To Coat Is To Replace Gas at Surface of Solid by Liquid

Where Does the Gas Go?

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To coat substrate is to replace air or other gas at its surface by a continuous liquid layer. To start up is to displace gas and bring liquid into contact; this must begin at one point-like place yet is optically resolvable only after the place expands and light refraction and reflection at its perimeter give it a looped contact "line." Start-up of dip coating of a partially immersed roll turning in a liquid bath can be thwarted by an entrained thick, stable gas layer. Start-up of slot coating of narrow moving substrate can succeed only after the lubricating air film between liquid and substrate ruptures and contact is made. The contact's perimeter, a wetting front, evolves into a nearly straight dynamic contact "line" upstream, joined at the coating's sides to two virtually static contact "lines" and a connecting "start line" downstream. Start up of wider substrates is marked by multiple contacts, from which the wetting fronts may merge into a jagged or serrated "start line," a successful start, or may not merge, leaving uncoated lanes with "side lines" trailing downstream. First contact is nucleation of wetting. Wetting front advance is spreading that displaces all or most of the gas ahead. Surface diffusion bounds spreading speed below. Vapor diffusion and adsorption of volatile liquid can enhance it. Local liquid convection by viscous drag, capillary pressure gradient, surface tension gradient, electrostatic and disjoining forces can speed, slow, or even reverse it to retraction. Coating amounts to continuous restart with acceptable gas displacement.

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Coating Archetype. Smooth uniform vertical strip slowly lowered end-first into a pool can so nucleate wetting that a smooth dynamic contact "line" encircles it and advances upward at the strip's descent speed. If lowering is halted, equilibrium contact line location and contact angle at it, as measured optically, are ultimately established. The process is diffusional — from molecular surface hopping to coherent ripplon action — governed by surface-excess free energies rooted in surface forces at sub-optical scales; it is also mechanical, governed at all scales by capillary pressure from surface tension in curved meniscus, gravity, and viscous stress. Because sub-optical contact angle may differ, what is measured is *apparent* contact angle at an *apparent* contact line; likewise, at dynamic contact lines.

When slow lowering is resumed, apparent dynamic contact line (ADCL) sinks, pool's surface bends in a meniscus down to it, apparent dynamic contact angle (ADCA) rises, and a shallow cleft of flowing gas forms. When speed is raised the cleft deepens, becoming more cusp-like; ADCA mounts toward 180º. Wetted substrate drags liquid, pulling that along the meniscus downward; this flow and the descending dry substrate drag gas toward ADCL. Toward it the gas pressure builds to drive counterflow equal to inflow — unless gas passes ADCL. Modest speeds leave the pressure too small to alter meniscus shape, liquid flow, or force balance at ADCL. At higher speeds the cleft's near-cusp ends in a thin gas layer; ADCA becomes indistinguishable from 180º; and pressure climbs high enough to upset the balance at ADCL and drive gas past it. But any gas dissolving upstream lowers the pressure peak there. "Dissolution assist" by choosing soluble gas appears to lie behind 20 m/s slot-die coating of filaments. Gas escaping through permeable substrates is analogous. The highest successful coating speeds to date are around 50 m/s by "permeability assist" in blade coating of papers.

Physical Models. Forces other than pressure, viscous, surface tension, inertia and gravity must compete in the ADCL region. For mass and momentum conservation principles with those forces, together with established behavior of liquids and gases, interfaces between them, and their adherence to each other and to solid surfaces — "no slip" — show that abrupt displacement of gas by liquid at a true line would require *infinite* pressure and viscous forces there. That is physically impossible. A fix was found: over a short distance about the putative line, suppose fluid slips according to an empirical slip coefficient. Coefficient and distance can be chosen to relieve the infinities with negligible effect more that a few distances away. However, another empirical parameter is usually required: the ADCA. In theoretical analysis and modeling it is estimated from experiments. Potent for may ends, this approach cannot explain how liquid displaces gas in the submicroscopic region — the ADCL in experiments, the slip region in theories. Nor can it tell how complete the replacement, nor the fate of the gas that passes.

A complementary approach can: suppose that of gas dragged into and driven out of the cleft a net flow at given pressure at the ADCL passes through it in a thin uniform layer entrained between moving substrate and liquid layer's somewhat slower moving under-surface. Such states are known in certain start-ups and other experiments. They accord with principles and fluid behavior in ordinary fluid physics, including "no slip." But, with exceptions, they are *unstable*. High shear rate across the gas layer can roil the interface by 3D waves (Kelvin-Helmholtz instability) that grow and nucleate myriad wetting contacts; mergers of ensuing spreading fronts trap the entrained gas in easily visible bubbles at or near the substrate. Attractive force across the layer from imposed or induced surface charge can destabilize the liquid surface in wave-like pattern (an electrohydrodynamic instability) whose crests grow ever more quickly as they approach substrate; hence numerous wetting contacts become inevitable — "electrostatic collapse." The outcome is gas trapped in bubbles that may be small enough to dissolve soon owing to their rising capillary pressure as they shrink. Attractive disjoining pressure, or "conjoining" pressure, from van der Waals forces becomes appreciable across any nanoscale gas layer, similarly destabilizing liquid surface and nucleating multitudinous wetting contacts — "van der Waals collapse." The bubbles of trapped gas tend to be smaller still and faster dissolving — especially with more soluble gas, a second aspect of "dissolution assist," known from curtain coating. If the gas layer passing through the ADCL is still thinning and electrostatic or van der Waals collapse is fast enough, spreading fronts from leading wetting contacts can coalesce into a coherent front along which gas is expelled upstream except for fast-dissolving nanobubbles and adsorbed states. Submicroscopic leading edges of visible convective spreading fronts must be such. They are one candidate interior of ADCL; the other, a zone of areal collapse. Hysteresis between the two regimes would account for coating speed differences seen between onset and cessation of unacceptable gas bubble entrainment. Moreover, loci of continuous nucleation of the first regime, coupled with 3D gas and liquid flow, evidently underlie jagged and serrated ADCL's.

Coating Archetype Continued. At the four lateral corners of strip descending into pool fast enough to create a gas layer around it, that layer is thinned at the corners by the capillary pressure of meniscus bent around them. Hence the gas layer collapses first at them, nucleating wetting at each. The convective spreading fronts (ADCL's) from each move across descending substrate until they meet those from adjacent corners; in frontal view the layer of counterflowing gas between liquid and substrate is vee-shaped, straight-sided if spreading-front speed is uniform. Gas flow in the vee is 3D; so is adjacent liquid flow. Layer thickness varies. Wetting may nucleate at a thin place and spreading from there may trap a bubble to be carried away in liquid — another kind of bubble entrainment. Raising descent speed deepens and sharpens a vee until gas pressure at its tip leads to a slim finger of air and then bubble detachment — yet another kind of bubble entrainment. On broader substrates, or with more viscous liquid, or under greater flow confinement, wetting contact nucleates not at just corners but multiple steady or shifting places, producing jagged or serrated ADCL's. At higher speeds visible bubbles detach from some or all of their tips — a mode of entrainment different from that along submicroscopic "electrostatic" or "van der Waals" frontal collapse.

Beyond the Coating Archetype. Critical to displaced gas's fate are flow rate and pressure of gas that arrives at ADCL, it appears. Upstream meniscus shape largely controls these, just as entry profiles between flexible web and winding roll or cambered flotation plate dictate entrained air layer pressure, thickness, and flow rate. The difference is that continuous electrostatic or van ther Waals frontal collapse at ADCL can virtually block gas flow, if it would otherwise not be too high. Externally accessible meniscus shapers, and thereby gas-flow modifiers, are confinement of meniscus, electrostatic force on it, and forces in flowing liquid behind it influenced by confinement by rigid and compliant boundaries and by inflow conditions (strips descending into pools are atypical!). Increases in coating speed at onset of unacceptable entrainment are possible by "elastohydrodynamic assist" in deformable roll and tensioned web-over-slot die coating; by "electrostatic assist" in slot, slide, and curtain coating; by "gravity assist" or "inertia assist" (a.k.a. "hydrodynamic assist") in curtain coating . . . .

Closure. Drawn from many experimental observations, theoretical analyses, deductions and insights, the synthesis outlined here invites further confrontation with existing data and theoretical models. It also points to needs for new ones.