Delivery of a Practical Tool for Predicting the Effect of Solvents & Growth Inhibitors on Crystal Morphology

Michael F. Doherty, Tobias Mazal, Yongsheng Zhao, Neha Padwal

University of California Santa Barbara

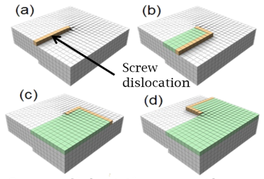
Objectives

- Develop a practical engineering tool for predicting the relative growth rates (growth kinetics) and morphology of solution-grown faceted crystals, including the effects of solvent, and impurities/additives

Crystal Growth Mechanisms

Layered Growth Mechanism

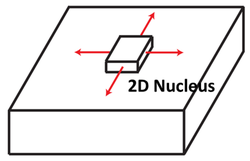
Spiral Growth



Absolute growth rate

$$G = \frac{h}{\tau}$$

2D Nucleation and Growth



Screw dislocations are the sources of steps

$$\tau_s = \sum_{i=1}^{N} \frac{l_{c,i+1}\, sin(\alpha_{i,i+1})}{v_i}$$

Step velocity v depends on[1]

- Density of kink sites along the edge (ρ)
- Net rate of attachment into kink sites (u)

$$v = a_p \rho u$$

2D Nuclei are the sources of steps

$$\tau_{2D} = \left(v^2 I\right)^{-1/3}$$

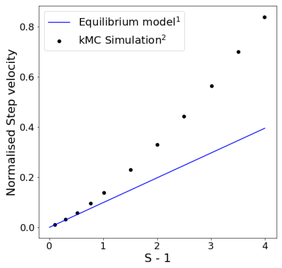
h : Height of a layer
$l_{c,i+1}$: Critical length of edge i+1
$\alpha_{i,i+1}$: Angle between edge i and edge i+1
a_p : Propagation length
I : Nucleation rate

Kink Density Modelling

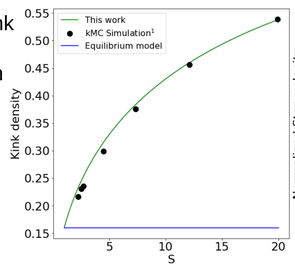
- Developing a novel framework for kink density model to be used within ADDICT's growth engine

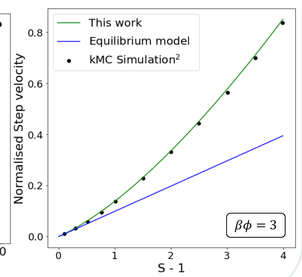
$$\sum_n F_n \pm T_n - A_n = 0$$

Rate of **creation** ± Rate of **transformation** − Rate of **annihilation** = 0



- Non-equilibrium kink density model matches simulation data
- Model has been extended to more complex cases (more than one growth unit)

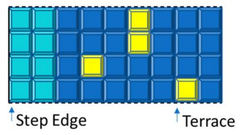




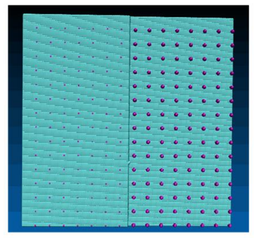
IFPRI
International Fine Particle Research Institute

Impurity Effects

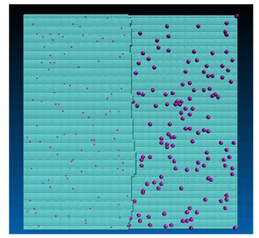
θ_I - fractional coverage of impurities on the terrace



Lattice Distribution

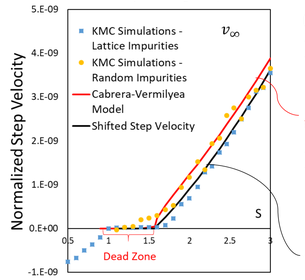


Random Distribution



- Terrace-bound impurities serve to pin the step

$S = 1.5 \quad \phi = 3\ k_B T \quad \theta_I = 0.016$



Cabrera-Vermilyea (C-V) Model

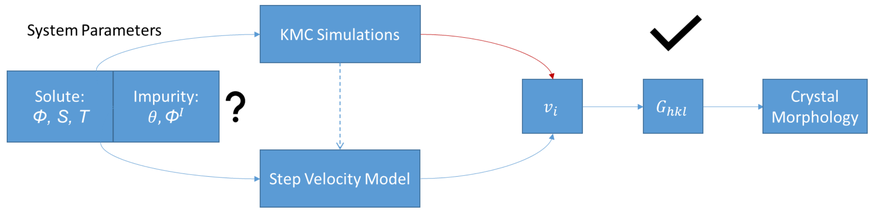
- Assumes that strongly adsorbed impurities pin the step to reduce the effective local supersaturation

$$v = v_\infty \left(1 - \frac{l_C}{\Delta}\right)^{0.5}$$

- Growth halted when the distance between impurities (Δ) is less than the critical length (l_C)

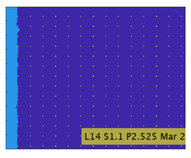
$$v = 0 \qquad 1 \le S \le S^*$$
$$v = a_P \rho u \qquad S > S^*$$
$$u = k^+ x_{sat}(S^* - 1)$$

Morphology Predictions

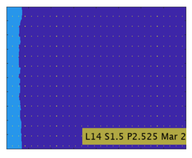


- KMC offers an alternative path as a method to determine step velocities and thus morphologies for more complex cases

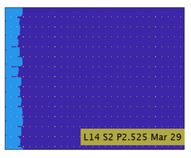
S = 1.1



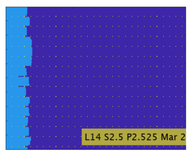
S = 1.5



S = 2

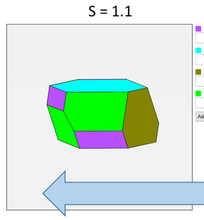


S = 2.5

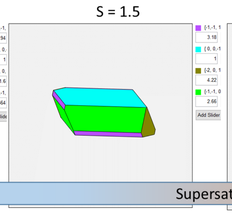


- Naphthalene system containing impurities at $\theta_I = 0.005$
- For centrosymmetric systems containing impurities, increasing S mitigates impurity effects

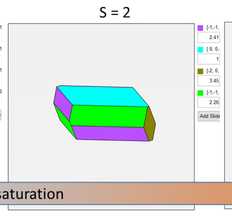
S = 1.1



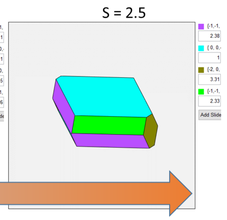
S = 1.5



S = 2



S = 2.5



Low

All faces slowed significantly
Results in Equant Morphology

Intermediate

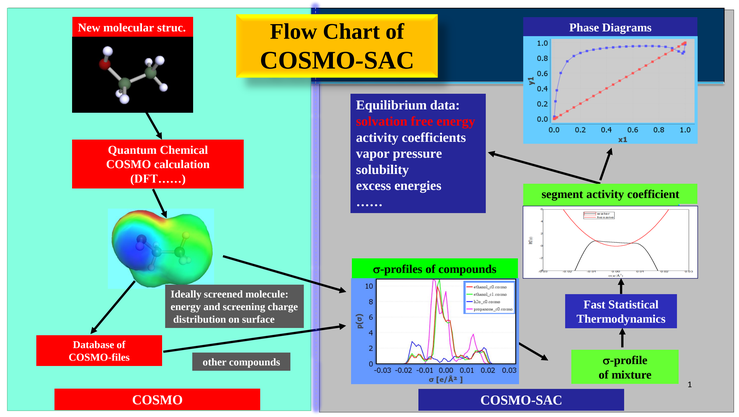
Fast lower energy / higher kink density faces disappear

High

Critical length <<< impurity spacing,
Impurity-free morphology adopted

Forcefield Developments

- COSMO-SAC ADDICT Workflow



- Case study of adipic acid compares morphologies from distinct forcefields and solvent models

FF	COSMO	vOCG	COSMO	vOCG
CLP	CLP opt.	CLP opt.	CSD	CSD
Amber	CLP opt.	CLP opt.	CSD	CSD
Lifson	CLP opt.	CLP opt.	CSD	CSD
CLP	QM opt.	QM opt.	Adipic acid grown from water	
Amber	QM opt.	QM opt.		
Lifson	QM opt.	QM opt.	Experimental habit	

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Future Work

- Non-equilibrium kink density model is finished - write "special code" for AB systems; ADDICT – test + compare with experiment and kMC
- Generalize non-equilibrium kink density model to any number of GUs
- Complete kMC simulations for AB crystals with and without impurities in solution
- Incorporate kMC simulations into ADDICT for step velocity prediction and integration into morphology prediction
- Extend COSMO-SAC to solvent mixtures (antisolvent crystallization)
- Automate CLP force-field in ADDICT

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