

Supplementary Information on “Thermally Enhanced Self-Propelled Droplet Motion on Gradient Surfaces”

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1. Gradient Preparation

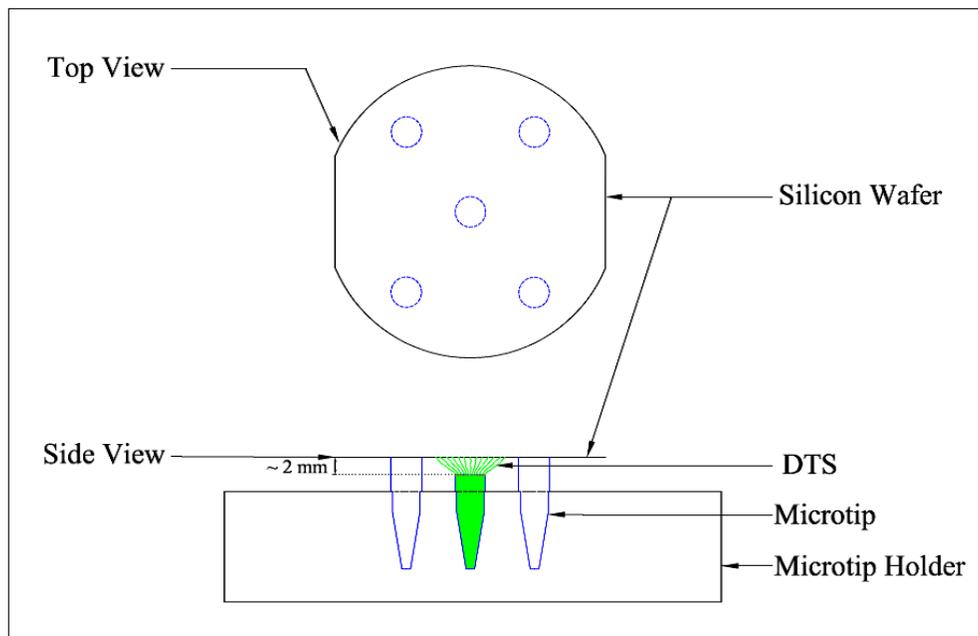


Figure S1 Schematic of gradient creation

2. Contact line description

We first aim to bring into light the subtle yet important distinctions between the underlying phenomena of ‘dynamic wetting’ and ‘droplet movement over wettability gradient surfaces’. In case of dynamic wetting, the local contact line dissipation can be explained by the usage of standard expressions for contact line velocity derived from Molecular Kinetic theory (MKT) only. In favor of this, we would like to cite the following excerpts from a recent publication in which the experimental results of dynamic wetting have been analyzed using various MKT models and parameters like ‘jump frequency’, ‘molecular displacement’ etc. *“The MKT asserts that the systematic deviation of the dynamic contact angle from its equilibrium value quantitatively reflects local energy dissipation (friction) at the moving contact line as it traverses sites of solid–liquid interaction¹”*. The connecting link in all experimental results (from a

number of experiments by different research groups) reported in the above reference is that all of those conform to dynamic wetting cases. By analyzing a series of such experiments it was shown that ‘contact line dissipation’ is adequate to account for the observable wetting phenomena. The experiments that we report herein concern not only droplet spreading due to dynamic wetting but dynamic wetting superimposed on physical ‘movement’ of the droplet. This phenomenon may be realized as a balance between the various driving and opposing forces, and cannot be attributed to contact line dissipation alone.

The evaluation of contact line velocity requires the numerical value of the static contact angle and dynamic contact angle at each location of the droplet¹ (see Equation 3, Pg.no.10134). However, the values of static contact angle cannot be evaluated at each spatial location in case of a moving droplet. Hence, extraction of the molecular or microscopic parameters for the reported experiments is not feasible. One might be tempted to evaluate these parameters by fitting various MKT models. However this might be detrimental and may not provide the actual picture as quoted from a recent reference²: *“Unfortunately, every model includes some molecular or at least microscopic parameters like the jump length, the jump frequency or the slip length which cannot be measured directly. Some numerical simulations such as the molecular dynamics are able to measure the jump frequency directly and therefore compare the fitted and measured parameter with success, but no experimental method has so far been devised to measure such quantities. Therefore, it is not straight forward to reject or accept the results of one fitting analysis.”*

We next talk about the implications of contact line hysteresis on the phenomena observed in our studies. Contact line dissipation can be manifested in the form of contact angle hysteresis or vice versa due to substrate heterogeneities. The substrates reported in our manuscript have been

prepared using diffusion controlled (from a point source) silanization of silicon wafers. Thus, the islands of silane can be classified as a well specified defect as per the following description of a ‘well specified defect’, based on the considerations outlined in Joanny and de Gennes³, wherein the authors have put forth a model for contact angle hysteresis for dealing with chemically heterogeneous and rough surfaces: *“If the chemical contaminants which create the defect were spreading from an initial point source, simple diffusion would indeed generate a Gaussian for³”* (Page no. 555); *“one could also generate the defects by chemical grafting (silanation ...) on surfaces which are accessible only at certain spots (using photoresist or photolabile film coverages and optical images to define these spots)³”* (Page no. 558). Indeed, the silane islands on the surface were accessible with varying surface coverage, which can be distinctly inferred from the microscopic images as reported in this Supplementary Information.

It is further important to note in this context that the contact angle hysteresis may be neglected if the surface coverage is minimal⁴. This has been reinstated by yet another group using AFM imaging analysis⁵. We pertinently quote here as reported in this reference: *“To address these points, we chose to study widely used model substrates, namely, silanized silicon wafers and low molecular weight ($9 < n < 12$) n-alkane droplets, therefore ensuring minimal heterogeneity and pure van der Waals interactions. We propose below an alternative description based on substrate heterogeneity according to the following scenario: Droplets are nucleated on the highest energy defects, and then grow preferentially on the most wettable areas, possibly slightly shifting their center of mass, in order to minimize the free energy. This tendency is balanced by surface tension which acts as an elastic restoring force maintaining an approximately spherical shape as observed in Figs. 2(a)–2(c). This is a case of weak heterogeneities, as discussed by Joanny and de Gennes[J. F. Joanny, P. G. de Gennes, J. Chem. Phys. **81**, 552 (1984)], where*

nearly no hysteresis is induced and fluctuations of the contact line are small at the observation scale.”

We further cite the following portion from a recently published article related to contact angle hysteresis: “It has been commonly accepted that roughness below $0.1\mu\text{m}$ has no influence on static wettability and contact angle hysteresis.”⁶ (Page No. 7160); “The theoretical description of contact angle hysteresis is complicated by the cooperative effect of long-range capillary interactions, and no simple relationship between the overall hysteresis and the energy dissipated by a single defect has been reported as yet.”⁶ (Page No. 7161)

3. Thermal Image of the Gradient Track

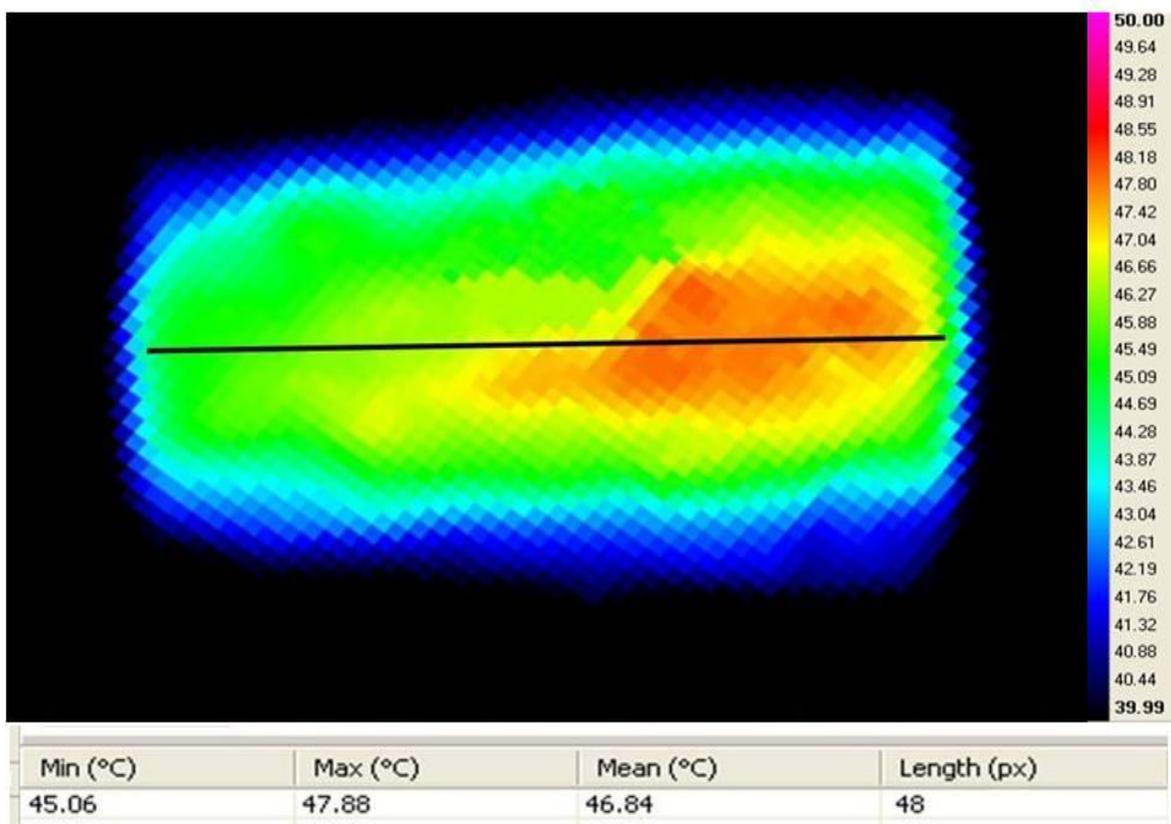


Figure S2. Thermal image of gradient track at 0.9W

4. Effect of variation of influencing parameters

Variations of the chemical coating (contact-angle and contact-angle hysteresis)

We performed additional experiments to check the variation. We varied the ratio of DTS (silane) to toluene at 1:10 , 1:5, 1:2 ,1:1 and with pure DTS. It was found that the 1:1 ratio gave the optimal wettability gradient necessary to drive droplet movement. The contact angle (advancing and receding) at each spatial location of the droplet has been characterized along with the contact angle hysteresis (experimentally).

Variation in the chemical coating may be brought about by the use of different silane apart from DTS, for eg. OTS. This will definitely lead to a different set of values of contact angles and contact angle hysteresis unique and limited to the coating in consideration. Accordingly, the numerical values of reported contact line friction will consequently undergo amendments. However, as pointed out by earlier researchers, the phenomenon reported herein will not alter qualitatively.

Variation in heating power

Effects of variation in heating power are summarized in **Table 1 & 2** of the main manuscript.

Variation in liquid viscosity and liquid thermal conductivity

The change in thermal conductivity due to change in temperature has no appreciable effect on droplet dynamics for the temperature range used herein. Appropriate viscosity values corresponding to the operating temperature has been incorporated in all calculations.

Effect of viscosity on droplet spreading on various coated surfaces has been studied previously and we cite a few relevant ones: “*Experiments of spontaneously spreading drops have been carried out through high-speed imaging (150 kfps) for different viscosities and coatings (oxide, silane, teflon) on Si wafers. The viscosity was changed by using different glycerin-water mixtures, with glycerin mass fractions of 0%, 50%, 65%, 72.5%, and 82.5%, corresponding to viscosities of 1, 6.6, 14, 31,*

and 85mPa-s, respectively. The different viscosities do not lead to any significant change in equilibrium contact angle ($\pm 2^\circ$), which was measured as $\theta_e = 20^\circ, 60^\circ, 109^\circ$ for oxide, silane, and teflon coatings, respectively⁷.(Page No. 2)

Variation in droplet volume

We have performed an extended set of experiments for droplet volumes ranging from 0.5 μ l to 7 μ l. Discernable droplet movement over the gradient surfaces even under applied local heat load was found to be in the size range of approximately 2.5-3 μ l. For droplet volumes lesser than 0.5 μ l, existing difference in the advancing and receding contact angles of the droplet could not provide necessary contact angle gradient for moving the droplets. Thus, the droplet volume of 2.5 μ l was used for all the reported experiments.

References

1. D. Duvivier, T. D. Blake, and J. De Coninck, *Langmuir*, 2013, **29**, 10132–10140.
2. D. Seveno, a Vaillant, R. Rioboo, H. Adão, J. Conti, and J. De Coninck, *Langmuir*, 2009, **25**, 13034–44.
3. J. F. Joanny and P. G. de Gennes, *J. Chem. Phys.*, 1984, **81**, 552.
4. S. Ramos and a Tanguy, *Eur. Phys. J. E. Soft Matter*, 2006, **19**, 433–40.
5. A. Checco, P. Guenoun, and J. Dailant, *Phys. Rev. Lett.*, 2003, **91**, 186101.
6. M. Ramiasa, J. Ralston, R. Fetzer, R. Sedev, D. M. Fopp-Spori, C. Morhard, C. Pacholski, and J. P. Spatz, *J. Am. Chem. Soc.*, 2013, **135**, 7159–71.
7. A. Carlson, G. Bellani, and G. Amberg, *Phys. Rev. E*, 2012, **85**, 045302.