

## Reversible Self-Propelled Droplet Movement: A New Driving Mechanism

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Reversible self-propelled movements of droplets of long chain alkanes are presented and analyzed. Slightly above the bulk melting temperature, solid alkane multilayers melt into droplets which move in a self-avoiding, random path. While moving, the droplets consume the solid alkane and leave behind a widening groove. At temperatures slightly below bulk melting this process can be reversed. Now the droplets move backwards leaving behind a narrowing solid trail which is nourished by the shrinking droplet. The speeds of the droplets are analyzed quantitatively and the melting enthalpy is identified as energetic source for their movement.

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A fascinating phenomenon in wetting research are “self-propelled” droplets [1] which are driven by unbalanced interfacial forces between their front and rear [2]. The surface energy gradient is caused by the droplets themselves when they modify chemically the surface during their temporary contact (“reactive wetting”). In all cases reported so far, the droplets serve as reservoir for the surface reactive ingredient. Thus their movement can barely be modified on-line, the moving direction is inherently irreversible, and the movement stops when the reactive ingredient is exhausted. In the following we will present a new type of self-propelled droplet movement. Its driving source is the melting enthalpy and the speed and moving direction of the droplets can be controlled externally and on-line via the sample temperature.

Long chain  $n$  alkanes ( $C_nH_{2n+2} = Cn$ ) have several special properties: (1) alkane molecules at a surface have a higher melting point than the alkane bulk material (“surface freezing”) [3,4]. (2) Liquid alkane melt does not wet its own surface-frozen monolayer. (3) Slightly below bulk melting alkanes preferentially solidify into multilayer terraces [molecules upright in all-trans configuration [5]] which coexist with droplets of undercooled alkane melt.

Our sample preparation starts with spin coating a suitable amount of alkane/toluene solution onto the substrate (=silicon wafers [6], i.e., an interface between air and  $SiO_2$ ) and heating the sample well above bulk melting. Upon lowering the temperature, slightly above the bulk melting point, a closed, “surface-frozen” monolayer forms at the  $SiO_2$  surface. On top of this solid monolayer, the excess alkane dewets into liquid alkane droplets. Upon lowering the temperature further to slightly below the bulk melting point, a nucleation barrier impedes bulk solidification. Instead, the excess alkane from the liquid droplets spreads out and forms terraces of solid mono- and multilayer on top of the surface-frozen layer [5]. This topography—solid terraces which partially cover the closed surface-frozen monolayer on the  $SiO_2$  surface—is the starting point for the creation of receding and advancing droplets presented and analyzed in the following. For typical droplet dimensions and speeds, both Bond (Bo)

and Reynolds numbers (Re) were  $\ll 1$  ( $Bo = \rho g R^2 / \gamma = 4 \times 10^{-5}$ ,  $Re = \rho v R / \eta = 10^{-2}$ , for  $\rho = 10^3 \text{ kg/m}^3$ ,  $R = 10^{-5} \text{ m}$ ,  $\gamma = 25 \times 10^{-3} \text{ N/m}$ ,  $\eta = 10^{-3} \text{ Ns/m}^2$ ,  $v = 10^{-3} \text{ m/s}$ ). Gravitational and inertial effects can be neglected. The sample topography was investigated via reflection optical microscopy with monochromatic light ( $\approx 500 \text{ nm}$ ). Silicon wafers with thick  $SiO_2$  layers ( $\approx 300 \text{ nm}$ ) generate sufficient contrast to visualize thickness steps of less than one monolayer ( $\approx 4 \text{ nm}$ ).

Figure 1 shows a sample whose  $SiO_2$  surface is completely coated by a “surface-frozen” monolayer. The surface is also covered partially by an additional solid monolayer with a few liquid droplets on top. These stationary droplets are typical leftovers from the preparation history [5] and not essential for the creation and properties of the moving droplets. Above a critical temperature,  $T_{adv}^{crit} = T_b + \Delta T_{adv}^{crit}$  ( $T_b$  = bulk melting temperature,  $\Delta T_{adv}^{crit} \approx 0.4 \text{ }^\circ\text{C}$ ), small droplets appear [7] at the steps between the areas covered with the monolayer and those areas covered only by the surface-frozen layer [8]. The droplets move “through” the monolayer area in a random, self-avoiding path and cut widening grooves. Obviously the droplets “consume” the solid alkane on their way [9]. At the terrace edges they are “reflected.” Each frame of Figs. 1 and 2 shows the paths of moving droplets within 40 ms, seg-

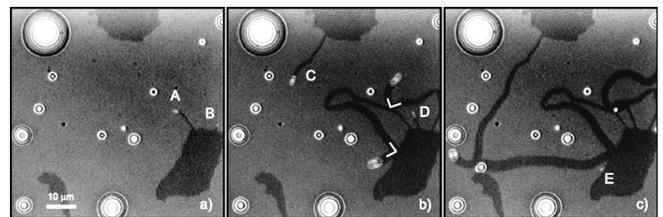


FIG. 1. Moving droplets (A, B, C, D, E) “eating” into a monolayer of C30 (brighter areas) on top of a surface-frozen monolayer at  $T \approx 0.4 \text{ }^\circ\text{C}$  above bulk melting. The dark spots are defects/dust on the CCD chip. The moving droplets appear elongated due to the stroboscopic illumination. In frame (b) ( $\Delta t = 0.8 \text{ s}$ ) the reflections of the paths at terrace edges are marked. In (c) ( $\Delta t = 1.3 \text{ s}$ ), droplets A and D are trapped and do not move any more.

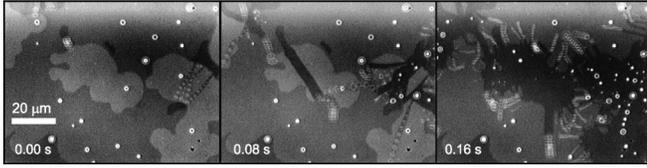


FIG. 2. Droplets of C24 moving into bilayers (bright gray) and monolayers (medium gray) on top of the surface-frozen monolayer (dark gray). During the imaging the temperature is increasing continuously. Stroboscopic illumination (10 flashes per frame).

mented into 10 steps due to a 250 Hz stroboscopic illumination in phase with the video recording (25 fps).

If there are terraces of different thicknesses, droplets appear first at the thicker edges and move first into the thicker solid terraces (Fig. 2) [10]. The critical temperature for the appearance of droplets at multilayer edges is  $T_b + (1/n)\Delta T_{\text{crit}}^{\text{adv}}$  ( $n = \text{number of layers}$ ). The droplets also move faster through thicker than through thinner layers.

The droplet speeds are proportional to  $T - T_b$  and increase with the terrace thickness (Fig. 3). They are, however, independent from the droplet size and the number of solid alkane layers underneath the moving droplets. For instance, droplets cutting a groove into a monolayer directly on top of the surface-frozen monolayer move like droplets consuming a monolayer on top of solid multilayers plus the surface-frozen monolayer.

The data of Fig. 3 can be unified into one master curve (Fig. 4):

$$U^* = \beta(T - T_{\text{adv}}^{\text{crit}}) \quad (1)$$

with speeds and critical temperatures rescaled:  $U^* = (1/n)U$ ,  $T_{\text{adv}}^{\text{crit}} = T_b + (1/n)\Delta T_{\text{adv}}^{\text{crit}}$  ( $\beta \approx 10^{-3} \text{ ms}^{-1} \text{ K}^{-1}$ ), i.e.:

$$U(n, T) = n\beta(T - T_b) - \beta\Delta T_{\text{adv}}^{\text{crit}} \quad (2)$$

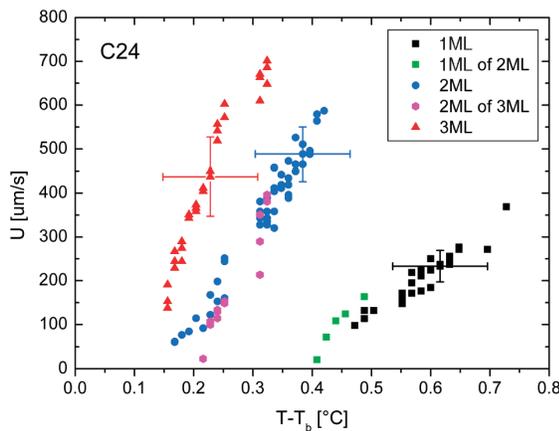


FIG. 3 (color). Velocity vs temperature for droplets melting into monolayers (1 ML), bilayers (2 ML), and three melting layers (3 ML) of C24 directly on top of the surface-frozen layer. Data indicated with 1 ML of 2 ML and 2 ML of 3 ML represent droplets melting into monolayers and bilayers on top of a plateau of 1 monolayer plus the surface-frozen layer, respectively.

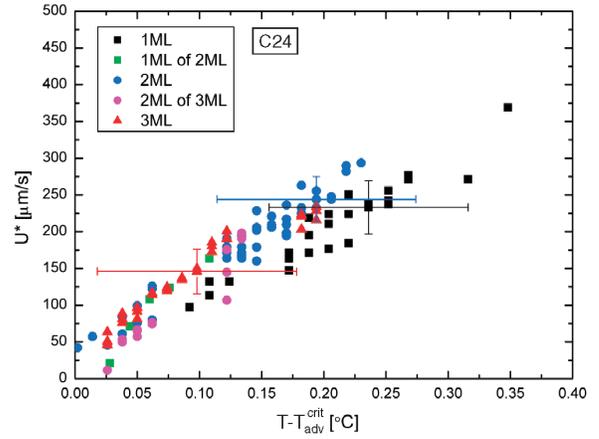


FIG. 4 (color). Unified plot of the data from Fig. 3 with a rescaled speed  $U^* = U/n$  and  $T_{\text{adv}}^{\text{crit}} = T_b + (1/n)\Delta T_{\text{adv}}^{\text{crit}}$  (with  $\Delta T_{\text{adv}}^{\text{crit}} = 0.38^\circ \text{C}$ ). As in Fig. 3 the error bars indicate absolute reproducibility. The relative temperature error within one measurement series is significantly smaller.

(valid only for  $U > 0$ ). Figure 5 explains the findings, in particular, the relation between droplet speed and the number of melting layers. Moving droplets touch on one side a solid alkane surface without the terrace. On the other side they contact the solid terrace. If this solid terrace melts at the perimeter “ahead” of the droplet it will create a local curvature whose capillary pressure will push the droplet towards the melting front. This quasi-two-dimensional tension originates from the melting enthalpy with:  $\gamma_{\Delta H} = n\Delta s(T - T_b)$  [as approximation,  $\Delta s$ , the specific entropy of melting per solid layer and area, is assumed identical for all (melting) layers]. When the droplet moves, a viscous drag,  $\gamma_{\text{vis}} = \alpha\eta U$ , arises ( $\eta = \text{viscosity}$ ,  $\alpha = \text{geometrical factor}$ ). At constant speed all components balance each other:

$$\gamma_{\text{SV}} + n\Delta s(T - T_b) = \gamma_{\text{LV}} \cos\theta + \gamma_{\text{SL}} + \alpha\eta U. \quad (3)$$

The droplet speeds are independent from size because both the driving force  $\gamma_{\Delta H}$  and the viscous drag increase approximately linearly with the droplet perimeter [11].

With  $\Delta s = \alpha\beta\eta$  one recovers from Eq. (3) the experimental findings [Eq. (2)]:

$$U(n, T) = n\beta(T - T_b) + \frac{1}{\alpha\eta}[\gamma_{\text{SV}} - (\gamma_{\text{LV}} \cos\theta + \gamma_{\text{SL}})]. \quad (4)$$

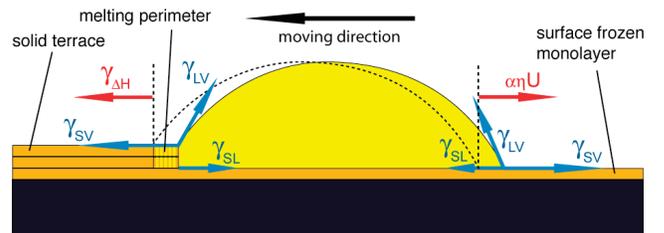


FIG. 5 (color). Forces acting on advancing droplets.

This reveals the origin of the temperature offset  $\Delta T_{\text{crit}}^{\text{adv}}$  ( $S_v =$  “moist” spreading coefficient):

$$\begin{aligned} \Delta s \Delta T_{\text{adv}}^{\text{crit}} &= -[\gamma_{SV} - (\gamma_{LV} \cos\theta + \gamma_{SL})] \\ &\cong -\left(S_v + \frac{1}{2} \gamma_{LV} \Theta^2\right) \quad (\text{for } \Theta \ll 1). \end{aligned} \quad (5)$$

In agreement with the current understanding of dynamic wetting, for the temperature range  $T_b < T < (1/n)\Delta T_{\text{crit}}^{\text{adv}}$ , all the free energy release due to melting alkane is burned in the thickening/spreading of a precursorlike film on top of the terraces and at the terrace edges. The existence of such a molecularly thin film has just recently been proven for this system [5]. At  $T = (1/n)\Delta T_{\text{crit}}^{\text{adv}}$ , the liquid alkane film is thick enough (most likely at the terrace edge where the droplets appear). It destabilizes into bulges and forms the droplets [8] [see also Gau *et al.* [12]]. The critical temperature is analogous to the critical angle of inclination for drops sliding down a tilted surface [13] which is also explained with the burning of free energy in molecular adsorption/desorption processes near the contact line and in a precursorlike film.

Our explanation agrees with another observation. If liquid droplets, which sit on top of solid terraces (remnants of the preparation history), are heated to slightly above  $T_{\text{adv}}^{\text{crit}}$ , usually the solid underneath does not melt and the droplet shape remains largely unchanged (see Figs. 1 and 2). In rare cases, however, the solid underneath melts, and the released melting enthalpy translates into a surface tension as described above. Yet, without additional disturbances [14], these droplets do not move because the tension acts all around the perimeter. Instead, the droplet flattens (Fig. 6). Thus  $\gamma_{LV} \cos\theta$  can be measured directly from the contact angle behavior  $\Theta(T)$  and compared to the predictions from Eq. (3):

$$\frac{\partial}{\partial T}(\gamma_{LV} \cos\theta) = n \cdot \Delta s. \quad (6)$$

With literature values [15] for C30 ( $\Delta H = 16 \times 10^4$  J/kg,  $\rho = 900$  kg/m<sup>3</sup>,  $d_{\text{monolayer}} = 4.2$  nm) one obtains  $\Delta s \approx 1.7 \times 10^{-3}$  Nm<sup>-1</sup> K<sup>-1</sup> in agreement with  $1.8 \times 10^{-3}$  Nm<sup>-1</sup> K<sup>-1</sup> derived from  $\Theta(T)$ .

The droplet movement can be reversed. Droplets, which simultaneously contact terraces of different heights, may start a receding movement if they are cooled below a certain threshold temperature  $T_{\text{rec}}^{\text{crit}} = T_b - \Delta T_{\text{rec}}^{\text{crit}}$ . Figure 7 shows an area with solid terraces up to 6 monolayers thick [16]. Prior to recording Fig. 7(a), the sample had been heated above  $T_{\text{adv}}^{\text{crit}}$  for a short time. Thus several advancing droplets together with their grooves were created. Figure 7(a) presents the situation after the sample has been cooled to below  $T_{\text{rec}}^{\text{crit}}$  for a short period of time. Receding droplets (A, B, C) have already left behind a trail of solid alkane (dashed lines). The receding movement continues in Fig. 7(b). In Fig. 7(c), droplet C “bumps” into the terrace edge and stops moving. In Fig. 7(d), B is “trapped” by the trail of A and also stops moving. As

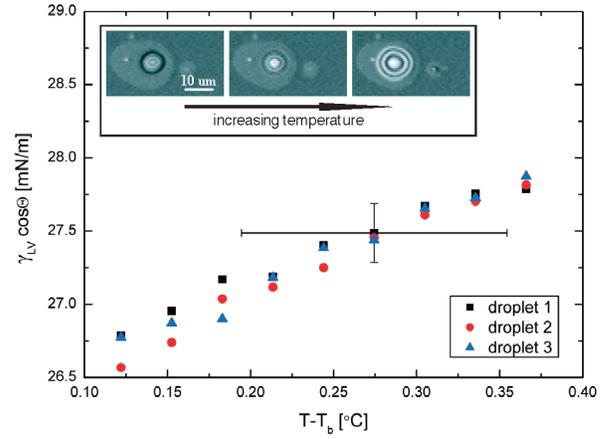


FIG. 6 (color). Temperature variation of the contact angle of three nonmoving droplets which melt into a terrace three monolayers thick. The contact angle changes from  $\approx 23$  deg at  $\square_b$  to  $\approx 11$  deg at  $\square_b + 0.4$  °C. Thus  $\Delta s \approx 1.8 \times 10^{-3}$  Nm<sup>-1</sup> K<sup>-1</sup> with  $\gamma_{LV}(T_b) = 28.6$  mN/m. The temperature error bar indicates absolute errors. Relative errors (relevant for  $\Delta s$ ) are smaller.

soon as they stop moving, droplets start to grow a solid terrace at their perimeter (barely visible with C because it is so small). Usually, receding droplets leave behind a solid trail as thick as the terrace edge from which they started. Solid terrace edges of any height are barriers and reflect or stop the movement. During the movement the liquid alkane from the droplet is fed into the solid trail; the droplet volume decreases during the movement. Up to now, only receding droplets creating traces at least three layers thick were observed.  $|\Delta T_{\text{rec}}^{\text{crit}}|$  is similar to  $|\Delta T_{\text{adv}}^{\text{crit}}|$ .

Receding droplets are harder to observe than advancing droplets because they “compete” with the terrace growth out of nonmoving droplets [5]. Both phenomena occur in the same temperature range (terrace growth can even occur already between  $T_b$  and  $T_{\text{adv}}^{\text{crit}}$ ) and the terrace growth will stop the receding droplet movement [17]. Receding droplets are best observed if a sample with advancing droplets is cooled quickly from above  $T_{\text{adv}}^{\text{crit}}$  to slightly below  $T_{\text{rec}}^{\text{crit}}$ . Thus the starting conditions (droplet contacting simultaneously terraces of different heights) and the running conditions ( $T < T_{\text{rec}}^{\text{crit}}$ ) for receding droplets are met. Terrace growth is suppressed if cooling between  $T_b$  and  $T_{\text{rec}}^{\text{crit}}$  is fast enough. Though too much cooling to only a few 0.1 °C below  $T_{\text{rec}}^{\text{crit}}$  will stop any droplet receding and circular terraces will grow from the halted droplets.

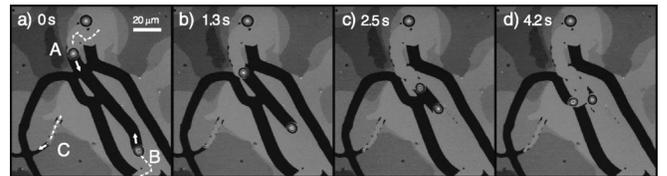


FIG. 7. Receding droplet movement. The solid terraces have thicknesses of up to 6 monolayers (C24). For details, see main text.

We assume that, as for the advancing case, the energetic source for the droplet receding is the melting enthalpy. However, the driving mechanism is probably different. There is no capillary force because the solid terrace grows into (underneath) the liquid droplet. The movement may be driven by surface energy differences between back and front [18]. Alternatively, edge effects from the transition between solid terrace and substrate or flows within the droplet caused by density differences between solid and liquid may move the droplets.

In conclusion, we present experimental observations and an analysis of reversible self-propelled droplet movements of long chain alkanes at solid/gas interfaces near the alkane bulk melting temperature. Above bulk melting, liquid droplets advance into the solid alkane film leaving behind (widening) grooves. Below bulk melting, the droplets move backwards, leaving behind a (narrowing) trail of solid alkane. Material conservation suggests an alkane exchange between droplets and grooves (advancing), or droplets and trails (receding), respectively. The droplet speed is proportional to the temperature and the terrace thickness. We propose that the melting enthalpy is the energetic source for the droplet movement. The driving force is counterbalanced by viscous dissipation leading to constant droplet speeds at fixed temperatures. The observed temperature offset (activation barrier) for the appearance of the droplets and start of their movement is attributed to energy dissipation in a precursorlike film at the sample surface. With these assumptions the experimental data from the advancing droplets could be rescaled into one master curve. The explanation is also in quantitative agreement with contact angle measurements.

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- [6] Glass or mica substrates show similar results.
- [7] See EPAPS Document No. E-PRLTAO-95-055538. The movie to Fig. 1 is presented as EPAPS document Adv,Mono,C30.mp4. This document can be reached via a direct link in the online article's HTML reference section or via the EPAPS homepage (<http://www.aip.org/pubservs/epaps.html>).
- [8] The droplet appearance can be explained as a nucleated process. A critical radius  $r_{\text{crit}}$  of nucleation of these droplets can be estimated by assuming partially wetting droplets on a planar solid alkane surface with a contact angle of  $20^\circ$  (derived from the interference rings of the droplets). With bulk values [ $\gamma_{LV} = 29$  mN/m,  $\Delta H(\text{C}_{36}\text{H}_{74}) = 173$  kJ/kg] [15] this yields a reasonable  $r_{\text{crit}} \approx 0.1$   $\mu\text{m}$  for  $\Delta T \approx +0.4$   $^\circ\text{C}$ .
- [9] The increase of the droplet volume, the terrace thickness, and the widening of the grooves is consistent with mass conservation.
- [10] See the file Adv,Multi,C36.mp4 in Ref. [7], which shows a similar situation as in Fig. 2 but for a different chain length (C36).
- [11] As an approximation the viscosity is assumed as constant. Within the investigated temperature range the viscosity changes much less as to account for the dramatic increase in droplet speeds. A temperature variation of the viscosity also cannot explain the dependence of the speed on the number of melting layers. A combination of temperature-dependent viscosity plus melting enthalpy results in a behavior [ $U \propto (T - T_b)^2$ ] inconsistent with the experimental results.
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