Thin Film Model of Crystal Growth and Dissolution

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We model growth and dissolution of a crystal in nano-confinement describing the non-equilibrium dynamics within the contact region using a continuum thin film equation. Our model accounts self-consistently (in the lubrication regime) for surface tension effects, for the microscopic interaction potential between the crystal and the substrate, and for non-equilibrium transport processes such as diffusion and liquid convection. Based on this model, we study dissolution under a macroscopic load (pressure solution) and growth under an applied supersaturation (crystallization force).

In pressure solution the functional form of the crystal-substrate interaction potential appears to strongly influence the dynamics. A divergent repulsion leads to flat contact, and to a dissolution rate which increases indefinitely with the applied load. In constrast, a finite repulsion implies a sharp pointy contact shape, and a dissolution rate independent from the applied load.

In confined growth it is well known that crystals can exhibit a rim in the contact region. Our model shows, at a given critical supersaturation and contact size, the generic formation and growth of a single cavity which ultimately leads to the formation of the rim. The results are supported by experiments on $NaClO_3$. This transition appears to be supercritical or subcritical, depending on the functional form of the interaction potential.

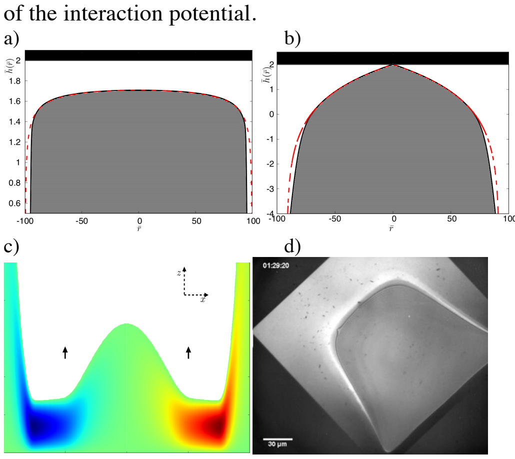

Figure 1: (a,b) Model results for pressure solution: (a) diverging repulsion, and (b) finite repulsion. (c,d) Cavity formation during growth : (c) model, (d) experiments.