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Author

Squires, Todd M

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COMMENTARY

Drops on soft surfaces learn the hard way

Todd M. Squires[1]

Department of Chemical Engineering, University of California, Santa Barbara, CA 93106-5080

A liquid drop sits on a solid surface and slides away when the surface is tilted. Few physical systems seem so mundane or would appear to be governed by such plain, predictable, and long-understood principles. Indeed, Young's fundamental understanding of the equilibrium gas/liquid/solid contact line (Fig. 1*A*) has remained intact for over two centuries (1). Nonetheless, static and dynamic contact lines continue to provide surprises (2), yielding qualitatively new insights, motivating new materials, and highlighting the mysteries that can remain overlooked within even the simplest of systems. In PNAS, Style et al. reveal yet another surprise hidden within this classic system: droplets spontaneously migrate along substrates that are chemically homogeneous, but inhomogeneously deformable (3). The Young (or Young–Dupré) equation,

$$\gamma_{lg}\cos\theta_Y = \gamma_{sg} - \gamma_{sl}, \tag{1}$$

relates the equilibrium angle θ_Y formed at the solid/liquid/gas contact line to the respective surface energies γ, which act as tensions pulling along each interface (Fig. 1*A*). Any nonzero vector sum of these three tensions would cause the contact line to move in response, unless some chemical or topographical inhomogeneity held it in place. Young's equilibrium contact angle, then, arranges the interfaces to balance these forces, giving Eq. **1**.

Significant modifications to this static picture—both conceptual and qualitative—have been discovered in recent years. Lotus leaves use microscopically rough surfaces to amplify their hydrophobic properties, achieving nearly perfect nonwetting and inspiring biomimetic superhydrophobic materials (4). Patterned surface wettabilities confine microfluids within wall-free channels (5). Namib Desert beetles combine both strategies to extract water from the air, using wings coated with a field of hydrophilic bumps, each separated by lotus-like superhydrophobic strips. Droplets of water nucleate onto the hydrophilic bumps from the blowing wind, eventually growing large enough to detach and drop into their mouths (6).

Superhydrophobicity and patterned wettability complement and enrich Young's picture in qualitatively new ways. Soft substrates (Fig. 1*B*), on the other hand, pose a more direct challenge to Young's equation, as probed by Dufresne and coworkers (7) and others (8). Notably, Eq. **1** balances only the tangential force on the contact line, ignoring the normal component with an implicit assumption that the solid is infinitely rigid. This contrasts with the complete (vector) force balance observed at three-liquid contact lines (Fig. 1*C*), following Neumann's triangle construction. Nonetheless, two centuries of apparent success have solidified Young's equation (Eq. **1**) as the consensus description of solid/liquid wetting, despite ignoring this unresolved normal force imbalance.

Capillary stresses can, however, deform sufficiently soft solids enough to alter a drop's apparent contact angle (9, 10). Elastic moduli (including, perhaps ironically, Young's modulus E) describe a material's stiffness and correspond roughly to the stress required to deform the material substantially. Moduli are often quoted in gigapascals (e.g., $E \sim 10^{-2}$ GPa for rubber vs. $E \sim 10^{3}$ GPa for diamond). Under partial wetting, the surface tension γ_{lg} exerts a force that is concentrated within the (molecular) width of the contact line, giving very high local stresses that deform the substrate. Substrate deformations decay away from the contact line (Fig. 1*B*), ultimately reaching an elastocapillary length scale,

$$L_{EC} \sim \frac{\gamma_{lg}}{E}, \tag{2}$$

beyond which sufficient elastic stress accumulates to reduce the "unbalanced" capillary stress below E and, thus, to recover a relatively flat interface. Given typical liquid surface tensions ($\sim 10^{-2}$ Pa·m), L_{EC} is immeasurably small for most solids (e.g., $L_{EC} \sim 100$ pm for water on glass). Instead, elastocapillary phenomena are typically observed involving slender structures, whose weaker bending rigidity succumbs more easily to wetting forces (11): wet hair forms clumps, microfabricated structures collapse under "stiction," and "capillary

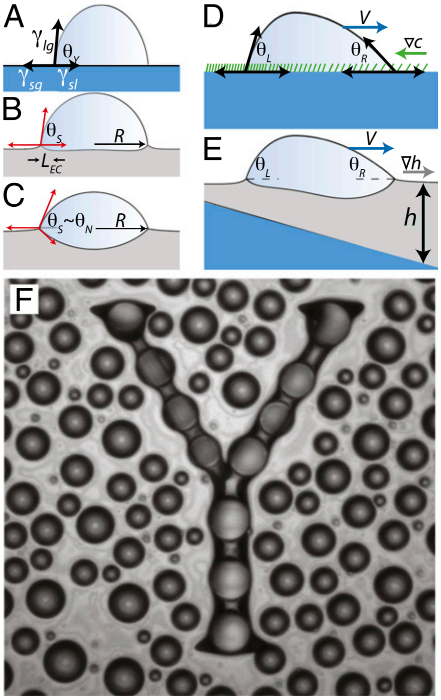

Fig. 1. (*A*) Young's classic concept of the solid/liquid/gas contact angle balances three interfacial tensions, each of which pulls on the three-phase contact line. Young's equation (Eq. **1**), which defines the equilibrium contact angle θ_Y, reflects a tangential force balance, assuming the normal force to be balanced by immeasurably small elastic deformation. (*B*) Capillary forces deform soft substrates over a elastocapillary length scale $L_{EC} \sim \gamma_{lg}/E$ (Eq. **2**), raising a ridge around the contact line and pressing into the substrate in the droplet interior. The apparent wetting angle θ_S over soft substrates, however, is lower than Young's equation would predict. Elastocapillary deformations are relatively insignificant for droplets that are much larger than L_{EC}, which are, thus, well described by Young's picture (*A*). (*C*) Drops smaller than L_{EC} deform the substrate so thoroughly as to give an apparent wetting angle θ_N given by Neumann's triangle construction for three-liquid contact lines. (*D*) Droplets placed on surfaces with wettability gradients (e.g., via graded surface chemistry) move spontaneously up the wettability gradient to lower the global free energy. (*E*) Coating a flat layer of soft gel (gray) atop a rigid substrate (blue) with variable height yields a substrate with stiffness variations. A droplet placed on a surface with a stiffness gradient is driven by the effective wettability gradient towards softer regions. (*F*) A rigid substrate with a Y-shaped groove, coated with a soft gel as in *E*, induces durotactic droplets migration and collection atop the Y, where the gel is thickest and the substrate most deformable. Adapted from ref. 3.

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[1] E-mail: squires@engineering.ucsb.edu.

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origami" structures self-fold with the addition of a drop of water. Conversely, drying a gel supercritically sidesteps the liquid/vapor interface that would otherwise cause its elastocapillary collapse and, instead, forms an aerogel.

Much softer moduli (∼ 1–10 kPa) are common with gels, and give ∼10-μm elastocapillary lengths that can approach or even exceed the size of wetting droplets. In such cases, where small drops wet soft substrates, Young's equation (Eq. **1**) can be violated appreciably, with smaller apparent contact angles than Young would predict. The apparent contact angle θ_S decreases with substrate softness (7, 8, 12) (Fig. 1*B*) and approaches the angle θ_N given by Neumann's triangle (Fig. 1*C*) in the limit of extreme deformability (13).

Gradients in surface wettability can be established with thermal (14) or chemical (14, 15) gradients (Fig. 1*D*), be imposed electrically (16), or form spontaneously from reactive liquids (17). Wettability gradients, in turn, drive droplet motion that continually reduce the overall surface free energy**.** Continuum hydrodynamics, however, predict that contact lines require infinite power to move (18). This aphysical prediction is only resolved by noncontinuum, molecular effects, causing contact line dynamics to depend strongly on minute variations in local chemistry or topography. Contact line pinning is, thus, common and plays a key role in coffee-ring stains (19, 20), the hysteresis of dynamic contact angles, and in wetting instabilities that ultimately limit the speed with which microchips can be produced via immersion lithography (21). Viscoelastic deformations of soft substrates—strongest around the contact line itself (Fig. 1*B*)—introduce a new mechanism for contact line hysteresis (22) and for the viscosity-independent "brake" on droplet spreading and sliding velocities (23).

Having shown substrate deformability to impact the apparent contact angle (7, 12), Style et al. now demonstrate that gradients in substrate stiffness (Fig. 1*E*) act effectively like wettability gradients (Fig. 1*D*) driving "durotactic" droplet migration down stiffness gradients (3). By spin-coating ∼10- to 100-μm layers of silicone gel ($E \sim 1–10$ kPa) atop rigid substrates with patterned or corrugated height profiles, they produce flat substrates that are chemically homogeneous and yet have inhomogeneous effective stiffness. Substrate regions with greater gel thickness have increased deformability. Droplets placed on these surfaces move up effective wettability gradients (Fig. 1*E*), eventually stopping in the softest regions (i.e., the soft "Y" pattern shown in Fig. 1*E*).

Style et al. have revealed a surprisingly simple mechanism by which solid/liquid wetting can be understood, engineered, and controlled.

With this work, Style et al. (3) firmly establish substrate deformability as a material property that can be engineered to influence surface wetting—like surface chemistry and topography—and even to direct the spontaneous migration of droplets. Like other gradient-driven migration phenomena, however, droplet durotaxis is quite slow, with patterns such as Fig. 1*E* developing over minutes. [By contrast, the ability to rapidly impose strong electric fields enables rapid electrowetting, heavily employed in "digital microfluidics" technologies (24).] Durotactic driving forces are fairly weak, and substantial energy is dissipated by moving solid/liquid contact lines. Increasing durotactic velocities would require reducing dissipative losses: for example, by tuning the substrate's viscoelastic loss moduli over the time scales relevant to migration or by reducing the contact line friction. The latter could potentially be achieved by developing deformable substrates with strong hydrodynamic slip: for example, by coating deformable surfaces with a mutually immiscible, fully wetting liquid or by engineering hydrogel or organogel substrates with (liquid-like) surfaces.

Most broadly, however, Style et al. (3) have revealed a surprisingly simple mechanism by which solid/liquid wetting can be understood, engineered, and controlled. In so doing, they affirm once again that even subjects that seem obvious may yet hold surprises for those curious enough to look.

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