

Supporting Information

Taming the Coffee Ring Effect – Enhanced Thermal Control as Method for Thin-Films Nanopatterning

Rafal Sliz^{†}, Jakub Czajkowski^{†‡}, Tapio Fabritius[†]*

[†] Optoelectronics and Measurement Techniques Unit, Faculty of Information Technology and Electrical Engineering, University of Oulu, Erkki Koiso-Kanttilankatu 3, 90570 Oulu, Finland

[‡] Microsoft, HoloLens Optics Finland, Keilalehdentie 2-4, 02150 Espoo, Finland

Corresponding author: Rafal Sliz, rafal.sliz@oulu.fi

Number of pages: 13

Number of figures: 7

Number of equations: 5

Number of tables: 1

Table of contents

- Modeling details.
- Modeled change of the vapor pocket for various temperatures and hosting liquids.
- Figures representing the drop shape in the whole spectrum (25–250 °C) of temperatures with a temperature step of 10 °C.
- Full set of cross-sectional profiles of the droplets at the various temperatures.
- Modeling results of the vapor pocket creation under a 2.17 pl droplet at various substrate temperatures.
- Modeling of the pressure distribution within the drop at the various substrate temperatures.
- Modeled velocity flow within the droplet and in the surrounding atmosphere at various heat transfer conditions.

Modeling details

MATLAB Environment was used to calculate the dimensions and shape of the vapor pocket under the droplet. We assumed that the drop is subject to gravitational forces (scaling as $\rho R^3 g$) and tension forces at the liquid-gas interface (scaling as $R\gamma$, proportionally to the liquid-gas surface tension). The capillary length (l_c) can be obtained by balancing these two forces: $l_c = \sqrt{\gamma/\rho g}$, where γ is the surface tension, ρ stands for fluid density, and g denotes gravity constant. For water at 100 °C, capillary length equals 2.5 mm, which is about 250 times larger than the radius of the studied inkjet-printed droplets – volume 2.17 pl. Therefore, we assumed almost perfectly spherical drops as depicted in Figure 4a, and in our considerations we have applied the evaporation model proposed by Biance and Soto.¹

As demonstrated by de Laplace, there is a difference of pressure between the inside and the outside of the interface, defined by the Young-Laplace equation: $\Delta P = \gamma C$, where C is the curvature of that interface.² Furthermore, we are able to obtain the shape of the outside liquid-air interface of the droplet by numerically solving the following second-order differential equation:¹

$$\frac{1}{r(1 + \dot{r}^2)^{1/2}} - \frac{\ddot{r}}{(1 + \dot{r}^2)^{3/2}} = C_0 + \frac{z}{l_c^2} \quad (S1)$$

In the Leidenfrost (or air-levitated) situations, gas escapes from the axis of symmetry towards the external edge, indicating that the maximum pressure point is located right below the center of the drop. For small droplets, evaporation takes place through the entire surface of the drop R^2 . The bottom of the droplet undergoes deformation by gravity over a characteristic length $l \sim R^2/l_c$. The pressure exerted on the vapor by our droplet is then dominated by the Laplace pressure. As demonstrated by Snoeijer et al., Burton et al., and Caswell, the shape of the vapor layer underneath the droplet is rather complex and can be described either by using Bessel functions of the first kind (Snoeijer) or two parabolas with a continuous derivative (Burton), which are joined in point h .³⁻⁵ We can determine the thickness of a vapor layer h as:

$$h \sim \left[\frac{\eta \kappa \Delta T}{\rho_v \mathcal{L} \gamma l_c^2} \right]^{1/4} R^{5/4} \quad (S2)$$

where η describes the viscosity of vapor, κ corresponds to the thermal conductivity of vapor, ΔT is the difference between surface temperature and the boiling point, ρ_v stands for vapor density, $\mathcal{L}$ is latent heat, γ is the surface tension, l_c denotes capillary length, and R is the maximum radius of the droplet.

This model does not use the thermal conductivity of the liquid. Instead, it uses the thermal conductivity of the vapor. Similar logic applies to other models developed by Xu and Qian or Quere^{6,7}.

According to the Handbook of thermal conductivity (Vol 1 and 3, 1995), the thermal conductivities of water, IPA, and TGME are as follows: 0.67, 0.12, 0.08 W/m·K, respectively. The same publication iterates the thermal conductivity of the vapors of water, IPA, and TGME as 0.024, 0.023, 0.025 W/m·K, respectively. Since the values are very similar, we assume that the vapor's thermal conductivity is not the main contributor in this equation. At the same time, the denominator of the equation has the surface tension of the liquid and the capillary length to the power of two. The capillary length is equal to $l_c = \sqrt{\gamma/\rho g}$, where g is the gravitational acceleration, and ρ stands for liquid density. After replacing the l_c in the denominator, the surface tension in the denominator becomes to the power of two, and one of the most important factors in the equation.

$$h \sim \left[\frac{\eta \kappa \Delta T \rho g}{\rho_v \mathcal{L} \gamma^2} \right]^{1/4} R^{5/4} \quad (S3)$$

The surface tension of the water, IPA, and TGME are as follows: 72.8, 23, 34 mN/m, respectively. Figure S1 demonstrates how the vapor pocket size changes with temperature for water, IPA, and TGME hosting liquids.

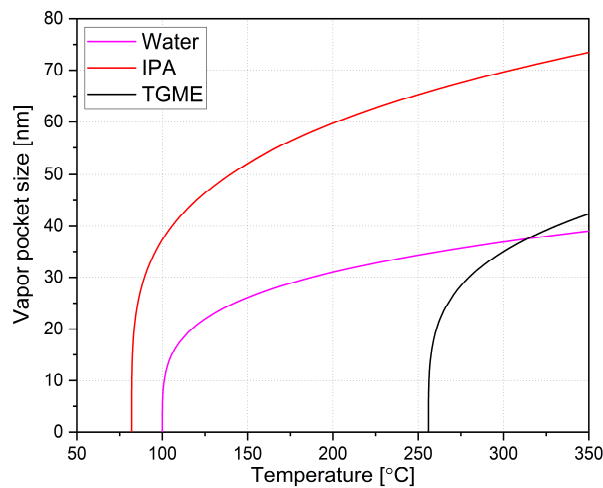


Figure S1. Change of the vapor pocket for various temperatures and hosting liquids.

As seen in the previous point, Soto's model considers the thermal conductivity of the vapor. We assume that the presence of the nanoparticles in the vapor is negligible, and therefore, their influence on the vapor thermal conductivity is minimal. However, we considered that the additions of nanoparticles might affect the surface tension of the liquids. For instance, M.H.U. Bhuiyan et al.

indicate that the nanoparticles raise the surface tension slightly ⁸. At the same time, Vafaei et al. suggest that the surface tension of the liquids firstly decreases and then increases with higher nanoparticle concentrations ⁹. Important work by Tanvir & Qiao demonstrates that concentrations of nanoparticles below 5% wt. have a negligible influence on the surface tension of the host liquid ¹⁰. Taking into account that there is no agreement on how the particular nanoparticles affect the surface tension of the liquids and that the amount of nanoparticles in our experiments is rather small (<2.5%), we have not taken into consideration their influence in the fluid behavior.

The achieved ultra-high-resolution profiles of the droplets at various temperatures were transferred to Autodesk AutoCAD environment for verification and further conversion to the DXF format. Furthermore, we used this format to simulate various aspects of the drop behavior by using the COMSOL Multiphysics software. Our model describes the 2D stationary behavior of the drop surrounded by ambient atmosphere and heated substrate at the bottom, for which the size of the vapor pocket is taken into consideration. The model includes the following physical aspects that we took into account during calculations: Laminar Flow, Heat Transfer in Fluids, Non-Isothermal Flow and Marangoni Effect.

We used a stationary momentum balance equation that describes the velocity field and the pressure distribution (Navier-Stokes equations). To incorporate the heating of the fluid, the flow of the fluid is coupled to an energy balance.

Consequently, we utilized the Boussinesq approximation to include the effect of temperature on the velocity field. In this calculation, variations in temperature generate a buoyancy force that lifts the fluid. Thus, the force is included into the source term representing external forces per unit volume (N/m³) in the Navier-Stokes equation as:

$$F = \begin{pmatrix} F_x \\ F_y \end{pmatrix} = \begin{pmatrix} 0 \\ \rho g \alpha (T - T_0) \end{pmatrix} \quad (S4)$$

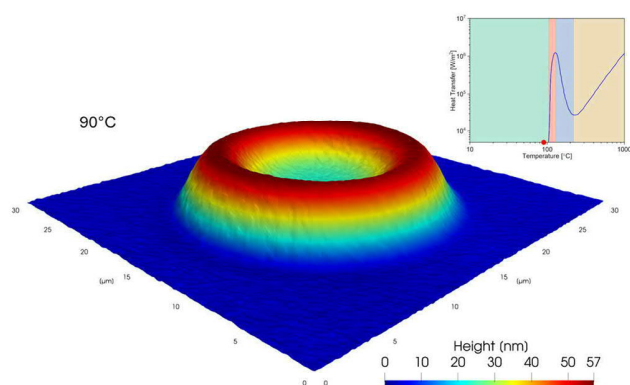
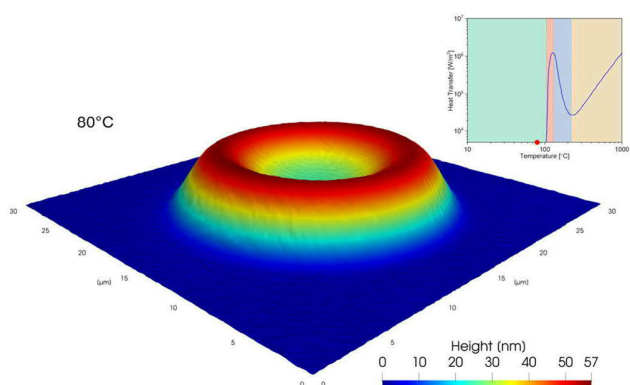
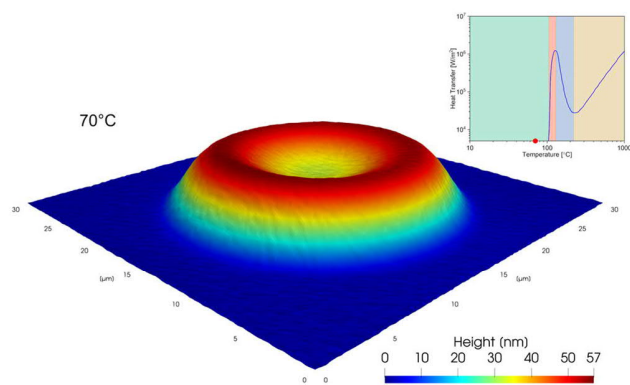
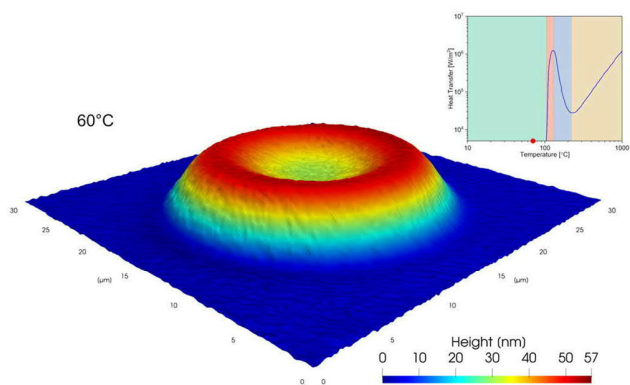
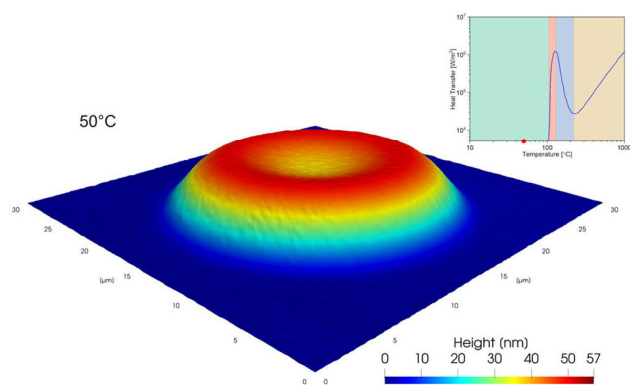
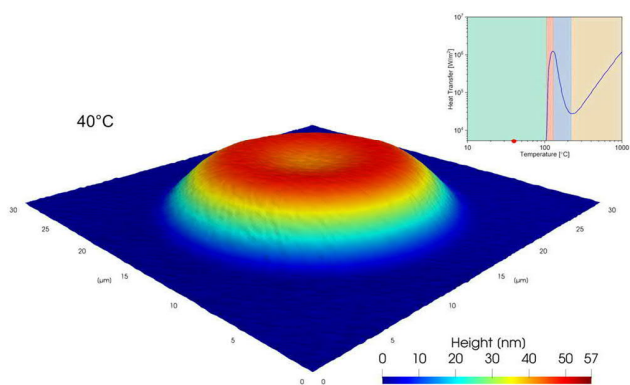
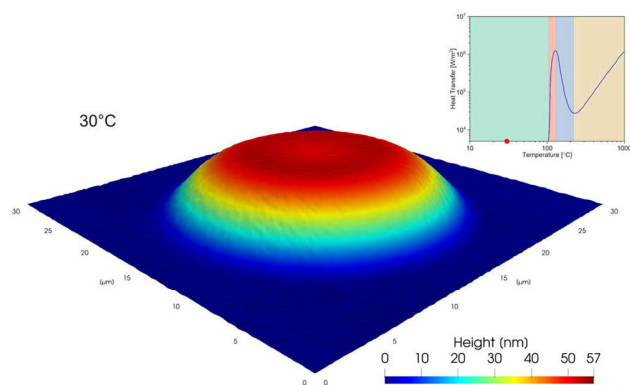
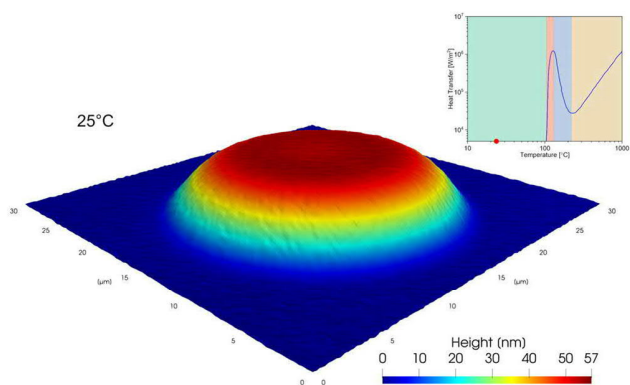
where ρ is the density, g is the acceleration due to gravity (m/s²), α is the coefficient of thermal expansion (1/K), T is the temperature in Kelvins and T_0 is the temperature at which ρ has been measured.

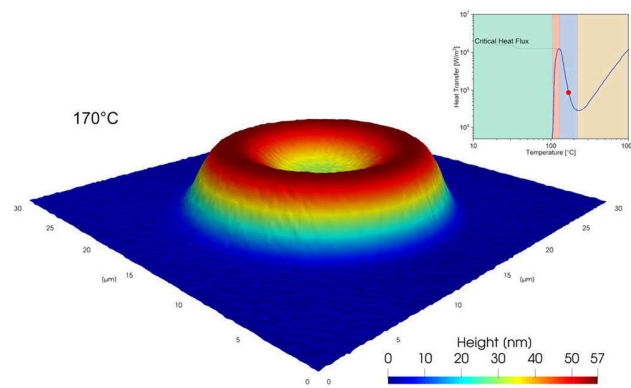
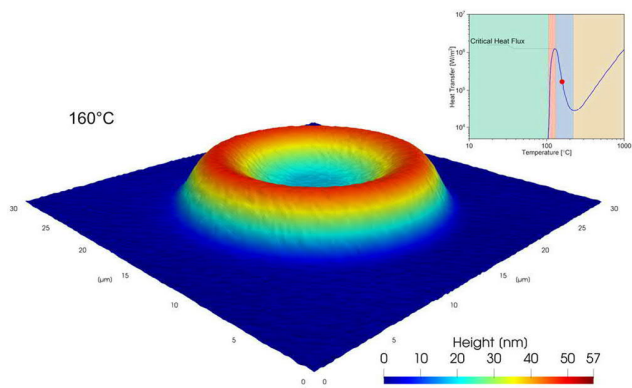
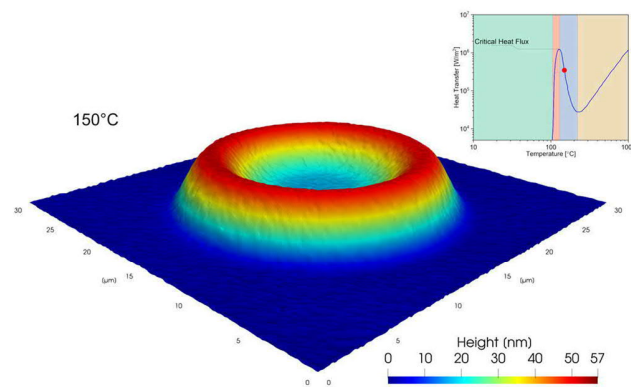
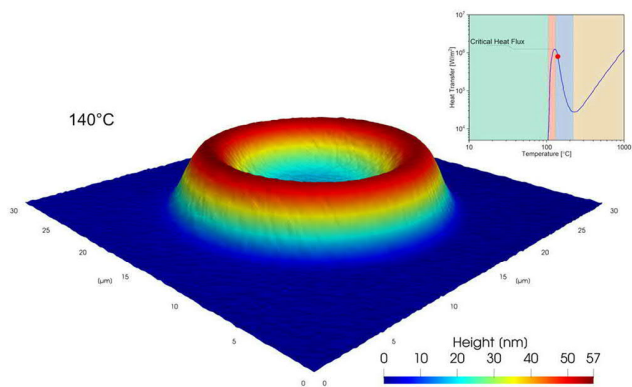
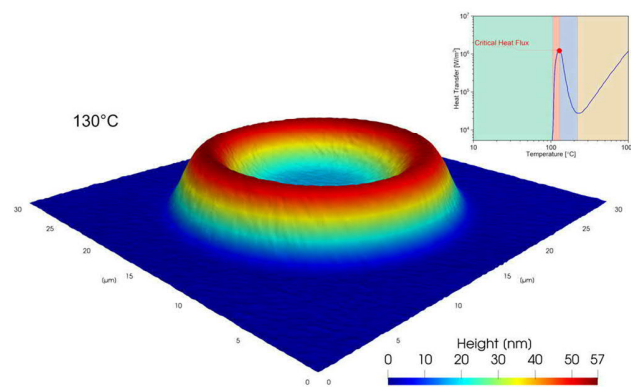
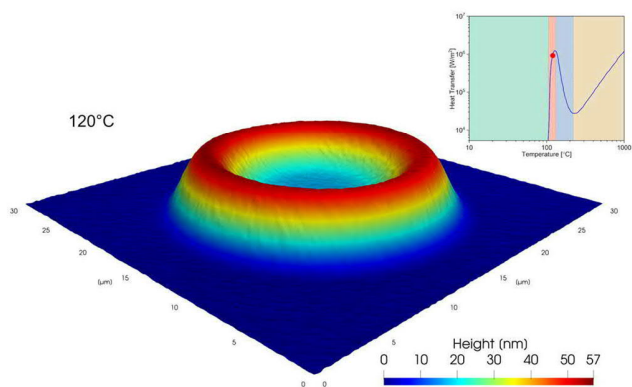
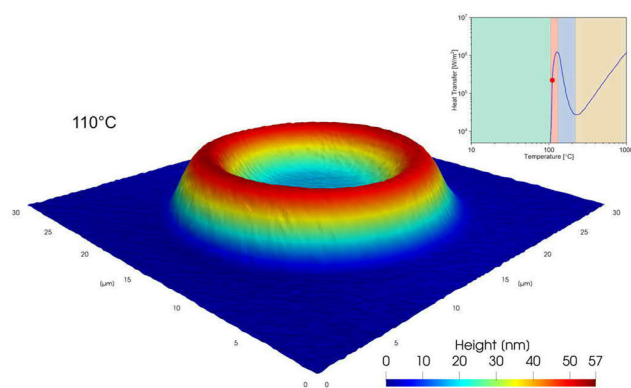
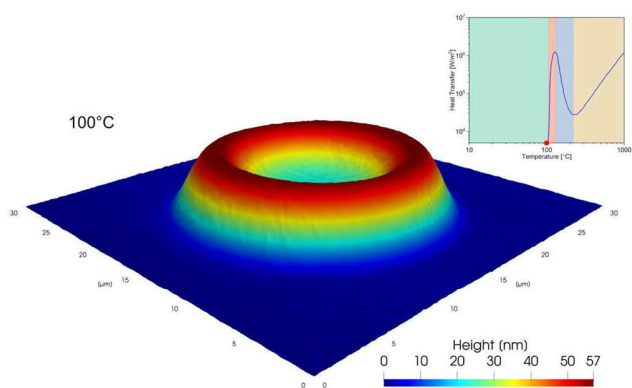
The following equation describes the forces that the Marangoni effect induces on the interface (liquid/air):

$$\eta \frac{\partial u}{\partial y} = \gamma \frac{\partial T}{\partial x} \quad (S5)$$

where γ is the temperature derivative of the surface tension ($\text{N}/(\text{m}\cdot\text{K})$). The equation says that the shear stress on a surface is proportional to the temperature gradient.¹¹

Taking into account the picoliter-scale regime, the following assumptions were applied in our model: the temperature of the air surrounding the drop is gradually decreasing by 1 °C between the substrate surface and approximately 60 μm over the droplet. The results illustrate the flow direction in the droplet indicated with arrows as well as the velocity of the flow shown with colors (Figure S6 & Figure S7).





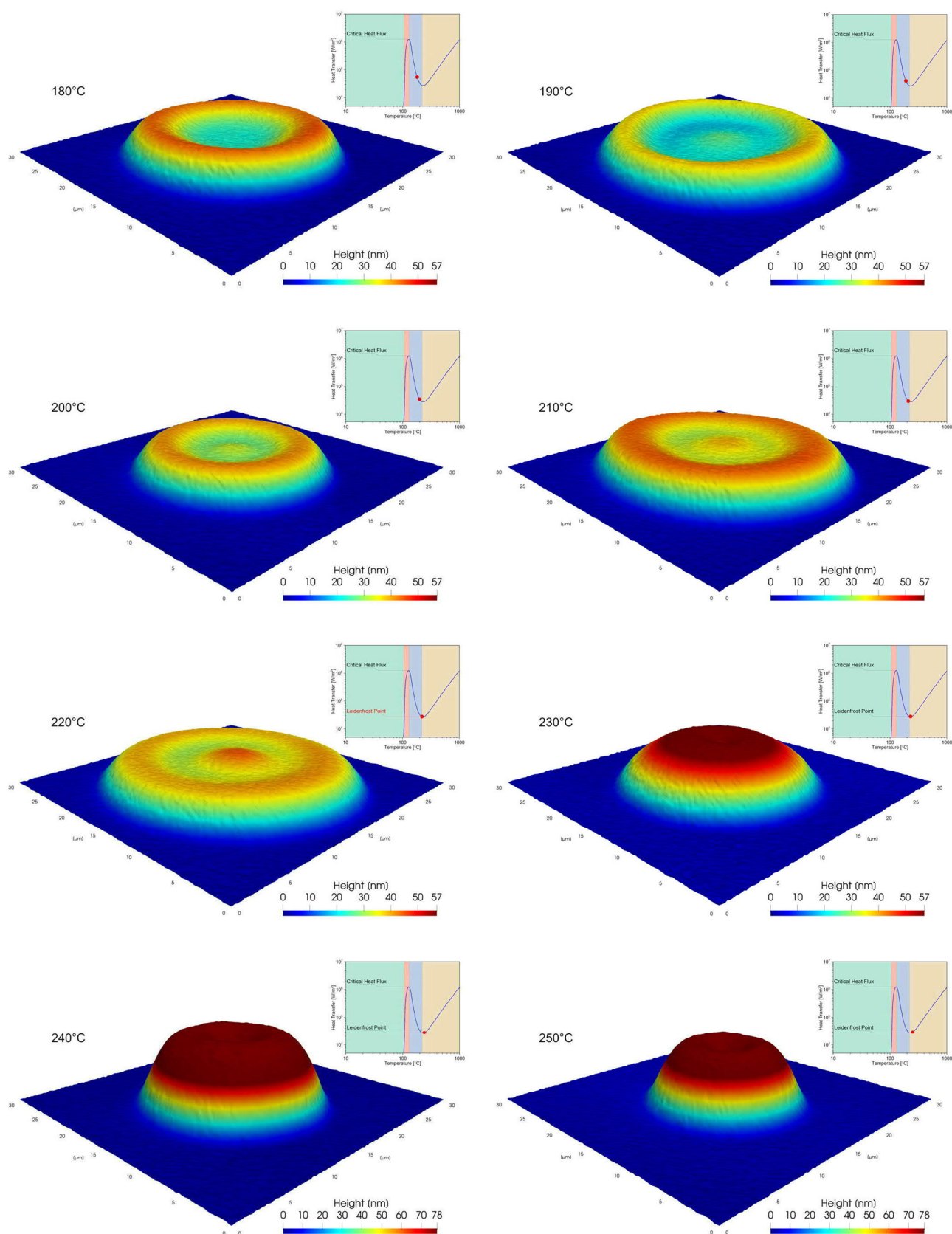


Figure S2. A full set of 3D profiles of the PEDOT:PSS droplets at various substrate temperatures 25–250 °C. The insert illustrates the heat transfer at a particular temperature, which is related to the Leidenfrost effect.

Figure S3 depicts the cross-sectional profiles of all the droplets used in this research. The plots have been divided into two temperature ranges to increase clarity. The division also emphasizes that the width of the droplet does not change at the lower temperature range.

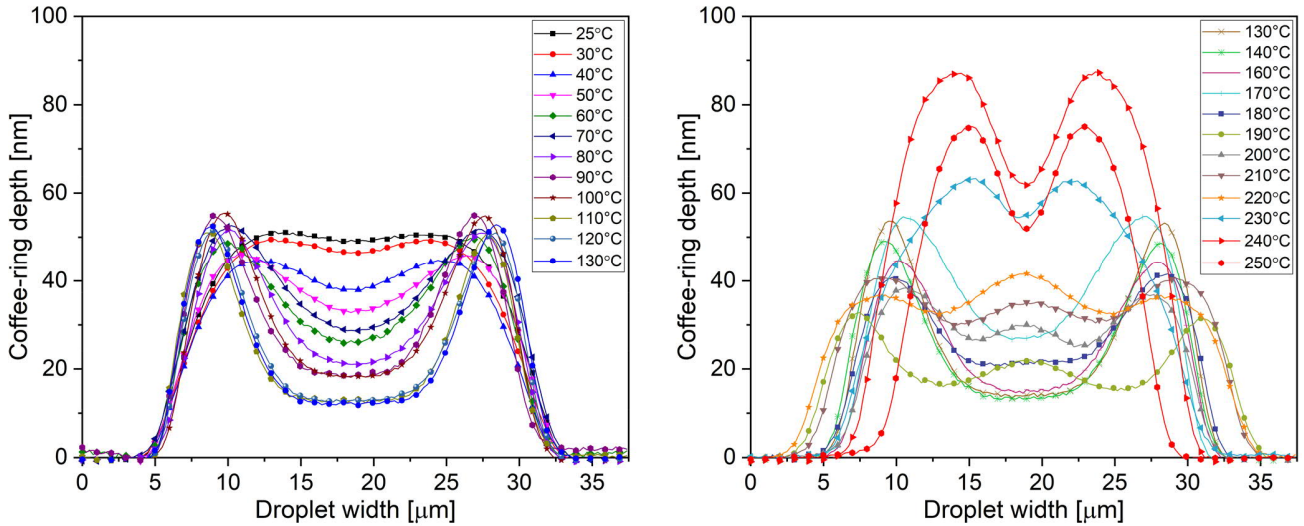


Figure S3. Cross-sectional profiles of the droplets at the various temperatures, divided into two sets for clarity (25–130 °C and 130–250 °C).

Figure S4 illustrates the results of modeling the vapor pocket dimensions under the droplet. At temperatures close to the boiling point (100 °C) the drop rises insignificantly. The change is more evident for temperatures above 110 °C. Importantly, regardless of the applied temperature, the spherical size of the droplet remains unaffected.

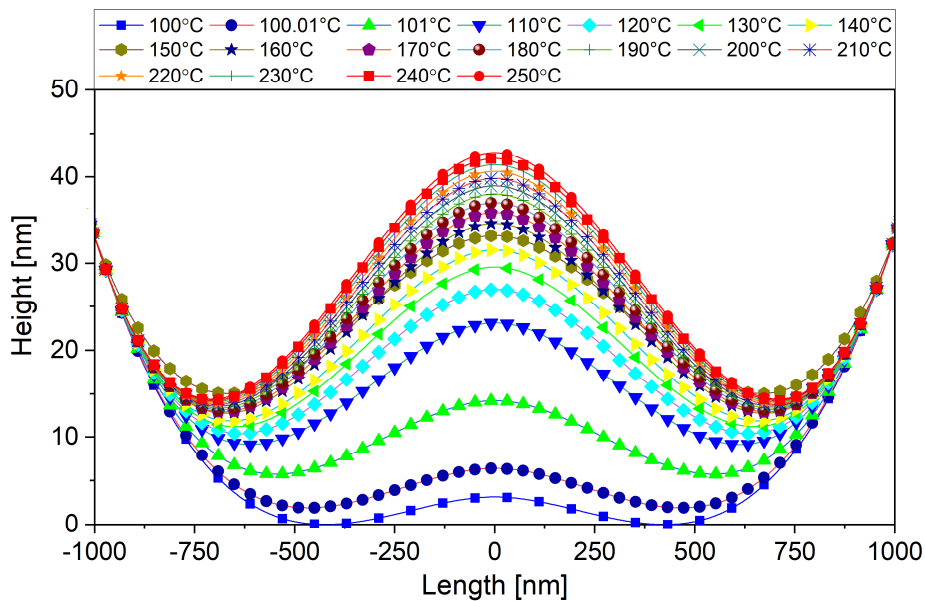


Figure S4. Modeling of the vapor pocket creation under a 2.17 pl droplet at various substrate temperatures.

Figure S5 depicts the pressure distribution within the droplet achieved during modeling. The difference in pressure distribution is rather low, but the important aspect is the location of the lower pressure points which is affected by the creation of the vapor pocket under the droplet. The larger the pocket, the more distant the lower pressure points.

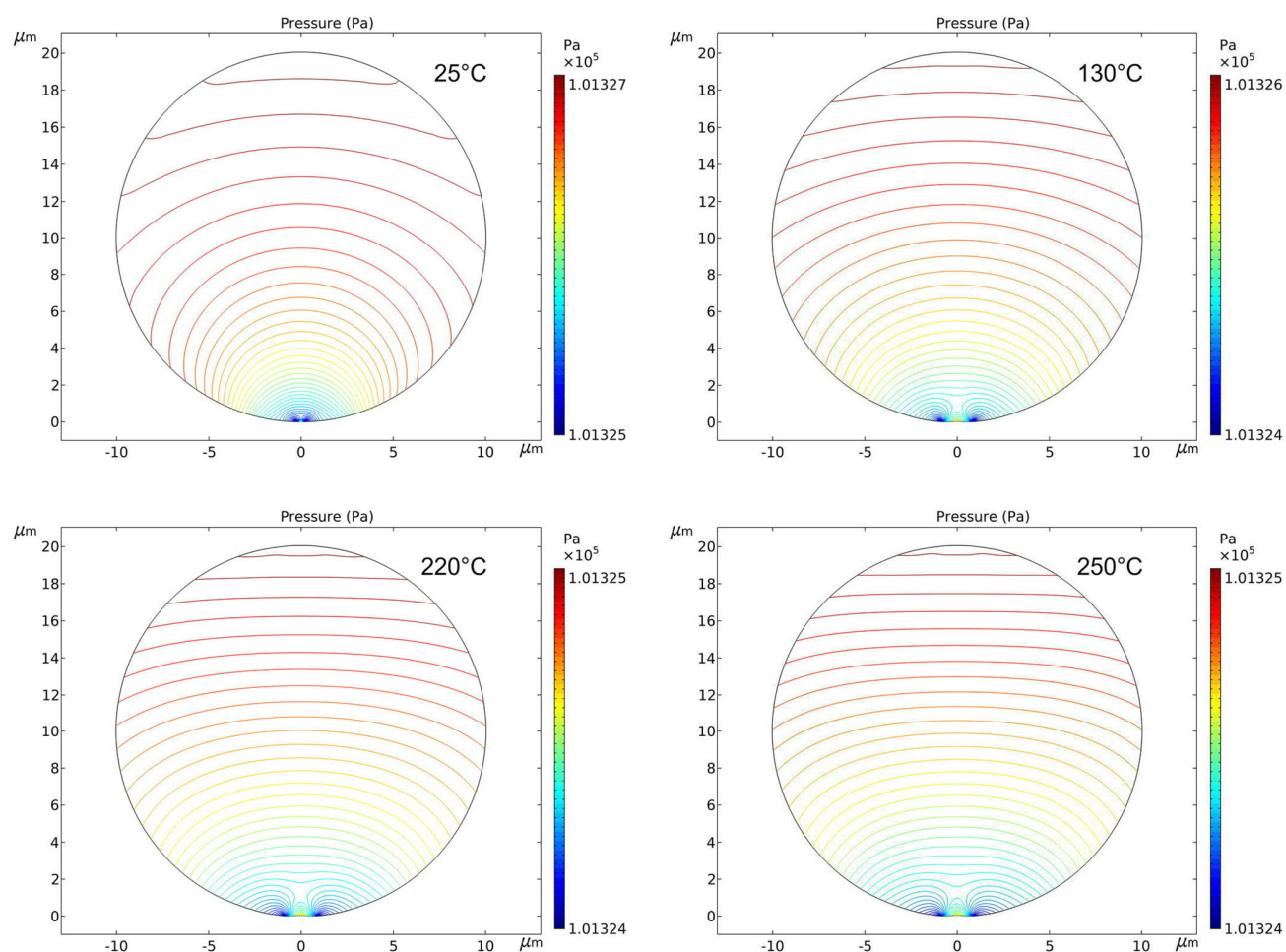


Figure S5. Pressure distribution within the drop at the various substrate temperatures. Due to the Leidenfrost vapor pocket creation, the lower pressure point splits into two separate points.

Figure S6 depicts information regarding the flow of the liquid in the droplet and the behavior of the surrounding environment. Although the direction of the flow is not affected, the flow velocity of the surrounding air is increasing significantly with the increasing temperature of the substrate.

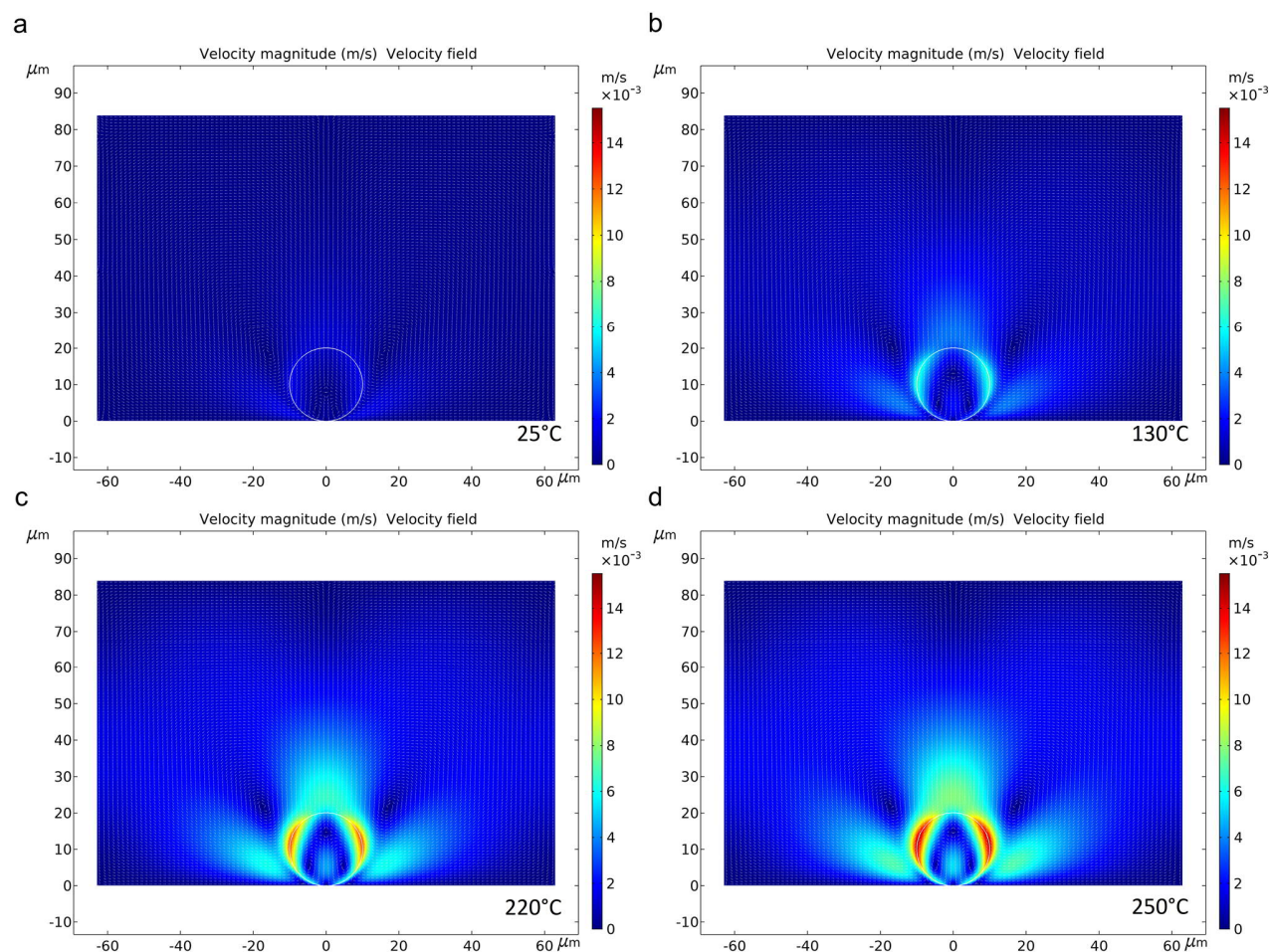


Figure S6. Velocity flow within the water droplet and in the surrounding atmosphere. The white contour illustrates the droplet shape on the surface of the substrate. a) 25 °C, almost negligible airflow surrounding the droplet. b) 130 °C, increased flow velocity within the droplet, especially on the sides. The surrounding atmosphere creates two vortices above the droplet. c) 220 °C, droplet internal flow increases significantly on the sides. The airflow creates three recognizable areas of increased flow – on the bottom-sides and on top of the droplet. d) 250 °C, the simulation indicates significant increase of the flows (internal and external) on the side of the droplet towards the top center.

Table S1. Roughness of PEDOT:PSS taken from the 2x2 μm area of the nano/microstructure for various temperatures

	R_a [nm]	R_q [nm]
25 °C	1.96 (±0.36)	2.63 (±0.47)
130 °C	1.21 (±0.22)	1.62 (±0.46)
230 °C	1.17 (±0.15)	1.53 (±0.27)

Figure S7 depicts information regarding the flow direction and velocity for an artificially created environment where the drops is surrounded on top and sides by a perfect heat insulator.

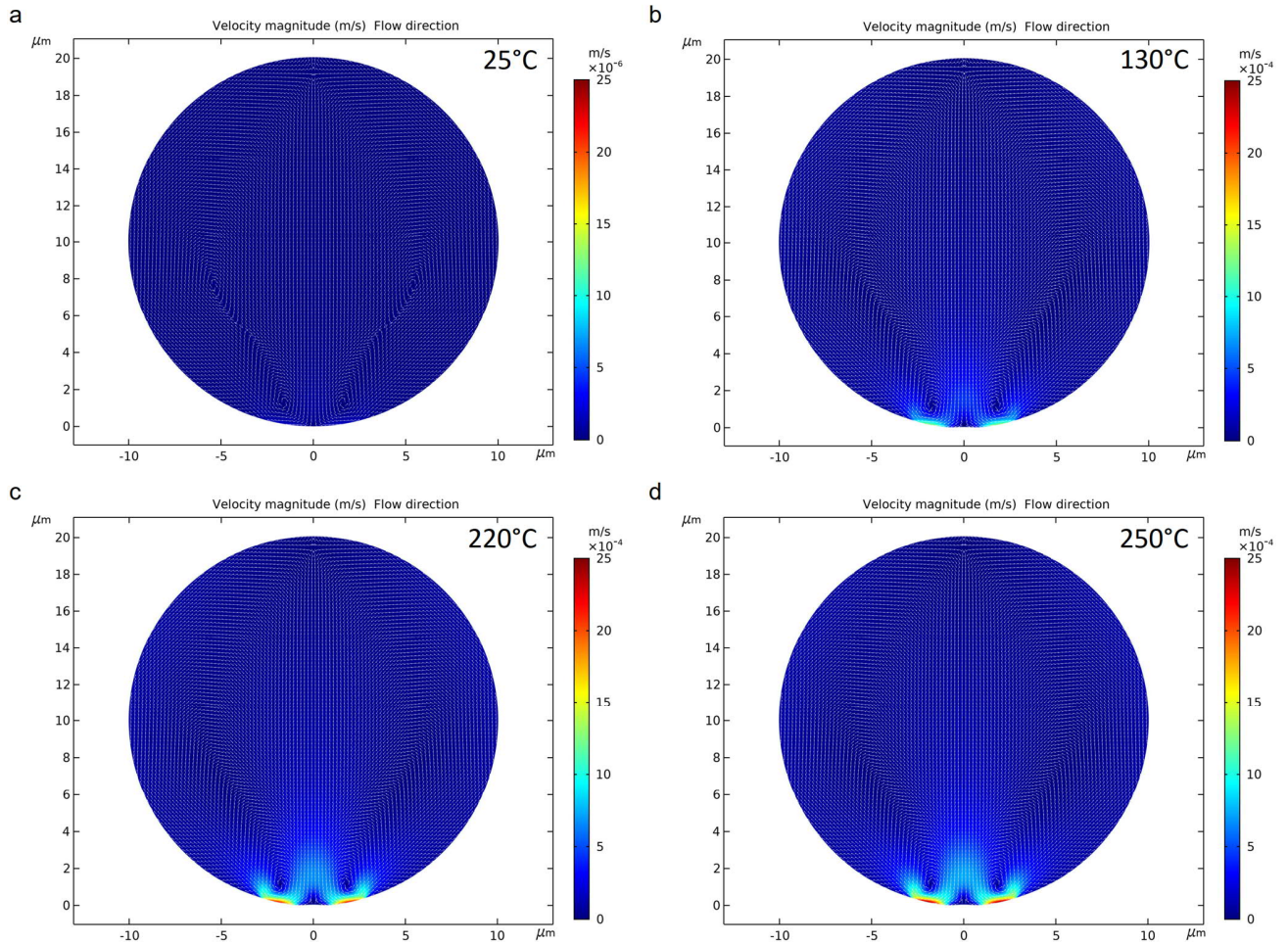


Figure S7. Modeling with an artificial environment where the droplet is surrounded (sides and top) by a perfect heat insulator, and the only source of the heat transferred to the droplet is the direct heat from the substrate through the vapor cushion, for a) 25 °C, b) 130 °C, c) 220 °C, and d) 250 °C. Without the heat from the surrounding air, the flow velocity within the droplet slows down significantly by order of magnitude, regardless of the temperature.

References

- (1) Soto, D. Non-Wetting Drops: From Impacts to Self-Propulsion, Université Pierre et Marie Curie, **2014**.
- (2) P. S. Laplace. *Traité de Mécanique Céleste*; 1805.
- (3) Snoeijer, J. H.; Brunet, P.; Eggers, J. Maximum Size of Drops Levitated by an Air Cushion. *Phys. Rev. E - Stat. Nonlinear, Soft Matter Phys.* **2009**, 79, 1–13.
- (4) Burton, J. C.; Sharpe, A. L.; Van Der Veen, R. C. A.; Franco, A.; Nagel, S. R. Geometry of the Vapor Layer under a Leidenfrost Drop. *Phys. Rev. Lett.* **2012**, 109, 074301.

- (5) Caswell, T. A. Dynamics of the Vapor Layer below a Leidenfrost Drop. *Phys. Rev. E - Stat. Nonlinear, Soft Matter Phys.* **2014**, *90*, 1–10.
- (6) Xu, X.; Qian, T. Hydrodynamics of Leidenfrost Droplets in One-Component Fluids. *Phys. Rev. E - Stat. Nonlinear, Soft Matter Phys.* **2013**, *87*, 1–14.
- (7) Quéré, D. Leidenfrost Dynamics. *Annu. Rev. Fluid Mech.* **2013**, *45*, 197–215.
- (8) Bhuiyan, M. H. U.; Saidur, R.; Amalina, M. A.; Mostafizur, R. M.; Islam, A. K. M. S. Effect of Nanoparticles Concentration and Their Sizes on Surface Tension of Nanofluids. *Procedia Eng.* **2015**, *105*, 431–437.
- (9) Vafaei, S.; Purkayastha, A.; Jain, A.; Ramanath, G.; Borca-Tasciuc, T. The Effect of Nanoparticles on the Liquid-Gas Surface Tension of Bi₂Te₃ Nanofluids. *Nanotechnology* **2009**, *20*, 185702.
- (10) Tanvir, S.; Qiao, L. Surface Tension of Nanofluid-Type Fuels Containing Suspended Nanomaterials. *West. States Sect. Combust. Inst. Spring Tech. Meet.* **2012**, 551–573.
- (11) Levich, V. G. *Physicochemical Hydrodynamics*; Prentice-Hall: Englewood Cliffs, NJ, 1962.