

Patterning droplets with durotaxis

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Numerous cell types have shown a remarkable ability to detect and move along gradients in stiffness of an underlying substrate—a process known as durotaxis. The mechanisms underlying durotaxis are still unresolved, but generally believed to involve active sensing and locomotion. Here, we show that simple liquid droplets also undergo durotaxis. By modulating substrate stiffness, we obtain fine control of droplet position on soft, flat substrates. Unlike other control mechanisms, droplet durotaxis works without imposing chemical, thermal, electrical, or topographical gradients. We show that droplet durotaxis can be used to create large-scale droplet patterns and is potentially useful for many applications, such as microfluidics, thermal control, and microfabrication.

droplet control | elasticity | soft matter | wetting | mechanosensing

The control of liquids on surfaces is essential for microfluidics (1), microfabrication (2), and coatings (3–5), to name but a few applications. Wetting is typically manipulated by controlling interfacial energies (6). Heterogeneous surface chemistries have been exploited to pattern (7, 8) and transport droplets (3, 9). Gradients in temperature or electric potential can drive droplet motion (3, 9). Alternatively, surface topography can control the spreading of fluids. For example, isotropically rough surfaces can exhibit superhydrophobicity (10, 11), whereas anisotropic surfaces exhibit anisotropic spreading (12) and even directed droplet transport (13–15). Here, we introduce a method to control droplets on surfaces inspired by the biological phenomenon of durotaxis—the ability of many eukaryotic cell types to move along gradients in the stiffness of their extracellular matrix (16–19). Although the current explanation of durotaxis involves active sensing of matrix stiffness and actomyosin-based motility (18), we show here that even simple liquid droplets display durotaxis. Furthermore, we show that durotaxis can be exploited to achieve large-scale droplet patterning. A simple theory explains how drops move toward softer parts of a substrate, and quantitatively captures the droplet distribution on patterned surfaces. Droplet durotaxis is prominent on soft substrates, which are significantly deformed by liquid surface tension (20, 21).

The spreading of liquid droplets on stiff, flat surfaces is primarily described by the contact angle. In equilibrium, a small droplet takes the shape of a spherical cap with uniform contact angle θ determined by Young's law: $\gamma_{LV}\cos\theta = \gamma_{SV} - \gamma_{SL}$. Here, indices L , S , and V of interfacial energies, γ , represent liquid, solid, and vapor, respectively (6). Spontaneous droplet motion typically occurs in two main cases. First, if the actual contact angle of a droplet differs from its equilibrium contact angle, the droplet will be driven to spread/contract until it reaches its equilibrium shape (6). Second, if there is a difference between the equilibrium contact angle on either side of a droplet, the droplet will be driven toward the more wetting side. This is typically achieved by modifying the interfacial energies across the droplet (9). Here, we show that gradients in substrate stiffness can also drive droplet motion on soft substrates.

Contact Angle Dependence on Substrate Stiffness

On soft substrates, the apparent contact angle varies with droplet size and substrate stiffness (22, 23). This breakdown of Young's law occurs because droplet surface tension can significantly deform soft substrates, as shown by the X-ray micrograph in Fig. 1A (22–23). Droplet surface tension pulls up at the contact line creating a ridge, while the droplet's internal (Laplace) pressure pushes down into the substrate over the contact area, creating a dimple. Dimple formation leads to a contact angle change: when the Laplace pressure is sufficiently large, the droplet bulges down into the substrate, taking a lenticular shape and causing it to appear more wetting, as illustrated in Fig. 1B and C. The apparent contact angle, θ , is defined here as the angle of the liquid–vapor interface at the contact line relative to the undeformed solid surface far from the droplet. For large droplets, we expect the contact angle to be consistent with Young's law. For very small drops, the shape mimics that of drops floating on a liquid with the same interfacial tensions as the soft substrate—the contact angle is determined from a Neumann triangle construction (22, 23, 34). The critical droplet radius below which the apparent contact angle starts to deviate from Young's law is $L = \gamma_{LV}/E$, where L is an elastocapillary length and E is the Young's modulus of the substrate (23). For hard solids, $L \sim$ molecular scales, so contact angle changes are insignificant. For soft solids, L can be macroscopic; gels with $E \sim$ kPa have $L \sim 10 \mu\text{m}$.

Two examples of the dependence of the macroscopic contact angle on droplet size are shown in Fig. 1D. Here, glycerol droplets rest on thin, flat silicone gel layers (CY52-276A/B; Dow Corning; $E = 3$ kPa) spin coated on a stiff glass coverslip. In the samples shown, the film thicknesses are $h = 3, 35,$ and $38 \mu\text{m}$. We measured θ using a laser scan (laser profilometer with white-light probe sensor; Solarius) and an optical profilometer (NewView 7300; Zygo Corporation). Further details are given in *Materials and Methods*. For droplets larger than $50 \mu\text{m}$, θ approaches the macroscopic value of 95° , measured for millimetric droplets. For droplets smaller than $50 \mu\text{m}$, θ is significantly reduced. For a given droplet size, the contact angle is smaller on the thicker substrate. In other words, small droplets appear to wet thick substrates more strongly than thin substrates.

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microscopy at the 32-ID-C beamline in the Advanced Photon Source (APS) of the Argonne National Laboratory. High-resolution, 50 nm/pixel micrographs were recorded using bright light at a photon energy of 8 keV generated by the APS (37). As we used a short exposure time of less than 0.2 s per snapshot, X-ray effects—such as polymer degradation—should be negligible (38). A Zernike phase-ring provided sufficient phase contrast to clearly visualize the droplet interfaces, so no contrast agent was required (39, 40).

Contact Angles. We measured droplet contact angles using two separate techniques: first, with an optical profilometer (NewView 7300; Zygo Corporation), and second, with a laser-scan device (laser profilometer with white-light probe sensor; Solarius). First, we measured the height from the undeformed surface h_d of droplets on a range of substrate thicknesses. Second, we used an image of the droplet to measure its apparent radius, R . When $\theta > 90^\circ$, R represents the actual radius of the droplet. When $\theta < 90^\circ$, R represents the footprint radius of the droplet. We calculated the contact angle θ by assuming that the droplet surface is a spherical cap of height h_d and radius R : if $R > h_d$, $(1 - \cos \theta)/\sin \theta = h_d/R$, whereas if $R < h_d$, $\theta = \sin^{-1}((h_d - R)/R) + 90^\circ$. On a rigid substrate with no

wetting ridge, this technique will give the correct contact angle. However, on soft substrates, this value systematically overestimates θ by an amount on the order of the ratio of the ridge height divided by the droplet radius. This systematic error is $\approx 5^\circ$ for the smallest droplets and decreases with increasing radius (23).

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