Substrate Curvature Gradient Drives Rapid Droplet Motion

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Making small liquid droplets move spontaneously on solid surfaces is a key challenge in lab-on-chip and heat exchanger technologies. Here, we report that a substrate curvature gradient can accelerate micro- and nanodroplets to high speeds on both hydrophilic and hydrophobic substrates. Experiments for microscale water droplets on tapered surfaces show a maximum speed of 0.42 m/s, 2 orders of magnitude higher than with a wettability gradient. We show that the total free energy and driving force exerted on a droplet are determined by the substrate curvature and substrate curvature gradient, respectively. Using molecular dynamics simulations, we predict nanoscale droplets moving spontaneously at over 100 m/s on tapered surfaces.

Most observations of the spontaneous motion of droplets on solid surfaces or substrates are due to wettability gradients [1–5]. Many techniques, such as thermal [4–7], chemical [8–10], electrochemical [11], and photochemical methods [12,13], can be used to make a flat substrate exhibit a continuously varying liquid contact angle. Droplets on such substrates tend to move toward the region with lower contact angle. Although spontaneous motion has also been observed for droplets on substrates with uniform surface energy but varying surface roughness [14], its mechanism can still be categorized as driven by a wettability gradient because of the varying effective contact angle. Droplet transportation can also be induced on some geometrical surfaces without wettability gradient [15–17], but the direction of motion is determined by both the contact angle and the arrangement of the structures on the substrate. The speed of spontaneous droplet motion resulting from all the above effects is typically in the range of micrometers to millimeters per second [6], far too low for applications in areas such as liquid-based thermal management of fuel cells and semiconductor devices.

Here, we report a mechanism that can result in ultrafast spontaneous motion of even micro- and nanoscale droplets. In contrast with the above-mentioned methods, neither surface energy gradient nor surface roughness variation is required. The purely geometrical consequence of the substrate curvature determines the total free energy and the substrate curvature gradient provides the driving mechanism. We will not only present the experimental and simulation-based evidence for the effect, but also explain these results using a simple model, and show that it accounts quantitatively for both the increase of the velocity at the nanoscale and the persistence of the effect on hydrophobic substrates.

To observe the effect experimentally, tapered surfaces were sharpened from glass tubes of 1.5 mm in diameter with half-cone angle $\alpha = 3.2^\circ$ by a flaming-brown micro-pipette puller (model P-1000, Sutter Instrument). The video frames shown in Fig. 1(a) illustrate a typical spontaneous motion of a 1 mm$^3$ water droplet in experiments under ambient conditions on the tapered surface. The droplet moves toward the direction of increasing cross section radius, $R$, of the tapered tube. The velocity, $v$, of the droplet is measured as a function of $R$ along the tapered tube, plotted as blue square dots in Fig. 1(b). The surface was treated first in an oxygen plasma and then in MTS solution, yielding measured advancing and receding water contact angles of about $\theta_a = 10.8^\circ$ and $\theta_r = 9.3^\circ$. The green and purple dots in Fig. 1(b) show the velocities of identical droplets on the same tapered tube just after being cleaned ($\theta_a = 43.2^\circ$ and $\theta_r = 39.5^\circ$) and after treatment in an oxygen plasma ($\theta_a = 16.3^\circ$ and $\theta_r = 13.6^\circ$), respectively. The velocity is not monotonic along the surface but increases with decreasing contact angle. It is well-known that spontaneous motion of smaller droplets is usually harder to induce [18]. Surprisingly, for smaller droplets of a volume 0.0115 mm$^3$, we recorded a maximum speed of ~0.42 m/s (red triangles) that is 2 orders of magnitude higher than those obtained by standard wettability gradients [19].

To reveal the mechanism, we first explore how the total free energy, $U$, of a droplet varies on a curved substrate. For droplets that have diameters smaller than the capillary length, $l_c$ ($l_c = 2.7$ mm for water at room temperature), we
where $\theta_s$ denotes the Young contact angle of the liquid on the substrate. For a droplet placed on a conical surface with half-apex angle $\alpha$, we can use a finite element code, SURFACE EVOLVER [28], to deduce its shape by minimizing $U$ for a fixed droplet volume. The points plotted in Fig. 2(a) show the resulting normalized total free energy, $u = (\gamma A_{LV} - A_{LS})/U$, versus the dimensionless substrate curvature $\xi = r_s\kappa$, where $r_s$ denotes the radius and $A_s = 4\pi r_s^2$ denotes the surface area of a droplet of the same volume, $\kappa$ denotes the local substrate curvature of the contact area which is equal to $-R^{-1}\cos\alpha$ or $R^{-1}\cos\alpha$ when the droplet is placed on the external or internal conical surface, respectively, and $R$ denotes the local cross section radius.

The results in Fig. 2(a) for various contact angles show that the total free energy is always monotonically decreasing as the substrate curvature increases, independent of whether the surface is hydrophilic or hydrophobic. Thus, the droplets always tend to move toward the larger or smaller end of the cone, whenever the droplets are on the external or internal surface of the cone, respectively. We term the driving force, $F_c = -dU/ds$, *curvi-propulsion*, because it is purely the result of the substrate curvature gradient, where $s$ is the coordinate along the generatrix of the cone pointing in the direction of increasing substrate curvature. The points plotted in Fig. 2(b) show the calculated values of $F_c$ versus $r_s\kappa$, indicating a rapid increase with increasing $|\kappa|$ or equivalently shrinking $R$.

The plotted results in Fig. 2 are scale independent and are thus valid for different sized droplets and cones. Furthermore, we find that the total free energy is almost independent of half-apex angles, as numerically validated in Fig. 2(a) with $\alpha = 0^\circ$ (circles for cylindrical tubes), $19.5^\circ$ (triangles), and $30^\circ$ (squares), and theoretically proven in the Supplemental Material [20]. The solid lines are the analytical approximation explained in detail in the Supplemental Material [20], showing perfect agreement with the numerical results.

In the lower speed region of spontaneous motion, the main obstacle arises from contact angle hysteresis, $\Delta\theta = \theta_s - \theta_a$, which generates a resistance force, $F_h$, that is usually modeled as $F_h = kr_s\gamma(\cos\theta_a - \cos\theta_s)$, where $k$ is a numerical constant that depends on the shape of the droplet [29], and $r_s$ is the radius of the droplet’s contact area on the substrate that can be approximately associated with $r_s$ in the form $r_s = r_s(\bar{\theta})$ with $\bar{\theta} = (\theta_a + \theta_s)/2$ and $\chi(\bar{\theta}) = 4^{1/3}\sin\bar{\theta}/(2 + \cos\bar{\theta})(1 - \cos\bar{\theta})^{-1/3}$ (see [20]). Therefore, the hysteresis resistance force per unit of droplet mass is proportional to $r_s^{-2}$. This property generally explains why it is...
harder to induce smaller droplets to move quickly on substrates by forces such as gravity, vibration, or air flow [30]. Finally, we can reformulate the equation of motion $mdv/dt + F_h = F_c$ as

$$dm/dt + \frac{3\gamma^2}{4\pi r_s^2} \left[ k \left( \cos \theta_t - \cos \theta_a \right) \chi'(\theta) + u'(\xi) \xi^2 \tan \alpha \right] = 0,$$

where $\gamma$ is the surface tension, $d$ is the distance between atoms, $r_s$ is the radius of the droplet, $\alpha$ is the contact angle, $\chi'$ is the derivative of the interfacial energy, and $u'(\xi)$ denotes the derivative of $u(\xi)$ with respect to $\xi$.

For a droplet with circular contact lines, the value of $k$ can be well approximated as $4/\pi$ [29]. With this value, we plot in Fig. 3 the dependence of $R_c$ on $\theta$, $\alpha$, and $\Delta \theta$ for droplets placed on the outer and inner conical surfaces, where $|R_c| = r_s \xi_{cr}^{-1} \cos \alpha$. The value of $F_c$ is larger or smaller than $F_h$ whenever $R$ is smaller or larger than $R_c$, respectively. In other words, when a droplet of radius $r_s$ is placed on conical surface at a position $R_0$ such that $R_0 < R_c$, then the droplet will always start a spontaneous motion toward the direction of locally increasing substrate curvature. This property is valid for droplets on both the outer and inner conical surfaces.

Further, for a droplet that is quasistatically placed at a position $R_0$ with $R_0 < R_c$, we can obtain the explicit solution of Eq. (2) as follows:

$$v^2 = \frac{6\gamma}{\rho r_s} \left[ u(\xi_0) - u(\xi) + u'(\xi_{cr}) \xi_{cr} \left( \frac{1}{\xi_0^2} - \frac{1}{\xi^2} \right) \right].$$

The speed of spontaneous motion increases at first, reaches its maximum at $R = R_c$, and then decreases. For comparison, the red dashed and the blue dash-dotted lines in Fig. 1(b) give the predictions of Eq. (4) with the initial positions $R_0 = 0.017$ mm and $R_0 = 0.07$ mm, respectively. The results show a good agreement with experimental measurements. We note that advancing and receding contact angles of water droplets during spontaneous motion are larger than those measured in a static state [for example, $\theta_a = 56.5^\circ$ and $\theta_r = 52.5^\circ$ at $t = 15$ ms in Fig. 1(a)], and we adopt these dynamic contact angles when making predictions. If we use the static values, the predicted speeds of spontaneous motion are the same but the maximum speeds are about 3 times the measured values.

In contrast with other mechanisms of spontaneous droplet motion, which favor motion of larger droplets, the curvature-propulsion described by Eq. (4) drives smaller droplets faster than larger ones. This potentially very useful property is experimentally confirmed in Fig. 1(b) as well as in the Supplemental Material [20]. Equation (4) even predicts spontaneous speeds of the order of 100 m/s for nanodrops on nanoscale conical surfaces. Since experiments with nanodrops are currently impractical, we complemented experiments with molecular dynamics (MD) simulations based on the LAMMPS platform [31], allowing us to study similar phenomena on the nanoscale. A nanoscale cone was modeled as a rigid framework of a monolayer of conically rolled graphene, as shown in Figs. 4(a) and 4(c). The water droplet was modeled by a standard model (SPC/E) [32] with the same parameters as in Ref. [33]. A Lennard-Jones potential, $\phi(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6]$, was used to characterize the cone-liquid van der Waals interaction [34], where $r$ denotes the distance between atoms. By fixing $\sigma$ at 0.319 nm and adopting two different values, 58.5 and 1.95 meV, for the well depth $\varepsilon$, we obtained two different contact angles $\theta = 51^\circ$ (hydrophilic) and $138^\circ$ (hydrophobic) with zero contact angle hysteresis in both cases. The model cone has a half-apex angle $\alpha = 19.5^\circ$ and a height of 20 nm. As illustrated in Figs. 4(a) and 4(c), for modeling the motion of a 2.5 nm-diameter droplet containing 386 molecules on the outer and inner cone surface, respectively. In the simulations, the temperature is kept at 300 K with a Nosé-Hoover thermostat, and the whole system is located in a finite vacuum box. Initially, the mass center of the droplet is fixed at a starting point for 1 ns, to reach thermal equilibrium. Then, the droplet is released to move freely along the conical surface for the next 1 ns.

When the droplet is released near the small tip of the external surface, it starts to move spontaneously toward the larger end, as illustrated in Figs. 4(a) and 4(b), with the maximum velocity exceeding 150 m/s. The red (solid) curve in Fig. 4(b) depicts the dependence of velocity, $v$, on the radius of the cone $R$ measured directly below the center of mass of the droplet, for contact angle $\theta = 51^\circ$. Snapshots of the droplet at three moments during this motion are illustrated in Fig. 4(a). Similar spontaneous motion is observed for the hydrophobic case ($\theta = 138^\circ$), a maximum
Thus, the slipping resistance force can be modeled as 

\[ F_s = \lambda \pi r_c^2 v \]

where \( r_c \) is the radius of the droplets contact area on the substrate as we defined before. Therefore, the equation of motion takes a form similar to Eq. (2) [see Eq. (S42) in the Supplemental Material [20]]. When we choose \( \lambda = 3.5 \times 10^4 \) Ns/m^3, the red dashed and the blue dash-dotted lines in Fig. 4(b) give model predictions that are again in good agreement with the MD simulations.

Creeping motion of droplets on cones has been observed previously [8,37–40]. We distinguish the results described here from previous observations and analyses, in several respects. Relatively large drops were considered in previous studies, which either encircled the cone externally or filled in a conical tube. The mechanism behind the creeping motion for such large drops is simply contact area gradient, while the driving mechanism for the spontaneous motion of the droplets we observe, which is small compared to the local dimensions of the cone, is substrate curvature gradient. As a result, the wettability-independent motion is always toward the larger or smaller end of the cone, for droplets on the external or internal conical surfaces, respectively. This contrasts with larger drops either encircling or filling a cone, which may tend to move in different directions, depending upon the wettability [37–40].

In conclusion, we have demonstrated ultrahigh velocity motion of droplets moving on tapered surfaces, by experiment on the submillimeter scale and by molecular dynamics simulation on the nanoscale. On the basis of molecular dynamics simulations, the peak velocities achieved this way are expected to reach of order 100 m/s on the nanoscale, so, this method is promising to realize spontaneous transportation of small droplet in fast motion. We explain this remarkable effect, which we term curvi-propulsion, as being due to the much higher substrate curvature gradients that nanoscale droplets can experience. We corroborate the effect using finite-element analysis and simple scaling arguments.

In previous experiments on spontaneous motion [6,41–45], external sources of energy such as vibrating or heating the surface were often applied in order to depress the influence of contact angle hysteresis. The same approach can be utilized to depress the hysteresis effect for spontaneous motion of droplets and thus achieve even higher droplet speeds.

If suitable substrates can be designed to exploit curvi-propulsion, for example, using arrays of nanoscale tapered structures, we speculate that this phenomenon could be useful for a range of practical applications where mass transport via droplet motion plays a key role, including rapid cooling, passive water collection, and microchemical synthesis. The curvi-propulsion mechanism may also prove useful in understanding biological phenomena such as intercell transport through cytonemes or filopodial bridges [46].

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