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 contrast, 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 NaClO3. 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.