Early onset of kinetic roughening due to finite step width in hematin crystallization

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Crystallization is an example of a highly non-equilibrium process, in which the flows of mass and energy are governed by dynamic structures comprising a two-dimensional interface between adjacent three-dimensional semi-spaces. During crystal growth, the structure of its interface with the growth medium dictates the molecular mechanism of solute incorporation, the response of the growth dynamics to temperature and composition gradients, the action of impurities and dopants, and, ultimately, the crystal perfection. Interfaces that are smooth at equilibrium may become rough during growth at elevated supersaturation. We observed a smooth to rough transition during the growth of hematin crystals from a biomimetic mixed organic-aqueous solvent. Hematin crystallization is the main pathway employed by malaria parasites to sequester toxic hematin, released during hemoglobin digestion; its inhibition is considered the most successful target for antimalarial drugs. We show that the transition occurs at a supersaturation significantly lower than that predicted by published criteria. Moreover, surface roughness varies non-monotonically with supersaturation and the rate constant for rough growth is slower than that resulting from nucleation and spreading of layers. We attribute these unexpected behaviors to the dynamics of step growth dominated by surface diffusion and the loss of identity of nuclei separated by less than the step width w. We put forth a general criterion for the onset of kinetic roughening using w as a critical lengthscale. The slow growth in the rough growth regime may relate to the high efficacy of antimalarial drugs that inhibit hematin layer growth by introducing negative feedback between elevated hematin concentration and crystal growth rate that enables accumulation of hematin and parasite demise.

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