

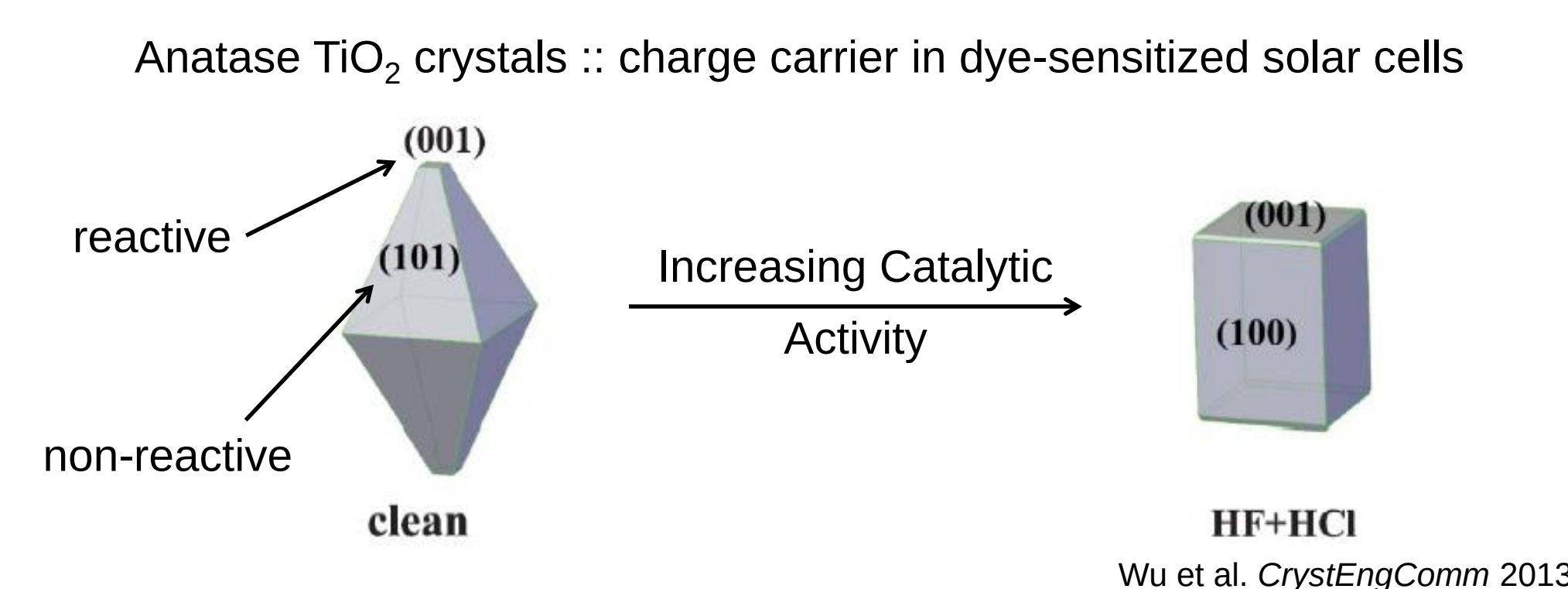
Goals

Derive the critical length of a 1D nucleus along a crystal edge

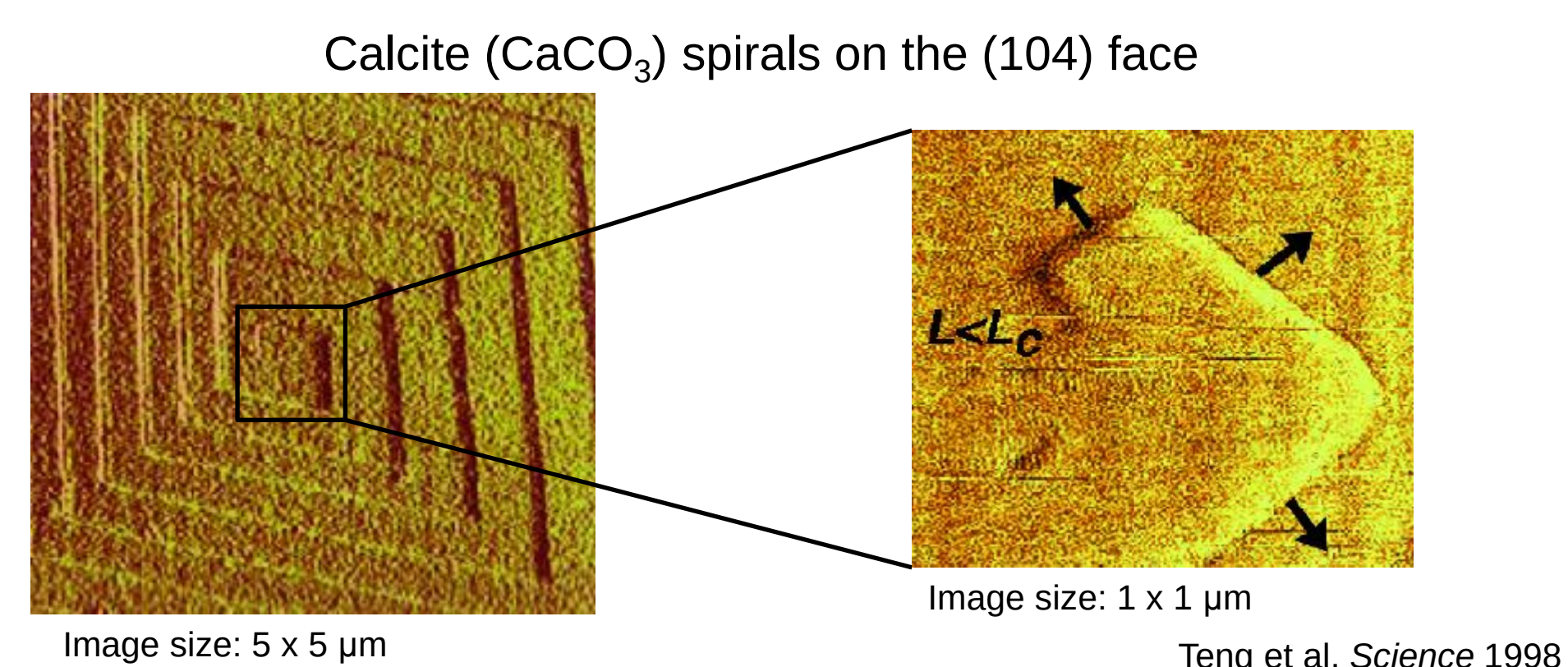
Compare our expression for the critical length to crystal growth experiments

Crystal Growth Modeling

- The morphology of a crystal largely determines its end-use efficacy, such as reactivity, bioavailability, etc.



- An efficient route to engineer the most effective crystal is to employ growth models which predict the crystal shape
- At low supersaturations, crystals grow layer-by-layer via a spiral growth mechanism



A nascent spiral edge will not spread across the surface until it reaches its critical length

- A mechanistic spiral growth model has accurately predicted the morphology of many crystals

$$G_{hkl} = \left(\frac{h}{\tau} \right)_{hkl}$$

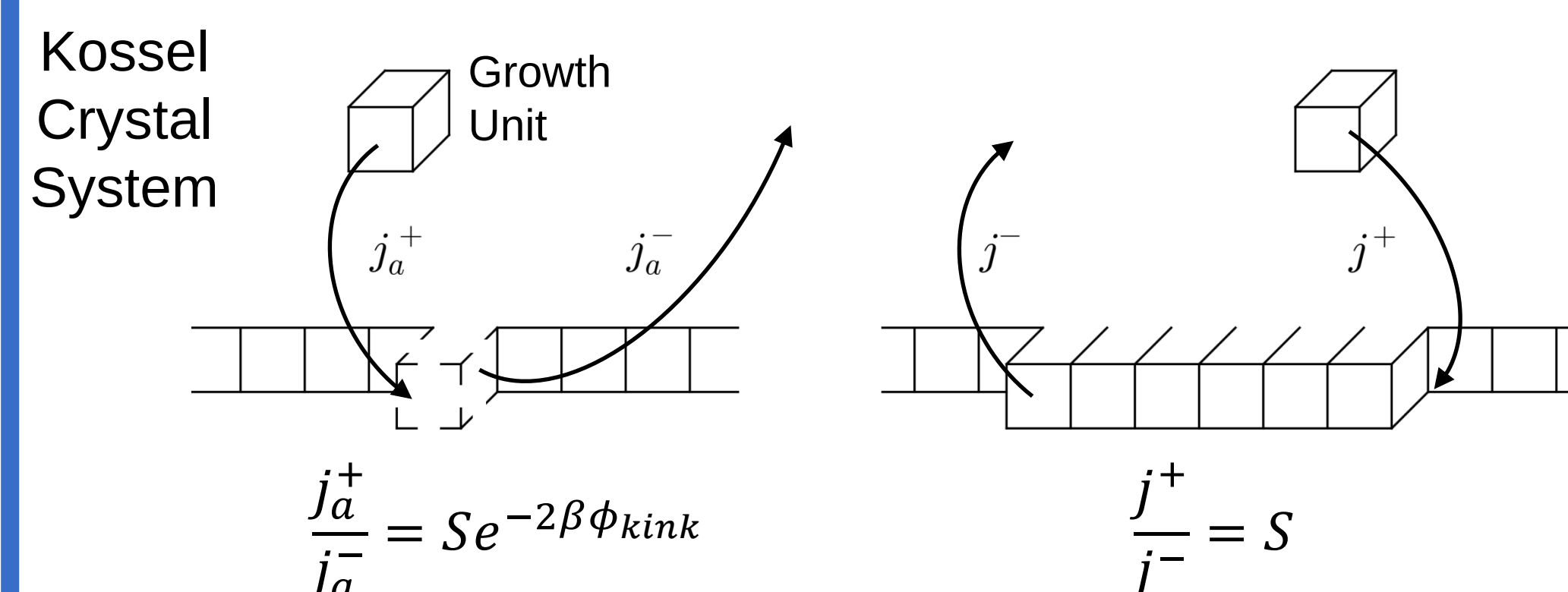
$$\tau = \sum_{i=1}^N \frac{l_{c,i+1} \sin \alpha_{i,i+1}}{v_i}$$

Kuvadia & Doherty, *Cryst. Growth Des.* 2011 Lovette et al. *Ind. Eng. Chem. Res.* 2008

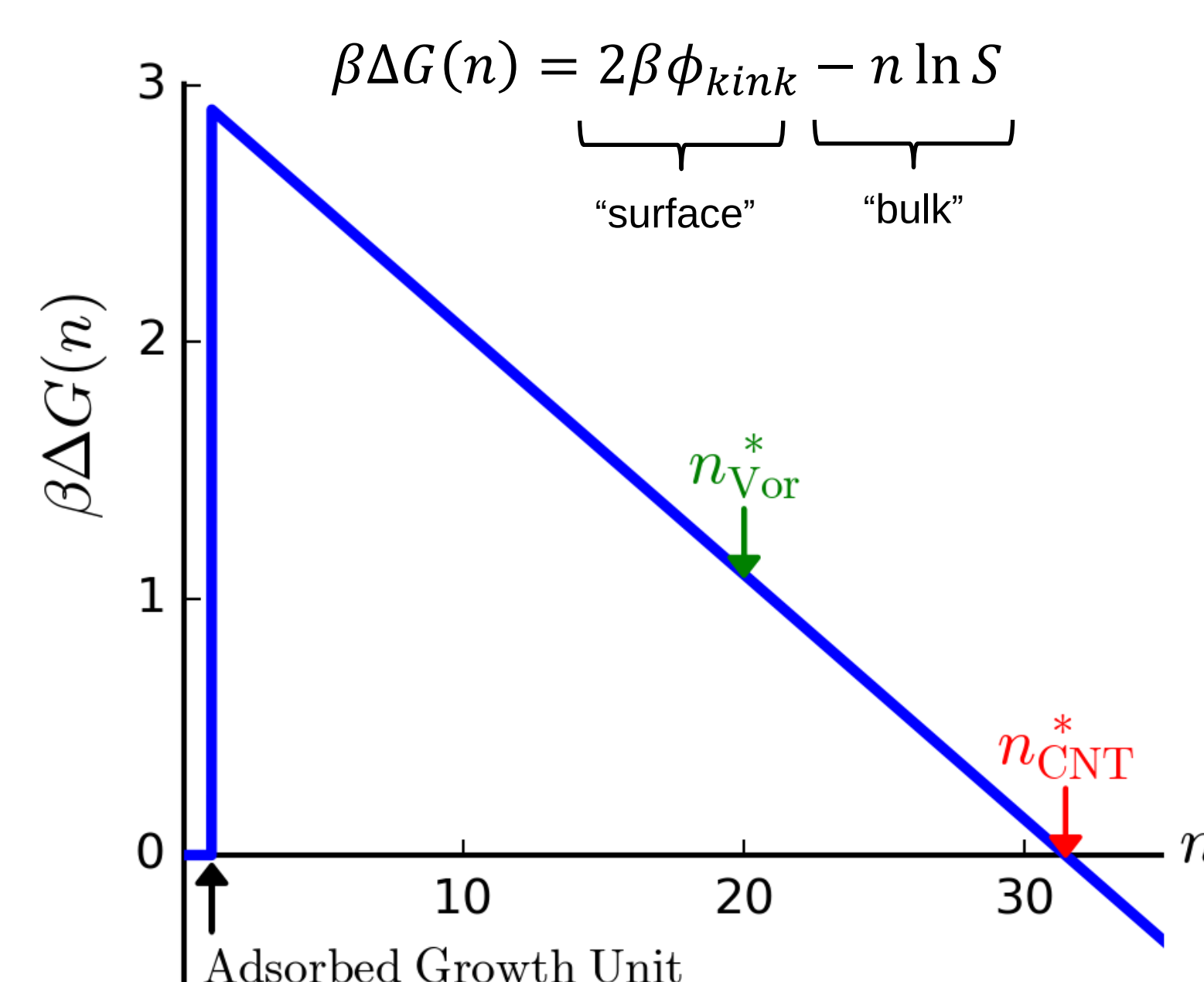
BUT crystal shape predictions are sensitive to the critical edge lengths

- Simplest model :: 1D nucleation
 - A variety of models are employed in the crystal growth literature, with different definitions of the critical length
- A unified approach to 1D nucleation may improve crystal morphology predictions

1D Nucleation



- The free energy of nucleus formation is like the Classical Nucleation Theory (for $n \geq 1$)



- No barrier is present in 1D nucleation...
 - therefore, 1D nucleation does not occur (Kashchiev)
 - however, 1D nucleation occurs because nuclei can still dissolve after surpassing the spike in free energy

- With the absence of a barrier, a thermodynamic definition of the critical length has been commonly used

$$\beta\Delta G(n_{CNT}^*) = 0 \longrightarrow n_{CNT}^* = \frac{2\beta\phi_{kink}}{\ln S}$$

- However, it is *always* favorable to add another growth unit to the nucleus
- This approach *does not* account for growth kinetics

- 1D nucleation is a biased random walk
 - Voronkov defines the critical length as the most probable "backward" movement of a kink site, which partially accounts for growth kinetics

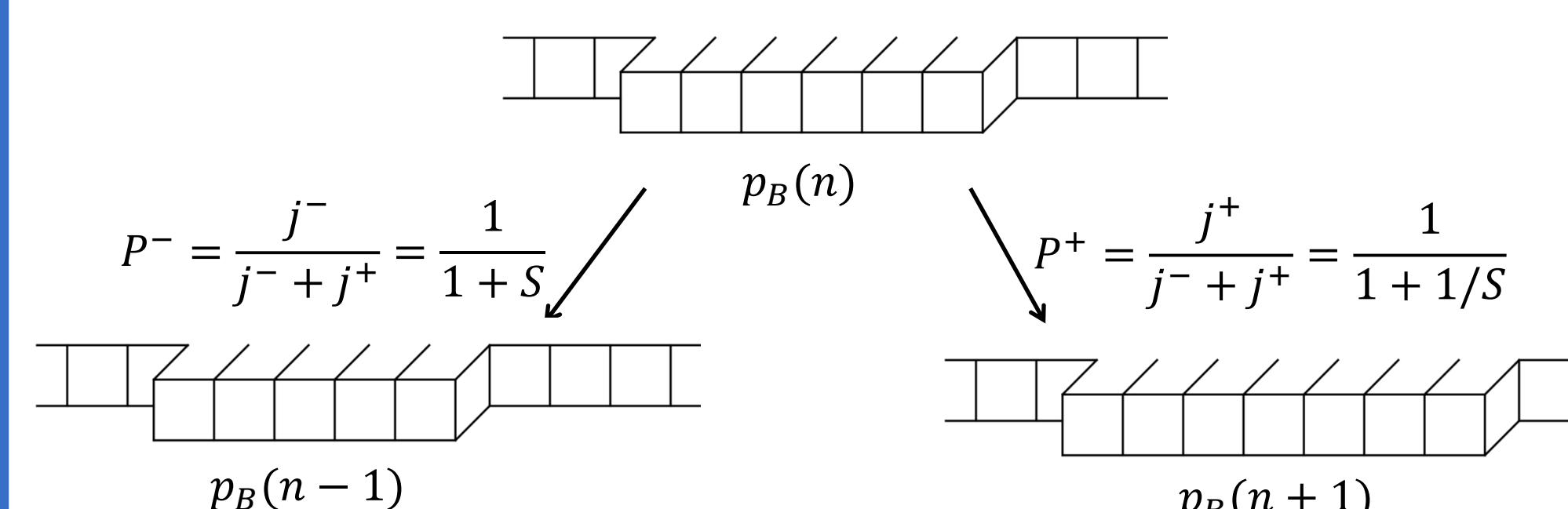
$$n_{Vor}^* = \frac{2}{S-1}$$

- A kinetic definition of the critical length is the length at which a nucleus has an equal probability of growth to an infinite size or complete dissolution
 - This approach has not been applied to 1D nucleation

- Several recent theories have converged on the committor for general definitions of transition states and for computing rates of complex barrier crossings in condensed phases, including nucleation
- For 1D nucleation, the committor, $p_B(n)$, is the probability that a nucleus of size n will grow to an infinite size before dissolving
 - The critical length is defined as $p_B(n^*) = 1/2$

1D Nucleus Critical Length

- Assumptions
 - Attachment and detachment rates are independent of size for $n \geq 2$
 - Growth and dissolution occurs 1 growth unit at a time
 - Attachment and detachment events are independent
- Consider a nucleus of size n



- We express the committor in a first step analysis

$$p_B(n) = P^- p_B(n-1) + P^+ p_B(n+1)$$
- We can obtain a recursive relation and cast in vector notation (for $n \geq 2$)

$$\mathbf{x}_n = \begin{bmatrix} p_B(n) \\ p_B(n+1) \end{bmatrix} \quad \mathbf{x}_{n+1} = \Omega \mathbf{x}_n \quad \Omega = \begin{bmatrix} 0 & 1 \\ -\frac{1}{S} & 1 + \frac{1}{S} \end{bmatrix}$$

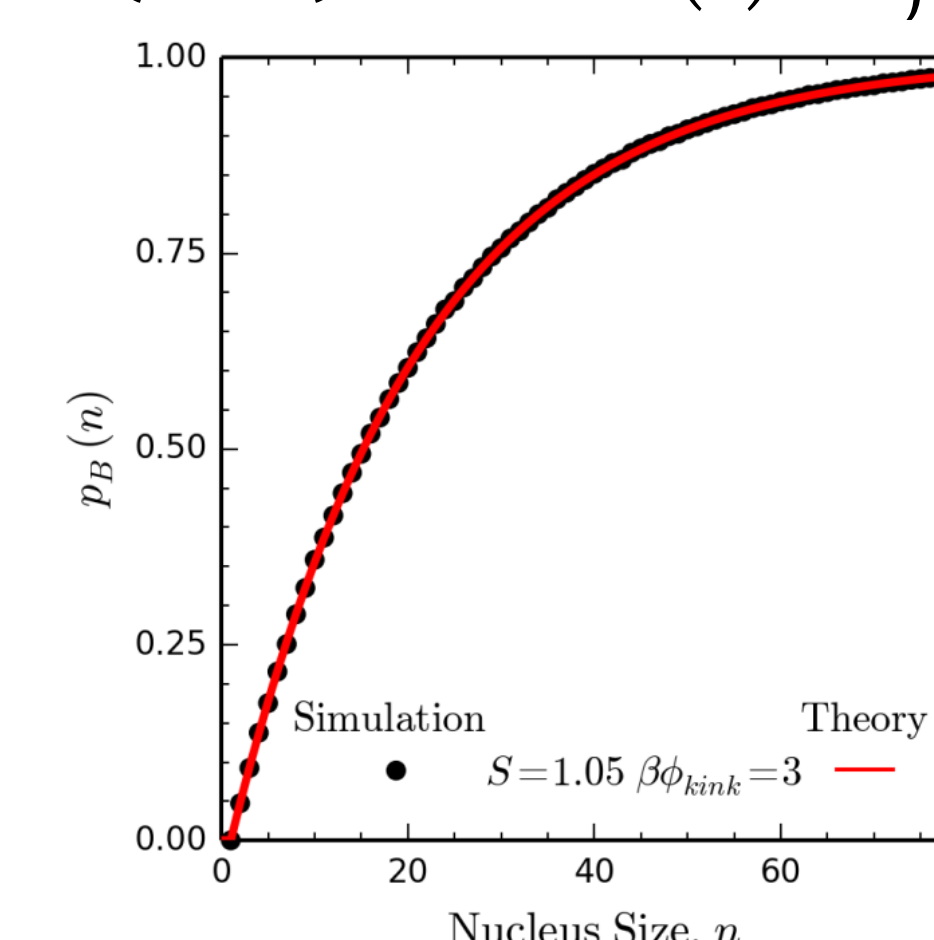
- Boundary conditions
 - $p_B(0) = 0$
 - $p_B(\infty) = 1$
- Match the committor at $n = 1$ by accounting for adsorption and desorption rates

$$p_B(1) = \frac{S-1}{e^{2\beta\phi_{kink}} + S-1}$$

- We derive the committor to be

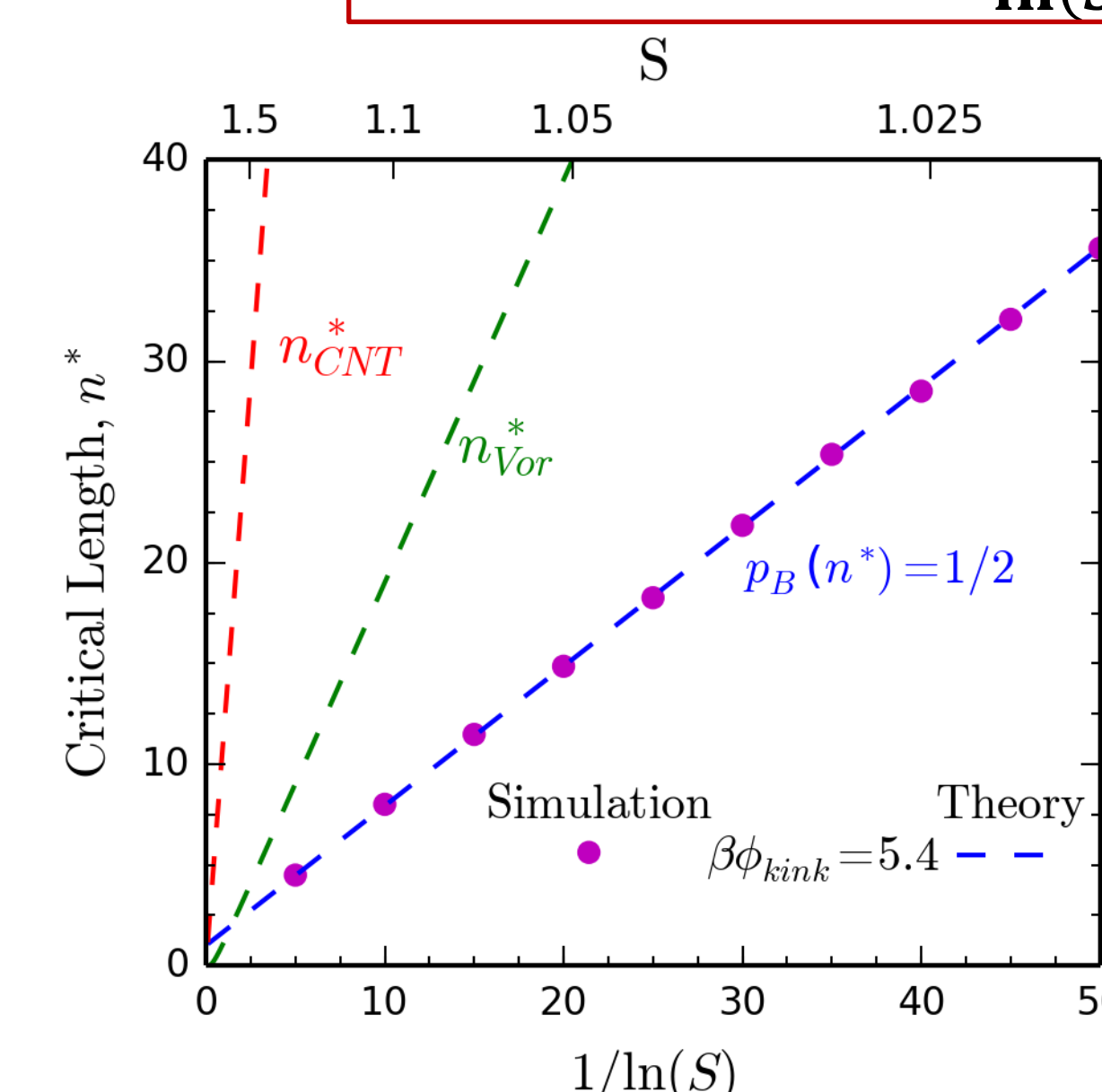
$$p_B(n) = 0 + \delta_{n \geq 1} \left\{ 1 - \frac{1}{1 + (S-1)e^{-2\beta\phi_{kink}}} \left(\frac{1}{S} \right)^{n-1} \right\}$$

We find excellent agreement with kinetic Monte Carlo simulations



- The critical length of a 1D nucleus is

$$n^* = 1 - \frac{\ln \left(\frac{1}{2} [1 + (S-1)e^{-2\beta\phi_{kink}}] \right)}{\ln(S)}$$

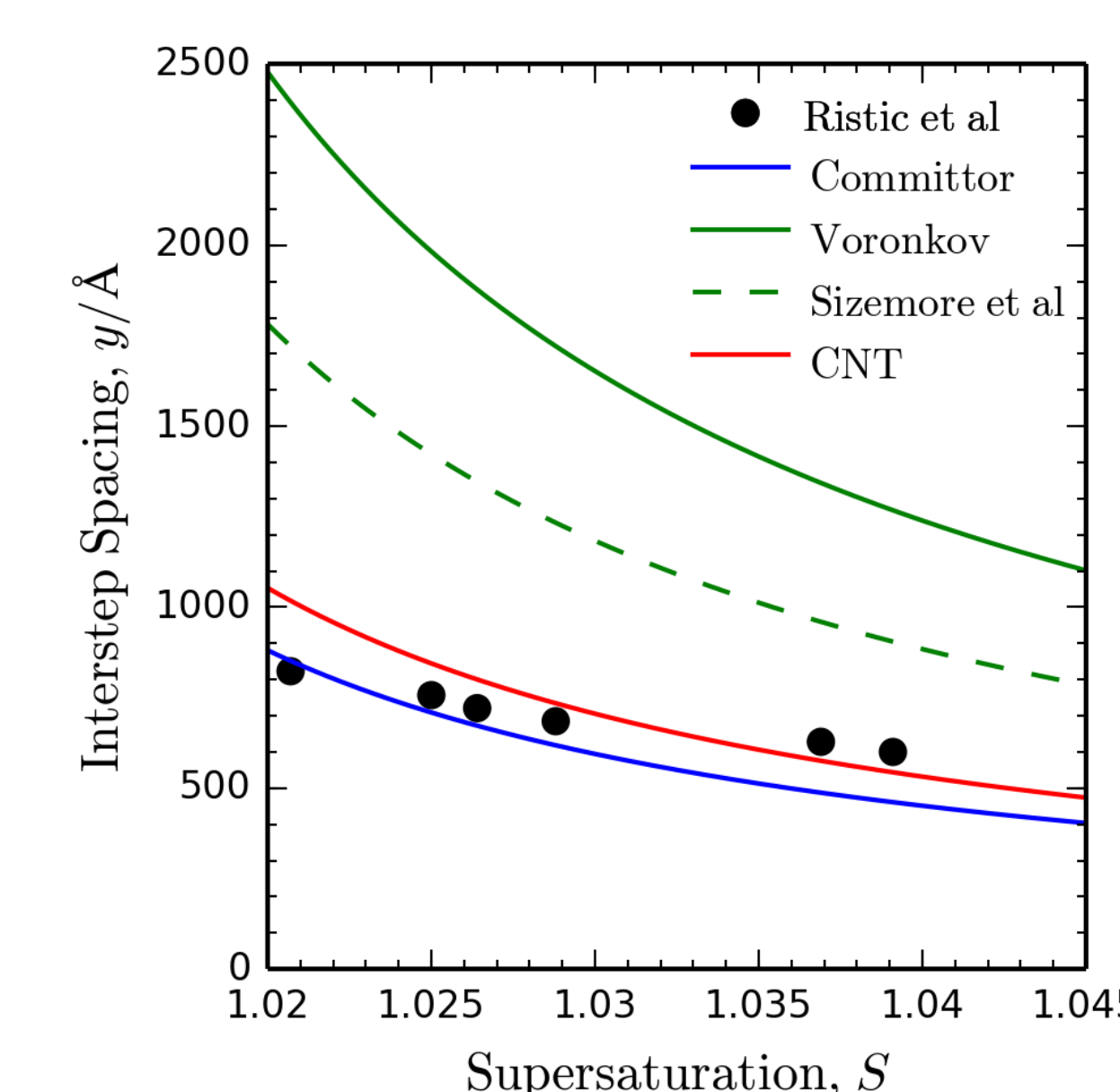


The critical length is nearly independent of $\beta\phi_{kink}$

Other models predict a much larger critical length compared to our model

Critical Spiral Edge Length

- We propose that the critical length we derive is applicable to the critical edge length of a nascent spiral
- Sizemore & Doherty proposed that the critical edge length was twice the rounding distance of an edge
 - Their result is nearly equivalent to that of Voronkov, except with a different rate expression model
- We compare our model to a study of N-methyl urea, a nearly-Kossel crystal
 - Ristic et al. measured the interstep distances for spirals, which we can calculate from our predicted critical length



- We find excellent agreement between experiments and our committor model
- CNT also yields great interstep distance predictions
 - Note that CNT and our committor model are equivalent for $\beta\phi_{kink} \approx 0.4$. For N-methyl urea, $\beta\phi_{kink} = 0.48$.

Summary

A unified approach to calculate the critical length of a 1D nucleus is necessary. Such a theory may improve crystal morphology predictions and assist in the development of more effective crystals.

We derive the critical length of a 1D nucleus with the committor, which yields excellent agreement with simulations.

We find great agreement between experimental results and our committor model.

References

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Acknowledgments

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