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# Reactive Leidenfrost droplets

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**Abstract** – We experimentally investigate the reactivity of Leidenfrost droplets with their supporting substrates. Several organic liquids are put into contact with a copper substrate heated above their Leidenfrost temperature. As the liquid evaporates, the gaseous flow cleans the superficial copper oxide formed at the substrate surface and the reaction maintains a native copper spot below the evaporating droplet. The copper spot can reach several times the droplet size for the most reactive organic compounds. This study shows an interesting coupling between the physics of the Leidenfrost effect and the mechanics of reactive flows. Different applications are proposed such as drop motion tracking and vapor flow monitoring.

1 In spite of its discovery more than two centuries ago [1],  
2 the Leidenfrost effect is still the subject of numerous ap-  
3 plied and fundamental researches. One can note the recent  
4 studies concerning the effect of an electric [2] or a magnetic  
5 field [3] on these droplets and the studies concerning the  
6 directed motion on structured surfaces [4, 5]. The unex-  
7 pected take-off of sub-millimetric Leidenfrost droplets has  
8 been also examined [6] and different theoretical analysis  
9 are now proposed to understand this phenomenon [7, 8].

10 Linking the Leidenfrost effect and chemistry has re-  
11 cently brought out the possibility to use droplets in cale-  
12 factation as micro-reactors giving rise to a new nanofab-  
13 rication method [9]. Already in his seminal paper [10],  
14 Boutigny dedicated a whole chapter to the specific chem-  
15 ical properties of Leidenfrost droplets. He made experi-  
16 ments with acid droplets that react strongly with metallic  
17 substrates. While he expected an increase of the oxida-  
18 tion rate as the temperature was increased, the reactiv-  
19 ity suddenly dropped when the temperature reached the  
20 Leidenfrost temperature of the acid due to the vanishing  
21 contact between the acid and the substrate.

22 In this letter we present a first attempt to induce a  
23 chemical interaction between a Leidenfrost droplet and  
24 the substrate on which it is standing. We experimentally  
25 show that the vapor escaping from a Leidenfrost droplet  
26 can react with the supporting substrate. To summarize,  
27 above a critical temperature, the vapor flow acts as a re-  
28 ducing agent and reacts with the copper substrate initially  
29 superficially oxidized. This leads to the formation of a

30 native copper spot that persists as long as the droplet is  
31 not evaporated. This effect was observed for several or-  
32 ganic liquids and the critical reaction temperatures are  
33 measured. A redox mechanism is proposed and the obser-  
34 vations are related to the reducing properties of the liquid.  
35 The spot size is comparable to the one of the droplet but  
36 can become very large with chemical compounds such as  
37 ethylene glycol. Finally, applications are given such as the  
38 surface cleaning, the tracking of a droplet on an inclined  
39 substrate and the monitoring of the vapor flow on a tex-  
40 tured surface.

## 41 **Experiments.** -

42 The experimental set-up consists of a hot plate on which  
43 a copper substrate is deposited. The copper substrate is  
44 sandblasted before any experiment to ensure an homoge-  
45 neous surface roughness. The substrate temperature is  
46 measured and controlled through a PT100 temperature  
47 sensor coupled to the heating system. The temperature  
48 in our range (200-500°C) is sufficiently high for an oxide  
49 copper film to form on the native copper substrate. For  
50 instance, it takes a few minutes for the oxide to form on a  
51 copper substrate heated at  $T = 380^\circ\text{C}$ . Images are taken  
52 using a high speed camera at a frame rate standing be-  
53 tween 5 and 1000 frames per second. Drops are deposited  
54 on the substrate and they levitate on their own vapor.  
55 They are maintained in place through the contact with a  
56 small capillary (Fig. 1).

57 Several organic liquids are tested: ethanol, isobutanol,  
58 isopropyl alcohol, tert-butyl alcohol, ethylene glycol and

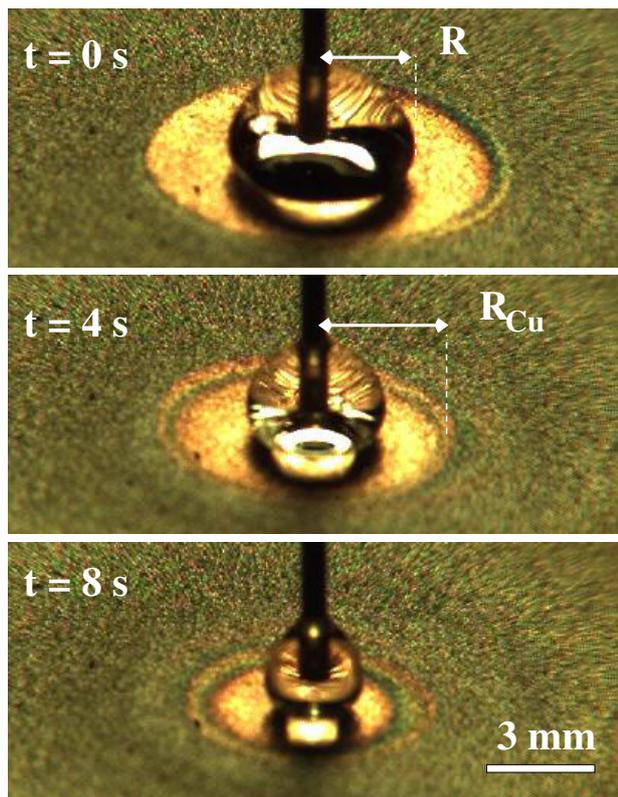


Fig. 1: (Color on-line) Evaporation of an ethanol Leidenfrost droplet of radius  $R$  standing on a copper substrate. The substrate is initially oxidized and appears dark. The radius of the native copper spot below the droplet is denoted  $R_{Cu}$ .

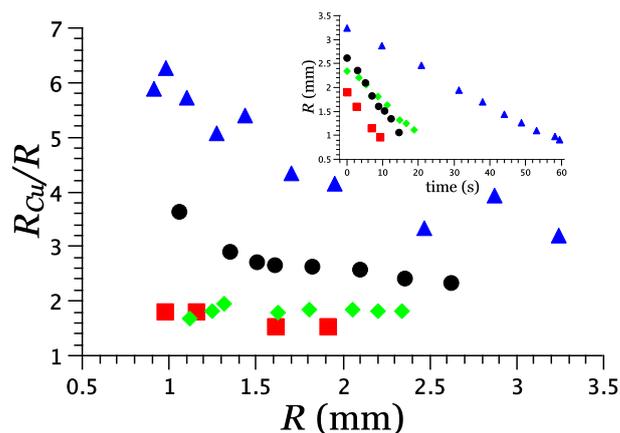


Fig. 2: (Color on-line) Ratio  $R_{Cu}/R$  as a function of  $R$  for droplets of ethanol (green diamonds), isobutanol (red squares), isopropyl alcohol (black dots) and ethylene glycol (blue triangles). The temperature of the substrate is fixed at  $380^\circ\text{C}$ . Insert:  $R$  as a function of time for the same dataset. The origin of time is taken arbitrarily as the first measurement time.

the supplementary material (Movie1.avi): under nitrogen atmosphere a cross is drawn by guiding an ethanol drop with the capillary. The cross remains as long as the nitrogen flux is maintained. When the latter is removed, the substrate is re-oxidized and the colored fringes are momentarily observed before the cross totally disappears.

To quantify the phenomenon we measure both  $R$  and  $R_{Cu}$  as a function of time (insert of Fig. 2) for experiments performed on different liquids and for a substrate heated at a fixed temperature  $T = 380^\circ\text{C}$ . We plot in Fig. 2  $R_{Cu}/R$  as a function of  $R$ . The value of this ratio strongly depends on the liquid used. The larger ratios are obtained for ethylene glycol (Fig. 3) while the lower values are observed for ethanol and isobutanol droplets. For two liquids (ethylene glycol and isopropyl alcohol) the ratio  $R_{Cu}/R$  is a decreasing function of  $R$  while for the two other liquids (ethanol and isobutanol) this ratio seems to be quite constant.

The critical reaction temperature  $T_c$  defined above strongly depends on the liquid. To measure  $T_c$  we slowly increase the temperature of the substrate until the reaction is observed. During this procedure droplets of the same size, roughly 1 mm in radius, are deposited on the substrate. The critical temperature measurements are reported in Table 1.  $T_c$  is always smaller than  $300^\circ\text{C}$  for the primary and secondary alcohols: we found between  $200$  and  $250^\circ\text{C}$  for ethanol, isobutanol and isopropyl alcohol, and the critical temperature for the ethylene glycol is smaller than  $250^\circ\text{C}$  and could not be measured since the Leidenfrost effect begin to disappear below this temperature. For the tert-butyl alcohol and the acetone, the reaction initiates at larger temperatures and develops over a temperature range  $[T_c^{min}, T_c^{max}]$ . At  $T_c^{min}$ , the reaction is

59 acetone. For almost all of them, from the Leidenfrost tem-  
 60 perature to a higher critical temperature the droplet lev-  
 61 itates on the substrate without any visible effect on the  
 62 substrate. Above this critical temperature, a reaction is  
 63 observed and a spot of native copper of radius  $R_{Cu}$  appears  
 64 below the droplet of radius  $R$  (Fig. 1). We note that the  
 65 reaction is different from a complete copper-catalyzed ox-  
 66 idation [11]: it does not emit any radiation in the visible  
 67 range and is not inhibited by working under oxygen-free  
 68 conditions (nitrogen atmosphere). As expected due to the  
 69 droplet evaporation,  $R$  decreases with time (insert of Fig.  
 70 2). We observe that  $R_{Cu}$  decreases too. This suggests that  
 71  $R_{Cu}$  results from an equilibrium between the copper oxida-  
 72 tion rate occurring naturally and the copper oxide reduc-  
 73 tion rate due to the reactive Leidenfrost vapor flow. Col-  
 74 ored fringes found in the vicinity of the native copper spot  
 75 give an indication about the copper oxide film thickness  
 76 resulting from the equilibrium between the two reactions  
 77 (Figs. 1 and 4). Once the droplet is totally evaporated, the  
 78 native copper spot disappears and the superficial copper  
 79 oxide layer covers all the substrate again. Working under  
 80 oxygen-free conditions prevents the substrate re-oxidation  
 81 and maintains the native copper aspect where the reaction  
 82 occurred. This point is illustrated in one movie given in

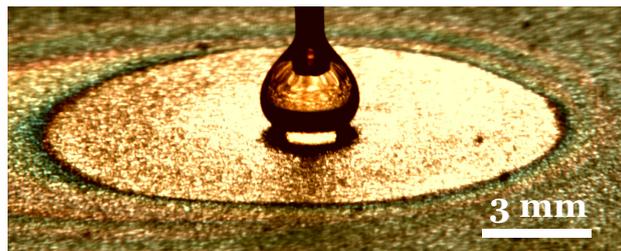


Fig. 3: (Color on-line) Evaporation of an ethylene glycol Leidenfrost droplet.

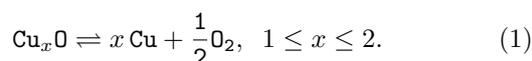
initiated but only a tiny spot is observed that corresponds to the colored fringes of the oxide film. Only for the temperatures larger than  $T_c^{max}$  the reaction is strong enough for the native copper of the substrate to be observed.

### Redox mechanism. -

We propose a heterogeneous redox mechanism to account for the chemical reaction. Copper oxides form redox couples with native copper (redox potentials  $E^0(Cu^+/Cu_{(s)}) = +0.52$  V and  $E^0(Cu^{2+}/Cu_{(s)}) = +0.34$  V), while primary and secondary alcohols are reducing agents with redox potentials around -0.20 V in standard conditions. The copper oxides-alcohols reactions are thermodynamically favored (but slow) at 25°C and we expect a larger reaction rate for increasing temperatures, which we observe.

Modeling the ratio  $R_{Cu}/R$  and the different values measured between the several chemical compounds is beyond the scope of the article. This is not obvious because it would require to precisely describe the exact shape of the flow field around the droplet and its chemical composition, a difficult task due to the mixing of the reactive vapor with the surrounding air. We have measured the evaporation rates for the alcohols analyzed in Fig. 2 (Tab. 1). We noticed that the largest copper spots were obtained for the least volatile chemical compound. This suggests that the reactivity with the substrate is probably the important parameter to understand the differences between the several organic species.

*Inorganic redox species.* Metal oxides may be used as oxygen carriers for the controlled redox reactions of simple organic species [11] to their possibility of chemical looping combustion with a view to achieve the sequestration of the produced carbon dioxide (see [12,13] for a review and current developments). Actually, the copper surface is a mix of copper(I) oxide ( $Cu_2O$ ) and copper(II) oxide ( $CuO$ ) that can produce some *adsorbed* oxygen species as:



*Oxidizing the organic species.* None of our tested compounds may carry out a direct spontaneous oxidation by gaseous  $O_2$ . So, in all cases, we consider only the first possible reaction of the species by the adsorbed oxygen, since we expect the partial pressure of the formed species

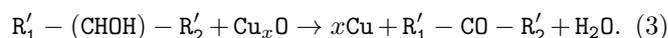
to vanish under the action of the natural convection. After that first reaction, a layer of copper is formed on the surface.

For a primary alcohol  $R_1 - CH_2 - OH$  ( $R_1 = CH_3$ : ethanol,  $R_1 = (CH_3)_2 - CH$ : isobutanol,  $R_1 = HO - CH_2 -$ : ethylene glycol), we have the formation of an aldehyde function as

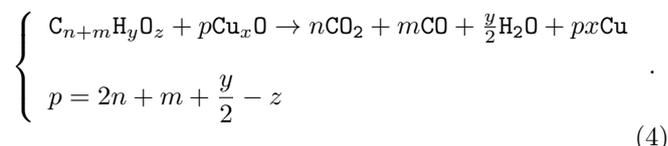


The loss of one molecule of water make this reaction very irreversible.

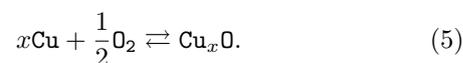
Analogously, for a secondary alcohol  $R'_1 - (CHOH) - R'_2$  ( $R'_1 = R'_2 = CH_3$ : isopropyl alcohol), we have the corresponding formation of a ketone function as



Unfortunately, the produced quantities are too small to allow specific characterizations, and devising a setup to trap the emitted vapour is far beyond the scope of this article. Moreover all the classical tests for carbonyl compounds would not stand the high temperature copper vicinity. For terbutanol and acetone, an oxidation occurred but at much higher temperature, with indicates that some minor or major organic skeleton changes are involved. Indeed, we could think of a possible dehydration/oxidation of terbutanol into epoxy-isobutylene, or the oxidation of the acetone *à la* Bayer-Villiger into methyl-ethyloate. Nonetheless, the temperature increase is quite significant, which indicates that the following generic oxidative degradation occurs



*Copper oxides regeneration.* If some dioxygen is available, the fresh copper layer shall be readily oxidized by the inverse reaction of (1)



For usual metal or metal-oxide catalyzed reactions we expect the released enthalpy to overheat the solid substrate (up to a glowing state), but here the heat is dissipated by convection. Inversely, if no oxygen is present, then the copper should remain visible, up to its diffusion inside the oxide layer.

### Applications. -

As seen previously, the reactive Leidenfrost effect emphasizes a simple way to clean locally, at the drop scale, the surface of a substrate (Movie1.avi in the supplementary material). This effect might be used to track droplet trajectories as well. As an example we followed the motion of an ethanol droplet on an inclined copper substrate

Chemical compound	Leidenfrost T (°C)	$T_c$ (°C)	Evaporation rate (mol/s)
ethanol $\text{CH}_3\text{CH}_2\text{OH}$ (I)	$136 \pm 5$	$245 \pm 5$	$(5.5 \pm 0.5) \cdot 10^{-5}$
isobutanol $(\text{CH}_3)_2\text{CHCH}_2\text{OH}$ (I)	$167 \pm 5$	$245 \pm 5$	$(5.1 \pm 0.7) \cdot 10^{-5}$
ethylene glycol $\text{HOCH}_2\text{CH}_2\text{OH}$ (I&I)	$240 \pm 5$	$\leq 250$	$(3.1 \pm 0.2) \cdot 10^{-5}$
isopropyl alcohol $\text{CH}_3\text{CHOHCH}_3$ (II)	$138 \pm 5$	$205 \pm 5$	$(6.5 \pm 0.7) \cdot 10^{-5}$
tert-butyl alcohol $\text{HOC}(\text{CH}_3)_3$ (III)	$140 \pm 5$	465 – 485	
acetone $(\text{CH}_3)_2\text{CO}$	$120 \pm 5$	300 – 385	

Table 1: Leidenfrost temperatures, critical reaction temperatures  $T_c$  and evaporation rates for several chemical compounds. I/II/III refer to primary/secondary/tertiary alcohols respectively. Evaporation rates are obtained from the data of Fig. 2 around a radius  $R = 2\text{mm}$  and assuming spherical droplets: for each chemical compound, the volumetric flow rate is converted into the amount of substance flow rate using the molar mass of the compound and its liquid density at the boiling temperature.

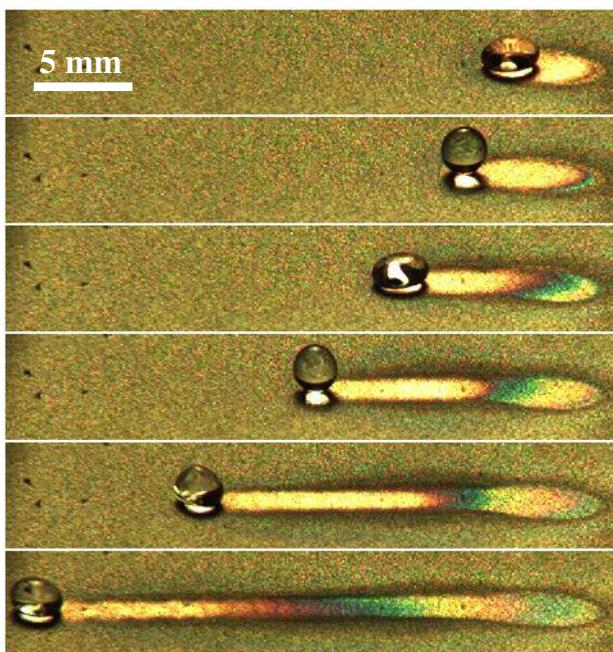


Fig. 4: (Color on-line) Motion of an ethanol Leidenfrost droplet on an inclined plane. The time interval between each picture is of 100 ms. The average sliding velocity between the first and last images is of 50 mm/s while the persistence time of the chemical pattern is of a few seconds.

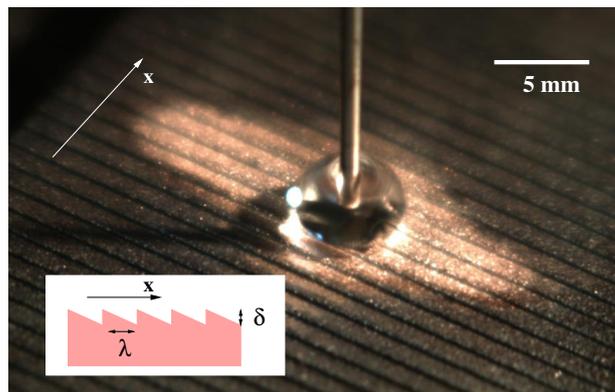


Fig. 5: (Color on-line) Ethanol Leidenfrost droplet standing on a textured copper substrate. The white arrow indicates the direction of the driving force, or equivalently, of the drop motion if the drop is not held by the capillary. Insert : sketch of the ratchet surface.

$x$  direction in Fig. 5) [4]. The origin of the driving force has been intensively studied in the recent years and several theoretical analyses have been proposed. In all of them the role of the rectified vapor flow by the asymmetric teeth of the ratchet is emphasized [14, 15]. To observe this, we manufactured a textured copper substrate as sketched in the inset of Fig. 5 with the values  $\lambda = 1.2\text{ mm}$  and  $\delta = 0.2\text{ mm}$ . An ethanol droplet is deposited on the substrate and is maintained by a capillary to prevent its motion. We observe that the native copper spot is not isotropic but extends more significantly in the direction of the ratchet features (perpendicular to the driving force direction  $x$ ). This is coherent with the hypothesis that most of the flow is evacuated in the direction perpendicular to the one of the driving force [15].

#### Conclusion, perspectives. -

In this article, we have observed and characterized a reactive Leidenfrost effect and some applications. This phenomenon opens a new route to couple thermodynamics, hydrodynamics, capillarity and chemical reactions. In our case it deals with organic liquid droplets standing on a copper substrate. We can easily imagine that such effect

158 heated at  $T = 450^\circ\text{C}$ . The inclination of the substrate is of  
 159 a few degrees and we use a high speed camera at a frame  
 160 rate of 1000 fps. Six pictures taken during the motion  
 161 are represented in Fig. 4. The trajectory is given by the  
 162 native copper tail. This latter is re-oxidized far from the  
 163 droplet as evidenced by the colored fringes. In the sup-  
 164plementary material we show one movie illustrating the  
 165 splash of an ethanol droplet (Movie2.avi). The reactive  
 166 Leidenfrost effect permits to visualize the bouncing of  
 167 the satellite droplets.

168 Another application deals with the vapor flow monitor-  
 169 ing. Linke et al. have shown that Leidenfrost droplets  
 170 are self-propelled on ratchet-like substrates in the direc-  
 171 tion perpendicular to the ratchet features (in the positive

could occur with any liquid/solid in a Leidenfrost state  
generating a reactive vapor flow over a reacting substrate.

\* \* \*

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