Ultrafast Propulsion of Water Nanodroplets on Patterned Graphene

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Supporting Information

ABSTRACT: The directed transport of liquids at the nanoscale is of great importance for nanotechnology applications ranging from water filtration to the cooling of electronics and precision medicine. Here we demonstrate such unidirectional, pumpless transport of water nanodroplets on graphene sheets patterned with hydrophilic/phobic areas inspired by natural systems. We find that spatially varying patterning of the graphene surfaces can lead to water transport at ultrafast velocities, far exceeding macroscale estimates. We perform extensive molecular dynamics simulations to show that such high transport velocities ($O(10^2 \text{ m/s})$) are due to differences of the advancing and receding contact angles of the moving droplet. This contact angle hysteresis and the ensuing transport depend on the surface pattern and the droplet size. We present a scaling law for the driving capillary and resisting friction forces on the water droplet and use it to predict nanodroplet trajectories on a wedge-patterned graphene sheet. The present results demonstrate that graphene with spatially variable wettability is a potent material for fast and precise transport of nanodroplets with significant potential for directed nanoscale liquid transport and precision drug delivery.

KEYWORDS: nanodroplets, graphene, nanofluidics, wettability gradient, wettability patterning

The structural patterning of surfaces is broadly encountered in natural systems, implying possible functional advantages for the organisms and their interactions with their environment. Nano- and microstructural and chemical surface patterns are encountered on insect bodies and plant leaves and are frequently associated with the vital functions of organisms.1,2 In turn, the interactions of natural nano/microstructures with liquids serve as inspiration for engineered surfaces meant to increase transport efficiency, liquid collection, or condensation and heat transfer of micro- and nanodroplets.3−9 A prominent example is the water-collection system of the Namib desert beetle, exhibiting surfaces exploited for water collection and directional transport.10 Experimental studies inspired by these surfaces have successfully demonstrated the water harvesting mechanisms in the microscale regime.11,12 Another example involves the structure of the vein network of the banana tree leaves, which has inspired the construction of patterned hydrophilic surfaces for microscale systems of higher heat transfer efficiency.13−15 The effect of wettability patterning on heat transfer16 was also investigated by studies that were focused on enhancing the cooling efficiency of microelectronic devices by guiding water on a hydrophilic wedge-shaped track surrounded by superhydrophobic terrains.17−19

The potential of wettability gradients for enhanced unidirectional liquid transport at the nano- and microscale has received significant attention for fast drug delivery, efficient heat transport,20,21 and electricity generation;22 such gradients are considerably easier to manufacture than other structural patterns.8 The static contact angle exhibited by water droplets on graphene is one of the common fundamental configurations for comparing experimental and computational studies and validating MD potentials.23−27 In turn, MD simulations of water droplet transport on graphene surfaces or channels with a linear wettability gradient28−30 have shown that a droplet can maintain unidirectional as well as nonlinear trajectories.28 Experimental studies have revealed the advantages of a wedge-shaped hydrophilic track for pumpless, rapid, unidirectional transport.30,31

Here, we examine graphene surfaces with patterned nanoscale wettability domains and show that such surfaces
 induce ultrafast unidirectional transport of water nanodroplets. We compute water droplet velocities of the order of $10^2$ m/s based on experimentally validated variations of surface energy corresponding to contact angles representing superhydrophobic ($\theta \geq 150^\circ$) or superhydrophilic ($\theta \approx 0^\circ$) surfaces. High transport velocities have been reported previously by few studies investigating propulsion due to chemical or large thermal gradients. Notably, the observed velocities are 2 orders of magnitude higher than the highest reported velocities of water in nanochannels and most studies featuring surface energy gradients. Our work is inspired by studies on water behavior on microscale-patterned surfaces that aimed to exploit surface patterning inspired by the Namib beetles and banana leaves.

At the nanoscale, we find that the effects of wettability differences are nonlinearly accentuated. In addition, we find
that there is a strong influence of the geometrical wettability patterning (shape and gradients) of the graphene surface on the nanodroplet transport. We evaluate the dependence of the induced transport velocities on the relative droplet size and attribute the ultrafast movement of the water droplets to the respective contact angle differences across the patterned surface. Finally, we derive a scaling law for the normalized friction coefficient of water on a graphene surface of variable wettability. We use this law to construct an analytical model describing the driving forces of the droplet motion on a wedge-patterned substrate. The analytical model is shown to predict reliably the results of the computationally intensive MD simulations. We expect that this law can be used for optimization of tapered-patterned surfaces in diverse applications, such as efficient drug delivery\cite{11} and cooling of microelectronics.\cite{18}

**RESULTS AND DISCUSSION**

We examine self-propulsion of nanodroplets on graphene surfaces patterned with the schemes shown in Figure 1. We perform MD simulations of water droplets placed on double-layer graphene, patterned either by a banded gradient scheme (Figure 1a) or a hydrophilic tapered track laid in a hydrophobic background (Figure 1b). The pattern in Figure 1a is defined by the bandwidth and wettability (each band has uniform wettability) or by the initial width and the angle of the wedge track, $\phi$ (Figure 1b). We vary the wettability of the inner zone of the wedge-shaped track, tuning it to represent a zone of hydrophilic, neutral, or hydrophobic interaction with water. The patterns are inspired by biological systems for water collection\cite{17} and directed fluid transport.\cite{15} As discussed below, the MD simulations reveal that these patterns induce motion of the water droplets with velocities up to 2 orders of magnitude higher than those observed in other nanoscale systems.\cite{37,38} We quantify the droplet transport by the position and velocity of the droplet’s center-of-mass (CoM), $P_{\text{CoM}}$ and $V_{\text{CoM}}$, and the difference ($\Delta \theta$) between the contact angles of the advancing and receding interfaces (see following sections and the Supporting Information (SI)).

**Water Droplets on Two Wettability Patterns: Uniform Gradient vs Wedge Track.** We compare the nanodroplet motion on surfaces with a uniform wettability gradient and a wedge-shaped track (Figure 1a,b, respectively). We observe two distinct behaviors characterized by markedly different values of $\Delta \theta$, as shown in the starting and final side view of each droplet over the corresponding patterned sheet (Figure 1c,d, respectively). Over the wedge-patterned surface, $\Delta \theta$ decreases steadily after the droplet settles on the surface, eventually falling below $5^\circ$ (Figure 1f). In contrast, $\Delta \theta$ remains almost constant on the uniform gradient surface (Figure 1f).

In the wedge-shaped pattern, the droplet initially accelerates nearly at the same rate as on the gradient surface, but, soon, under the resistance of interfacial friction, it decelerates; thus, its maximum attained velocity is below that on the uniform-gradient surface (Figure 1e). In the following sections, we investigate the effects of the track’s geometry on the droplet trajectory, with the aim to maximize the induced CoM droplet velocity.

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**Table 1. Values of the Interaction Strength between Water and Graphene Atoms Used in the Different Stripe Zones of the Wettability-Gradient Surface Shown in Figure 1a**

<table>
<thead>
<tr>
<th>zone</th>
<th>$\epsilon_{\text{CO}}$ [kcal/mol]</th>
<th>contact angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.05994</td>
<td>121°</td>
</tr>
<tr>
<td>2</td>
<td>0.07494</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.08994</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.10494</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.11994</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.12994</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.13864</td>
<td></td>
</tr>
</tbody>
</table>

“The most hydrophobic (zone 1) and most hydrophilic (zone 7) values of this table are the ones used for the two regions in the wedge-shaped patterned graphene surface in Figure 1b.
terminal value, whereas for the two higher values of \( \phi \), as expected. These values designate \( \theta_{\text{ext}} \) for the five cases listed. The value of \( \epsilon_{\text{CO}} \) for the inner (more wettable) zone in all cases remains constant, \( \epsilon_{\text{CO}} = 0.13864 \text{ kcal/mol} \), and corresponds to \( \theta = 51^\circ \).

### Table 2. Values of the Interaction Strength \( \epsilon_{\text{CO}} \) between Water Molecules and Graphene Atoms in the Outer Zone of the Wedge-Shaped Pattern, Denoting the Different Wedge Cases in Figure 2a

<table>
<thead>
<tr>
<th>wedge case</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>outer zone ( \epsilon_{\text{CO}} ) [kcal/mol]</td>
<td>0.03994</td>
<td>0.05994</td>
<td>0.07994</td>
<td>0.09994</td>
<td>0.11994</td>
</tr>
<tr>
<td>water contact angle ( \theta_{\text{ext}} ) [deg]</td>
<td>147</td>
<td>121</td>
<td>107</td>
<td>88</td>
<td>68</td>
</tr>
</tbody>
</table>

These values designate \( \theta_{\text{ext}} \) for the five cases listed. The value of \( \epsilon_{\text{CO}} \) for the inner (more wettable) zone in all cases remains constant, \( \epsilon_{\text{CO}} = 0.13864 \text{ kcal/mol} \), and corresponds to \( \theta = 51^\circ \).

**Figure 3.** (a) Center-of-mass (CoM) position \( P_{\text{CoM}} \) and (b) respective velocity \( V_{\text{CoM}} \) vs time for water droplets moving on graphene surfaces with a wettability gradient (black curves) and the wedge-shaped track 2 in Table 2 (red curves), using a spherical droplet equilibrated in vacuum. The graphs extend up to the point when each droplet reached the end of the substrate.

We note that the initial droplet used for all simulations in this subsection is equilibrated on a “neutral” wettable surface with \( \epsilon_{\text{CO}} = 0.09369 \text{ kcal/mol} \) and equilibrium contact angle \( \theta = 89^\circ \).

**Effect of Structural Variations of the Graphene Substrate.**

**Effect of Wettability Contrast of the Wedge Track.** The wettability contrast of the wedge-track patterned surface is critical to the droplet transport characteristics (Figure 2a). For all cases in this section, the wedge (silver-colored in Figure 1b) is hydrophilic, with a constant interaction strength \( \epsilon_{\text{CO}} = 0.13864 \text{ kcal/mol} \) that corresponds to an equilibrium contact angle \( \theta = 51^\circ \). The interaction strength \( \epsilon_{\text{CO}} \) of the outer, less-wettable zone (black-colored in Figure 1b) is varied, as shown in Table 2. The original wedge pattern, discussed in the previous section, corresponds to case 2 in Table 2. We observe that a terminal CoM droplet velocity, \( V_{\text{CoM, max}} \), is reached only for the more hydrophilic cases 3 and 4, while the velocity in case 5 peaks early and declines steadily thereafter. As expected, \( V_{\text{CoM, max}} \) declines with decreasing wettability contrast (lower \( \theta_{\text{ext}} \) or higher \( \epsilon_{\text{CO}} \)) (see Figure 2a).

**Effect of Wedge-Track Angle.** The geometry of the wedge track, and more specifically the wedge angle, \( \phi \), greatly affects the early stages of the motion of the water droplet (Figure 2b). We consider three wedge tracks with angles \( \phi = 5^\circ, 10^\circ, \) and \( 25^\circ \). We observe that the droplet CoM velocity peaks at a terminal value, whereas for the two higher values of \( \phi \) it starts to decline in a shorter time, due to extensive friction in the larger hydrophilic zone. The acceleration of the droplet rises with increasing \( \phi \), as expected.\(^{17}\) We emphasize that, for both \( \phi = 10^\circ \) and \( 25^\circ \) wedge tracks, the initial acceleration is higher than the constant-gradient pattern, although the sustained influence of the wettability gradient eventually causes the droplet on the gradient surface to move faster. Note, again, that maximum droplet speeds exceed 150 m/s. We note that in previous experimental work with millimeter-scale tracks and droplets, the track angle \( \phi \) has been limited to values well below \( 10^\circ \) due to the rapid widening of the track at high values of \( \phi.\(^{17,30}\)

**Effect of the Droplet Shape and Size. Effect of Initial Droplet Shape.** The structural characteristics of the water droplet at the instance it is brought in contact with the patterned surface have an effect on its subsequent motion (see SI Section 3.2.1 for more details). The initial behavior of a spherical water droplet that is first equilibrated in vacuum has been found to depend on the pattern of the surface it is placed on (wedge track or gradient). The water droplet structure is affected as it is lowered (by applying a constant velocity on water molecules) onto the patterned surface. The initially spherical droplet approaching the wedge-patterned surface gets readily attached to the surface, onto the hydrophilic zone at the start of the track. Even though the terminal velocity of the droplet is lower in the case of the wedge pattern, the droplet reaches the end of the wedge-patterned substrate sooner than for the straight-patterned gradient surface (Figure 3). We remark that the wedge track sets the fluid to a more vigorous motion and imparts initially higher acceleration than that observed on the gradient wettability surface. However, for the latter, the sustained influence of the wettability-gradient-induced force eventually raises the fluid velocity to levels beyond those attained on the wedge-shaped track.

**Droplet Size Effects on Wedge-Track Transport.** We equilibrate three droplets of different sizes on a neutrally wettable surface (Table 3). The geometric parameters of the wedge-patterned surfaces, i.e., wedge angle, \( \phi \), and initial width of the hydrophilic zone, are scaled according to the droplet size so that the problem remains similar for every case (Table 3). The transport characteristics of the droplets along the track are only affected by the size of the droplet (see SI Section 3.2.2 for more details). For each case, the velocity initially rises under the influence of the Laplace pressure that forces the fluid onto
the wettable track to minimize its energy. As the liquid moves to the wider portions of the track, the propelling force (due to the Laplace pressure) weakens, while the friction resistance rises. This competition results in the velocity peaking, and then declining, as the friction force keeps rising further (due to the fluid—solid contact area rising toward the wide end of the track). The variation of maximum terminal velocity with droplet size is shown in Figure 4. This trend is expected, as larger droplets have increased inertia as well as a larger contact area (i.e., higher frictional resistance) with the underlying wettable track.

Table 3. Values of the Mean Equilibration Radius \( R_{\text{equil}} \) of the Contact Interface of Water and Carbon, Number of Water Molecules, Equilibration Contact Angle \( \theta_{\text{equil}} \) and Corresponding Initial Width and Angle of the Wedge on the Patterned Surface

<table>
<thead>
<tr>
<th>case</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>no. of ( \text{H}_2\text{O} ) molecules</td>
<td>1474</td>
<td>3759</td>
<td>53331</td>
</tr>
<tr>
<td>( R_{\text{equil}} ) [Å]</td>
<td>57</td>
<td>79</td>
<td>180</td>
</tr>
<tr>
<td>( \theta_{\text{equil}} ) [deg]</td>
<td>89</td>
<td>96</td>
<td>94</td>
</tr>
<tr>
<td>track starting width [Å]</td>
<td>6.3</td>
<td>8.7</td>
<td>20.0</td>
</tr>
<tr>
<td>wedge angle ( \phi ) [deg]</td>
<td>1.6</td>
<td>2.2</td>
<td>5.0</td>
</tr>
</tbody>
</table>

\( \theta_{\text{equil}} \) here corresponds to the measured contact angle of the droplet when equilibrated prior to its release on the patterned graphene surface (see Methods section for more details).

Interfacial Friction Coefficient. We have performed a systematic study to extract the area-normalized friction coefficient of water droplets moving on surfaces of different wettabilities. This quantity is used in the following section to determine the friction force applied at the interface between the droplet and the patterned substrate. For each surface with different wettability, we apply a constant force on all water molecules and let the droplet move until the interfacial friction force between water and substrate equals the driving force (i.e., the droplet attains a steady velocity). We then correlate the steady (terminal) velocity of the droplet, \( U \), and the friction force, \( F_{\text{fr}} \), which is the pair force between water and the surface and equals the applied force at equilibrium. Plotting the friction force versus the steady terminal velocity for different values of the applied driving force (Figure 5a), we extract the friction coefficient for that surface via a linear fit of the data. The friction coefficient is defined as \( \mu = \frac{F_{\text{fr}}}{AU} \), where \( A \) is the wetted area of the substrate. Finally, collecting the results from the cases with different wettabilities, we deduce a quadratic relation between the friction coefficient and the surface wettability, as seen in Figure 5b, which can provide estimates for the friction coefficient for all wettability values over the tested range.

Analysis of Droplet Transport on Wedge-Shaped Patterned Surfaces. We now establish a simple, analytical model for the forces acting on the water droplet when it is moving on a wedge-patterned surface. We establish the driving force induced by the wettability contrast between the two zones of the wedge track, \( F_{\text{dr}} \), and the friction force between the droplet and the underlying surface, \( F_{\text{fr}} \) which hinders the droplet’s motion (Figure 6a). The propelling force \( F_{\text{dr}} \) is linearly dependent on the wettability jump \( \delta S \) along the separation line of the two zones, \( \delta S = \frac{5 \cos(\theta)}{\delta(\theta)} \), where \( \theta \) is the contact angle of each wettable region, and \( w \) defines the direction perpendicular to the separating line between the two zones. Thus, in the direction of motion, \( x, F_{\text{dr}} = 2\gamma A \delta S \sin \phi/2 \), where \( \gamma \) is the water surface tension and \( A \) the total contact area of the droplet with the substrate that contributes to the motion actuation. The wettability of the outer hydrophobic and inner hydrophilic zones is characterized by the contact angles \( \theta_A \) and \( \theta_\mu \) respectively. The friction force at the direction of the droplet’s motion is calculated as the sum of the friction forces on the two distinct zones of wettability: each force is calculated as the product of the friction coefficient of each wettability zone (\( \mu_A \) and \( \mu_\mu \) for the hydrophobic and hydrophilic zones, respectively), as described in the previous section, with the droplet-wetted area \( A \) of each zone, and the terminal velocity of the droplet, \( U \). \( F_{\text{fr}} = \mu AU \). Further details about the analytical force evaluation can be found in SI Section 4.

The input to the analytical model is the initial position and velocity of the droplet from the MD simulation results. The output of the model defines the instant acceleration of the droplet and, in turn, the instantaneous velocity and position of the droplet on the track. We compare the evolution of the velocity of the droplet along its trajectory, as calculated from the analytical model, against the velocity evolution derived from the MD simulations. We find good agreement between the simulation and the model for the three droplet sizes in Table 3 (see Figure 6b and SI Figure S7 for all three sizes). We note that the current model matches the simulation results for a section of the overall trajectory, as our analysis does not account for end effects (i.e., the force induced by the wettability jump at the start of the wedge track or for the decelerating force when approaching the right periodic end of the substrate). Our analytical estimates indicate that the observed fast pumpless transport of water droplets at the nanoscale can be observed in experimental setups involving millimeter-scale droplets (see SI Section 4).

CONCLUSIONS

We presented molecular dynamics simulations of ultrafast (~O(10^2 m/s)) transport of water nanodroplets on bio-inspired wettability patterns laid on graphene surfaces. We showed that the motion of water droplets on gradient band-wettability patterns can be rationalized by the time evolution of the difference of advancing and receding contact angles. The water droplet transport on the wedge tracks is unidirectional with a terminal speed of transport that can be enhanced by...
changing the geometry of the track. We demonstrated the advantage of the wedge-track pattern over a straight gradient wettability pattern with respect to the directionality of the droplet motion. We identified the driving mechanisms for these phenomena and formulated an analytical model that evaluates the instantaneous acceleration of the droplet and could facilitate the design of such patterned surfaces. The results of this study can further assist ongoing research on spontaneous actuation of water transport due to interfacial phenomena, crucial for high-efficiency drug delivery and ultrafast heat dissipation for nano- and microscale systems.

Given the plethora of the available nanoscale fabrication methods to generate such wettability gradients, the present study supports the feasibility of moving minute amounts of fluids with very high velocities that are not attainable with macroscopic devices.

METHODS

We perform MD simulations of water droplets placed on double-layer graphene, patterned either by a banded gradient scheme (Figure 1a) or a hydrophilic patterned track laid in a hydrophobic background (Figure 1b). The pattern in Figure 1a is defined by the bandwidth and wettability (each band has uniform wettability) or by the initial width and the angle of the wedge track, ϕ (Figure 1b). We vary the wettability of the outer zone of the wedge-shaped track, tuning it to represent a zone of neutral or hydrophobic interaction with water. The inner zone of the wedge track remains hydrophilic for all simulations. For all simulation cases, the water droplet has been equilibrated on a graphene surface with a neutral wettability. We tune the wettability of the graphene surface by modifying the value of the Lennard-Jones interaction strength (\(\epsilon_{CO}\)) between carbon and oxygen atoms.23,25 The baseline simulation setup uses a droplet of 1474 water molecules and is equilibrated on a “neutrally wettable” surface with interaction strength \(\epsilon_{CO} = 0.09369\) kcal/mol, corresponding to an equilibrium contact angle of 89°.41 All MD simulations are performed with the LAMMPS42 package. A time step of 1 fs and periodic boundary conditions are applied to all simulations. The interactions of the water molecules are modeled with the TIP4P-Ew water model43 with molecular topology constraints applied using the SHAKE algorithm.44 For short-range interactions, we use a cutoff of 1.0 nm for the pair C−O45 and a cutoff of 0.9 nm for the pair O−O.46 From a sensitivity analysis for the settings of short-range interactions on our results, we find that the end value of the CoM velocity of the droplet varies approximately 4−5% for a 10% variation of the cutoff distance (see SI Section 1.3). For the computation of long-range electrostatic interactions, we set the cutoff distance at 0.85 nm43 and we use a particle−particle particle-mesh (P3M) algorithm47 with a root-mean-squared error in the force calculation of 10−5.

Figure 5. (a) Friction force \(F_f\) versus terminal velocity for surface wettability corresponding to \(\epsilon_{CO} = 0.5994\) kcal/mol. The extracted friction coefficient \(\mu\) is analogous to the slope of the line fitting the force data. For this case, we find \(\mu = 5554\) N/(m/s)/m2. (b) Friction coefficient \(\mu\) versus surface wettability, as defined by the interaction strength \(\epsilon_{CO}\). A quadratic fit is found to describe the relation of \(\mu\) and \(\epsilon_{CO} : \mu = a\epsilon_{CO}^2 + b\epsilon_{CO} + c\), with \(a = 57696\), \(b = 5726\), and \(c = 0\). The top x-axis denotes the respective contact angle \(\theta\) values corresponding to the ticks of the wettability \(\epsilon_{CO}\) axis.

Figure 6. (a) Water-droplet transport over a graphene substrate in the direction of the velocity vector \(V_{CoM}\) under the influence of the capillary driving force, \(F_{dr}\), and the resisting friction force, \(F_f\). The contact angles designating the wettability of the outer or inner zone of the wedge track are denoted as \(\theta_A\) and \(\theta_B\), respectively, whereas the respective friction coefficients are \(\mu_A\) and \(\mu_B\). (b) Comparison of the droplet velocity evolution from MD simulations (red) and from the analytical model presented in this section (black) for a droplet with \(R_{equil} = 180\) Å (case 3 in Table 3).
The graphene atoms remain fixed for the majority of simulations, in order to eliminate further noise in the results due to phonon vibrations.\textsuperscript{46,49} We tested how the phonon excitation of the top layer of graphene would affect the results; we found that the end value of the CoM velocity of a water droplet on the graphene with the band gradient varies by 8% but only by 1.5% with the wedge pattern. We attribute this discrepancy to the spatial constraints the wedge pattern imposes on the droplet, enhancing its unidirectional translational motion (see SI Section 1.5). We tune the wettability of the graphene surface by varying the value of the Lennard-Jones interaction strength ($\epsilon_{\text{CO}}$) between carbon and oxygen atoms.\textsuperscript{25,26} Visualizations were performed with the Visual Molecular Dynamics (VMD) package.\textsuperscript{28} Postprocessing of the results has been partially performed using the MDAnalysis package.\textsuperscript{23}

We build the various-sized graphene sheets with the WCCNT package, developed within the CSELab.\textsuperscript{23} The package works within the VMD software interface\textsuperscript{25} as a TCL plugin, and it integrates different routines to generate and analyze LAMMPS-compatible files of graphene sheets (GRSs) and carbon nanotubes (CNTs) with water. Preparation of the systems, including defining the various wettability zones on the graphene sheets, was also performed with TCL scripting within the VMD package. The water droplets preparation is performed with the following procedure: For each case of droplet size, a water box is deposited on a graphene surface with the same wettability as the inner zone of the wedge track and is left to equilibrate to a droplet in an isothermal–isobaric (NVT) ensemble at 298 K for 2 ns. The equilibration is over when the measured contact angle of the droplet does not change further.\textsuperscript{41}

The majority of MD simulations are conducted with equilibrated droplets, placed on patterned GRS’s, and left to move under the influence of interfacial forces (as described in SI Section 4). For all simulations, the water molecules are kept at 298 K, with the Nose–Hoover thermostat,\textsuperscript{27} adjusting only the thermal component of temperature, which was found to be equivalent to employing an NVE ensemble.\textsuperscript{45} (see SI Section 1.4). The simulations performed in the Results section are summarized in SI Section 2. For the friction coefficient study, we apply a constant force on all oxygen atoms and let the droplet move until the interfacial friction force between water and substrate equals the driving force. We then measure the steady terminal velocity of the droplet, $U_t$, and the friction force, $F_f$. This is the pair force between water and the surface and equals the applied force at equilibrium. We extract the friction coefficient by performing a set of 6 simulations, varying the applied force on the water molecules. This is repeated for different values of surface wettability (varying the interaction strength $\epsilon_{\text{CO}}$), in order to construct the collective graph in Figure 5b. This required 24 MD simulations of 5 ns.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.9b00252.

Droplet equilibration; change of surface wettability; effect of cutoff distance of short-range interactions; effect of thermostatting; effect of phonon excitation of the top graphene layer; simulation campaign; complementary graphs for the effects of structural variations of the graphene substrate on the water droplet transport; relation of difference of hysteresis and maximum achieved velocity of the droplet; complementary graphs for the effects of the shape and size of the droplet on its transport; and analytical evaluation of forces (PDF)

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E.P., J.H.W., C.M.M., and P.K. designed the MD studies. E.P. performed the MD simulations and the analysis of the MD results. C.M.M. and P.K. coordinated the project and participated in the analysis of the results. All authors contributed to writing and editing of the manuscript.

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
This work is supported by the European Research Council Advanced Investigator Award (Grant No. 341117). We acknowledge the Swiss National Supercomputing Centre (CSCS) for computing time through project c17.

REFERENCES
(2) Ball, P. Patterns in Nature: Why the Natural World Looks the Way it Does; The University of Chicago Press: Chicago, IL, 2018.


