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Critical stresses and cracking in thin films of colloidal dispersions
WEINING MAN, WILLIAM RUSSEL, Princeton Univ. — Colloidal dispersions are often coated on a substrate to leave a uniform thin film after solvent evaporating. However, during drying, a negative capillary pressure develops as the air-water interface is pulled down into the interstices between particles, putting the drying film in tension. The film responds by collapsing normal to the surface but is constrained from shrinking laterally unless cracks open. In this study, we use a high-pressure ultra-filtration device to measure directly the pressure responsible for cracking in uniform films of latex or silica dispersions containing particles of varying radii, avoiding a drying process with edge effects that generate lateral flows and propagating fronts. The results confirm that cracking is controlled by the recovery of elastic energy with the critical pressure increasing with the modulus of the particle, decreasing with film thickness, and independent of particle size. The Griffith's criterion for equilibrium crack propagation along with the nonlinear stress-strain relation provides a necessary, but not sufficient, condition for cracking. When pressure increases beyond the critical value, additional cracks open in qualitative agreement with our elastic energy recovery model. We also find that films with randomly close packed particles crack at a higher pressure than predicted, while those with hexagonally ordered domains particles crack at the critical pressure. These observations suggest an important role for defects that nucleate cracks.

Weining Man

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