, but just those cubes where the concluding transition occurs at a kink. This is equivalent to assuming that all crystal growth events occur via adsorption to kinks. Furthermore, we approximate the life cycle of each cube ($V \to \ldots \to C$ or $Y$) as a Markov chain where the transition probabilities depend both on the state of the subject cube (V, C or Y) and on the states of its nearest neighbours. This combination of states will be collectively referred to as the Markov state. To make the model tractable, we assume that only five Markov states are important to the growth process (Fig. 1b):

CVV: A vacant kink. This Markov state initiates the Markov chain. It can transition to either CYV or CCV (see below). The transition $CVV \to CYV$ occurs if an impurity adsorbs to the kink (rate $k^+c$),

and $CVV \to CCV$ occurs if a crystal unit adsorbs to the kink (rate $j^+$). Hence the transition probabilities:

$$P_{CVV \to CYV} = \frac{k^+c}{k^+c + j^+}, \tag{4}$$

$$P_{CVV \to CCV} = 1 - P_{CVV \to CYV}. \tag{5}$$

CYV: An impurity adsorbed at the kink. From here either the impurity dissolves (rate $k^-$) to return to the start, $CYV \to CVV$, or an antikink arrives (rate $\frac{v}{2a}$) and captures the impurity, $CYV \to CYC$:

$$P_{CYV \to CVV} = \frac{k^-}{\frac{v}{2a} + k^-}, \tag{6}$$

$$P_{CYV \to CYC} = 1 - P_{CYV \to CVV}. \tag{7}$$

CCV: A crystal unit adsorbed at the kink. The kink is free to randomly walk in either direction until it either returns to the start, $CCV \to CVV$, or annihilates with an antikink an average distance $a/\rho$ from the start, $CCV \to CCC$. This is equivalent to a random walk on the number line, starting at 1 and terminating at either 0 or $a/\rho$, where increments occur $S\times$ quicker than decrements (a textbook problem [28]):

$$P_{CCV \to CVV} = \frac{S^{1/\rho - 1} - 1}{S^{1/\rho} - 1}, \tag{8}$$

$$P_{CCV \to CCC} = 1 - P_{CCV \to CVV}. \tag{9}$$

CYC: The impurity is captured between a kink and an antikink. The Markov chain terminates.

CCC: The kink annihilates with an antikink without capturing an impurity. The Markov chain terminates.

The process that links the five Markov states can be described by the recurrence relation

$$P_{CVV \to CYC} =$$
$$P_{CVV \to CYV}P_{CYV \to CYC}$$
$$+ P_{CVV \to CYV}P_{CYV \to CVV}P_{CVV \to CYC}$$
$$+ P_{CVV \to CCV}P_{CCV \to CVV}P_{CVV \to CYC}. \tag{10}$$

Finally, solving for $P_{CVV \to CYC}$ and identifying $\Theta \approx P_{CVV \to CYC}$, leads to

$$\Theta = \frac{J\theta}{J\theta + 1} \tag{11}$$

where $J = \frac{1}{2}\rho(1 - S^{-1/\rho})$.

## 3. Results and discussion

### 3.1. Kink occupancy

Eq. (11) relates the mole fraction of impurity inside the crystal, $\Theta$, to the fraction of kinks occupied by an impurity, $\theta$. When incorporation is low ($\Theta \ll 1$), Eq. (11) simplifies to a linear relationship, $\Theta \approx J\theta$.
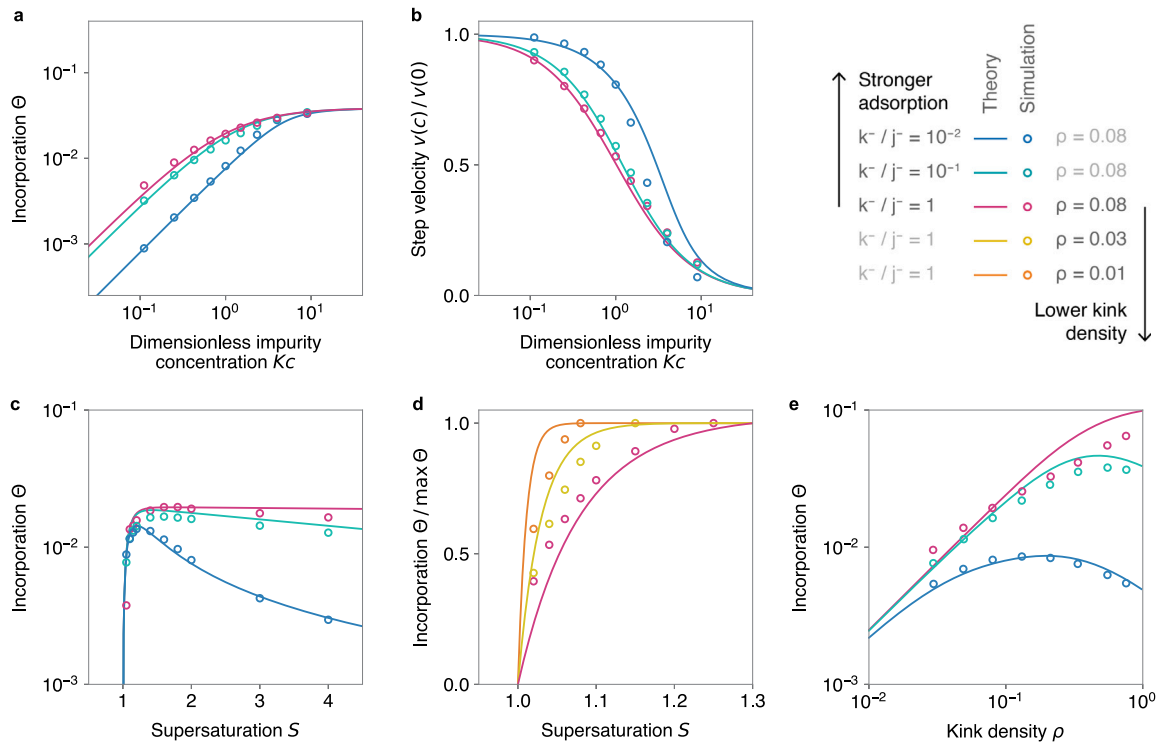
**Fig. 2.** (a–e) Our analytical model (lines) compared against kinetic Monte Carlo simulation (circles, see the Appendix). Unless stated otherwise, we chose parameters $Kc = 1$, $S = 2$ and $\rho = 0.08$ for this demonstration. The lines that correspond to $k^-/j^- = 1$ are also representative of weaker impurity adsorption ($k^-/j^- > 1$).

The concentration and properties of the impurity ($c$, $k^+$ and $k^-$) do not appear in $J$ and are therefore only relevant to $\Theta$ to the extent that they determine $\theta$. In other words, a weakly adsorbed impurity at a high concentration will incorporate to the same extent as a strongly adsorbed impurity at a low concentration provided that the kink occupancy $\theta$ is the same. An increase in the rate of impurity adsorption ($k^+c$) or a decrease in the rate of impurity desorption ($k^-$) will increase $\theta$ and therefore increase $\Theta$.

When all other conditions are the same, more impurity outside the crystal always translates to more impurity inside the crystal ($d\Theta/dc > 0$), although there are diminishing returns ($\theta \to 1$ as $c \to \infty$), see Fig. 2a. It is not obvious that $\Theta$ should increase monotonically with $c$ since high impurity concentrations poison growth (Fig. 2b) which hinders incorporation. In fact, for models that suppose that a fixed time interval elapses between the adsorption of an impurity and its capture, the degree of incorporation is predicted to rapidly decline as the step is increasingly inhibited ($\Theta \sim \exp(-b/v)$ for some constant $b$ as $v \to 0$) [15,16]. By contrast, when impurity capture is a stochastic event, as it is in our model, any amount of impurity in the mother phase will always boost incorporation more than it hinders it.

### 3.2. Supersaturation

Higher supersaturations bring about faster crystal growth, and faster crystal growth has two opposing effects on incorporation:

1. The crystal is more likely to trap the impurities adsorbed on its surface.
2. The impurities must compete against a greater influx of crystal solutes.

At low supersaturations, effect (1) dominates and $\Theta$ increases with $S$ (Fig. 2c). As $S$ increases, effect (2) increasingly attenuates effect (1) until $\Theta$ hits an upper bound. The initial ascent of $\Theta$ from zero to its maximum value goes approximately as $\Theta \sim (1 - S^{-1/\rho})$, which is

more abrupt when the kink density $\rho$ is low (Fig. 2d). What happens at even higher $S$ depends on the impurity. If the impurity is weakly adsorbed ($k^- \gg v/a$ and so $\theta$ is independent of $S$), then $\Theta$ will plateau to a maximum value because effects (1) and (2) cancel each other out at high $S$. On the other hand, if the impurity is strongly adsorbed ($k^- \ll v/a$ and so $\theta$ depends on $S$), then $\Theta$ will peak and subsequently decline with $S$ because effect (2) dominates over effect (1) at high $S$.

### 3.3. Kink density

The mole fraction of incorporation $\Theta$ is directly proportional to the kink density $\rho$ except in the following cases:

1. On the approach to saturation ($S \to 1+$), $\Theta$ loses its $\rho$ dependence since $\rho(1 - S^{-1/\rho}) \to (S - 1)$.
2. If the kink density $\rho$ were increased from a small value to a large value, then $\Theta$ would increase linearly with $\rho$ before reaching a maximum value and subsequently declining (Fig. 2e). Strongly adsorbed impurities reach their maximum $\Theta$ at lower kink densities than weakly adsorbed impurities.
3. When the crystal becomes substantially loaded with impurities ($\Theta \gtrsim 10^{-1}$), the dependence of $\Theta$ on $\rho$ (and on all other parameters) is weakened as the denominator ($J\theta + 1$) in Eq. (11) attenuates the numerator $J\theta$. Such high levels of incorporation, however, might not be attainable in practice (see the next section).

### 3.4. Maximal incorporation

There is a limit to how much kink-blocking impurity can incorporate into a crystal. Irrespective of the growth conditions, it cannot exceed

$$\Theta < \frac{1}{1 + \frac{2}{\rho}} \approx \frac{\rho}{2}. \qquad (12)$$

More generally, if the impurity occupies a volume equal to $\omega$ crystal units, then

$$\Theta < \frac{\rho}{2 - \rho(\omega - 1)}. \tag{13}$$

For low kink density crystals, this limit is highly restrictive. For example, $\Theta < 0.05$ (i.e. 5 mol%) when $\rho = 10^{-1}$ and $\omega = 1$. For high kink density crystals, the limit is less restrictive and possibly irrelevant as other physical effects, such as the crystal solubility, might constrain incorporation before the ceiling of Eq. (13) is ever reached.

### 3.5. Accuracy of the model

To assess the accuracy of Eq. (11), we compared it to the results of an analogous numerical model (details in the Appendix). The quantitative agreement between the numerical and analytical models is satisfactory, and the qualitative dependencies of $\Theta$ on its parameters are faithfully reproduced (Fig. 2). The deviation between the two models is greatest at low supersaturations (Fig. 2d) and high kink densities (Fig. 2e), which is unsurprising given the assumptions of the model.

It should be noted that the numerical model is not an entirely suitable reference case since it contains a number of parameters that are underdetermined by the specification of the analytical model; for example, the parameters $j^-$, $S$ and $\rho$ in the analytical model do not uniquely determine the rate of kink nucleation in the numerical model, which influences the kink distribution and thus $\Theta$. Critically, the degrees of freedom within the numerical model affect $\Theta$ to an extent comparable to the differences between the analytical and numerical models. For this reason, it would not be possible to significantly improve our analytical model without accommodating the nuances of kink distribution.

### 4. Conclusions

On the assumption that an impurity completely blocks kink growth and incorporates if and only if captured by a kink–antikink pair, we have derived an equation for the amount of impurity that incorporates via the elementary step. How accurately this mechanism describes any particular impurity/crystal system may be judged by the validity of our analytical predictions for that system. There are two predictions in particular that seem to distinguish this mechanism from other mechanisms of capture: (1) for weakly adsorbed impurities, incorporation is independent of mother phase supersaturation at high supersaturations, and (2) the degree of incorporation via a low kink density step is limited by a proportionally low ceiling.

### CRediT authorship contribution statement

**Robert Darkins:** Investigation, Writing – original draft. **Alexander Broad:** Resources, Writing – original draft. **Dorothy M. Duffy:** Supervision, Writing – original draft. **Ian J. Ford:** Supervision, Writing – original draft.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Data availability

Data will be made available on request.

### Acknowledgements

### Appendix. Numerical simulation

In the numerical model the crystal is represented by a two-dimensional grid of size $2^{10} \times 2^{10}$, where each cell is in a state of either V, Y or C. A single row $(i, 0)$ is permanently assigned state C, with all other cells initially in state V. The $x$-axis has periodic boundaries and the $y$-axis has reflecting boundaries. Only the transitions V → C, C → V, V → Y and Y → V are possible. Each cell transitions to a new state at a rate determined by both the initial and final states as well as the states of its first-nearest neighbours. The model is implemented using kinetic Monte Carlo [29].

Extending an existing numerical model [30], the transition V → C occurs at a rate $j^- S$ when there are two or more C neighbours (and any number of Y neighbours), and at a rate $j^- S \exp(-2\beta\phi)$ when there is exactly one C neighbour and zero Y neighbours, where $\phi$ is the step free energy and $\beta$ is the inverse thermodynamic temperature. The reverse reaction C → V occurs at a rate $j^-$ when the total number of bonds (counting both C and Y) is no greater than two, and C → V occurs at a rate $j^- \exp(-2\beta\phi)$ when there are three bonds (counting both C and Y). The transition V → Y occurs at a rate $k^+ c$ but only when there are exactly two C bonds and zero Y bonds. The reverse reaction Y → V occurs at a rate $k^-$ but only when the number of C bonds is no greater than two. The simulation is run until either the grid is exhausted or $10^8$ integration steps have been performed.

Note that the analytical model is parametrised by a kink density $\rho$ whereas the numerical model has a step free energy $\phi$ that serves as an indirect control on the kink density. To allow direct comparisons between the two models, the numerical model is evaluated for some value of $\phi$, and then $\rho$ is measured numerically (by measuring the uninhibited step velocity $v_0$ and evaluating $\rho = v_0/(aj^-(S - 1))$) and then fed into the analytical model. In Fig. 2, kink densities $\rho = 0.08$, 0.03 and 0.01 correspond to $\beta\phi = 3$, 4 and 5, respectively.

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