Evaporation of microliter water droplets on a hot copper substrate coated with single-walled carbon nanotubes

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Abstract. This paper presents an experimental study of evaporation of a millimeter-sized sessile water droplet into open atmosphere in a wide range of the temperature difference (from 0 to 76 K) between the solid substrate and the atmosphere. The study was performed using two substrates made of copper. One of them had no coating and was polished to the root mean square roughness of about 20 nm. Another one was coated with a micrometer-thick film of single-walled carbon nanotubes. With the help of precise drop shape analysis system, the mode of droplet evaporation with pinned contact line was studied. No appreciable difference was detected in evaporation droplet dynamics between the two substrates for the substrate temperatures from 24 to 100 °C.

1. Introduction
The study of evaporating liquid droplets is important for a number of applications including medical diagnostics, production of nanostructured surfaces, cooling of microelectronic equipment, and also to understand the mechanisms that occur in complex systems (clouds, fog, etc.) [1]. The greatest interest is caused by the fact that evaporation of liquid drops substantially intensifies heat transfer and affects the flow within the droplet.

Picknett and Bexon [2] were among the first to study evaporation of a sessile liquid drop on a solid substrate. They found that droplet evaporation occurs in two main modes: constant contact radius (pinned contact line) and constant contact angle (moving contact line). Sobac and Brutin [3] showed that substrate wetting properties play an important role in the process of the drop evaporation. Hu and Larson [4] studied vapor diffusion during sessile droplet evaporation both numerically and analytically, and proposed correlations for evaporation rates. Popov [5] derived an improved vapor diffusion model that can be used to calculate the evaporation rate for a droplet in a wide range of contact angles. In the majority of experimental studies, evaporation of sufficiently large droplets was studied with relatively small temperature difference between the heated substrate and the ambient gas (see, for example, recent papers [6-10]).

In our paper, the process of evaporation of liquid droplets having an initial volume less than 1 μl is studied under the temperature difference between the solid substrate and the atmosphere of up to 76 K. One of the working substrates is smooth, whereas the other one is coated with a thin film of single-walled carbon nanotubes. The main objective of our work is to study the effect of nanotube coating on the dynamics and evaporation of the sessile liquid drop. It is assumed that due to various factors...
(increased thermal conductivity of the substrate surface layer, surface structure at micro- and nanoscale, …) the use of the nanotube coating may intensify the evaporation process. This intensification is expected to be more pronounced for smaller droplets under higher temperatures of the substrate.

2. Experimental setup and methods

Studies of the sessile liquid drop evaporation were performed with the use of DSA100 drop shape analysis system produced by KRUSS (figure 1). This device consists of three main subsystems: a high-precision dosing system with the dosing step of 0.1 μl, a motorized object table with program-driven movement in 2 horizontal axes, and the optical shadow system, which includes 50 W light source and a CCD camera with a resolution of 780x580 pixels (viewing field from 3.7x2.7 mm to 23.2x17.2 mm). Also, we used a Peltier heating chamber, opened into atmosphere, which can maintain the specified temperature of the bottom wall with an accuracy of about 0.1 K. To achieve high temperatures, we had to use the cooling circuit of the Peltier chamber. We used water as a coolant, the temperature of which was maintained by a thermostat at 20 °C. The working substrate (copper block with thickness of 10 mm) was installed in the center of the Peltier chamber using heat-conducting paste KPT-8.

Figure 1. The experimental setup consisting of DSA100 drop shape analysis system (top image) and Peltier heating chamber installed on the coordinate table (right image).
Measurement of the surface temperature of the copper substrate was carried out using a thermocouple, fixed at the distance of 1-2 mm from the liquid drop. The substrate surface temperature in each experiment was constant and varied in the range from 24 to 100 °C. The temperature and relative humidity of the ambient air during the experiments was 24-25 °C and 20-30 %, respectively. Distilled deionized nano-filtered Milli-Q water is used as the working fluid. The initial liquid drop volume is about 1 μl. Software of DSA100 allows us to process shadow photos of evaporating liquid droplets in fully automatic mode (real-time determination of the droplet volume, base diameter and contact angles).

Two substrates made of copper having size of 10x10x10 mm are used. The working surface of both substrates was polished so that the root mean square roughness was about 20 nm. The first substrate had no coating. The surface of the second substrate was spray-coated with single-walled carbon nanotubes. The thickness of the coating is estimated to be on the order of 1 μm. The morphology of this surface was analyzed using a scanning electron microscope (HITACHI S3400N), as well as using an atomic force microscope (Solver Pro NT MDT). The root mean square roughness of the coated substrate was about 60 nm. Figure 2 shows SEM images of the surface coated with single-walled nanotubes obtained before and after the experiments. Degradation or any significant change of the nanotube coating is not observed. The wettability of both substrates is very close. At room temperature, the static advancing contact angle for both substrates is 85 ± 8°, whereas the static receding contact angle is 23 ± 6°.

Before the experiment a thorough cleaning of the working surface was performed. Then the substrate was placed in a reservoir with the working fluid for a day. Thereafter, to remove the liquid from the working surface, the substrate was flushed with clean compressed air designed for cleaning optical components. After that the substrate was placed into the Peltier heating chamber. A liquid droplet of pre-set size was placed on the working surface using a high-precision dosing system of the DSA100 system. The objective of the shadow optical system was focused if needed; after that the measurement with frequency of several Hz started until complete evaporation of the liquid droplet.

3. Results
Figure 3 presents consecutive shadow images of an evaporating droplet on the substrate with nanotube coating for the substrate temperature of 50 °C (on the substrate without coating the dynamics of the droplet evaporation is very similar). Values of the contact angle obtained using the DSA100 KRUSS software are indicated. It is seen that the droplet evaporation occurs in the mode with constant contact radius (the contact line is pinned). After the contact angle reaches about 10° the contact line starts

![Figure 2. SEM images of the substrate coated with single-walled carbon nanotubes before (left) and after (right) the experiments.](image-url)
moving so that both the contact radius and the contact angle decrease (this was the case for all substrate temperatures studied from 24 to 100 °C). Unfortunately, the DSA100 KRUSS software is not capable to reliably measure contact angles less than 10°. That is why below we present data for the droplet evaporation mode with constant contact radius only.

Dependences of the main parameters of the sessile liquid drop during evaporation vs time are shown in figures 4-5. Results are presented for two different substrates for the substrate surface temperatures 50, 80 and 100 °C. The slight variation of the contact diameter (see figure 4 left) at the very last stage of the evaporation mode with pinned contact line is due to the measurement uncertainty of the software (as seen from figure 4 left, this uncertainty does not exceed 2%). From figures 4-5 one can see that

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**Figure 3.** Consecutive images of an evaporating water droplet on the copper substrate with nanotube coating. The substrate temperature is 50 °C, initial droplet volume is 0.89 μl, time interval between images is 15 s. Values of the contact angle obtained using the DSA100 KRUSS software are indicated.

**Figure 4.** Dependences of the droplet contact diameter (left) and contact angle vs evaporation time for different substrates and substrate temperatures: 1, 2 – 50 °C; 3, 4 – 80 °C; 5, 6 – 100 °C. Filled signs (1, 3, 5) – surface without coating; empty signs (2, 4, 6) – surface with single-walled nanotube coating.
Figure 5. Dependence of the droplet volume vs evaporation time for different substrates and different substrate temperatures: 1, 2 – 50 °C; 3, 4 – 80 °C; 5, 6 – 100 °C. Filled signs (1, 3, 5) – surface without coating; empty signs (2, 4, 6) – surface with single-walled nanotube coating.

Figure 6. Droplet mass loss per unit time divided by the droplet diameter vs substrate temperature. Circles – surface without coating (3 runs for each temperature); crosses – surface with single-walled nanotube coating (3 runs for each temperature).

Qualitatively the evaporation dynamics on both surfaces does not differ. However, quantitative comparison of data sets presented in figures 4-5 is difficult as we have some variation in the initial diameter, contact angle and volume of the droplets. It is known (see, for example, [3]) that for a sessile liquid drop in the evaporation mode with constant radius the mass loss per unit time is proportional to the droplet radius and does not depend on the droplet volume and contact angle. This allows us to quantitatively compare the data for droplets with different initial parameters. Figure 6 shows the droplet mass loss per unit time divided by the droplet diameter vs substrate temperature for both surfaces and for all temperatures studied. Within experimental error, no effect of the nanotube coating on the evaporation rate is seen.
4. Conclusions
We presented the results of the experimental study of evaporation of a microliter (millimeter-sized) sessile water droplet into open atmosphere in a wide range of the substrate temperatures (from 24 to 100 °C). The study was performed using two substrates made of copper. One of them was smooth and had no coating. Another one was coated with a micrometer-thick layer of single-walled carbon nanotubes. The mode of droplet evaporation with constant contact radius (pinned contact line) was studied. No appreciable difference was detected in droplet evaporation dynamics between the two substrates. This indicates that for static macroscopic droplets the nanotube coating has little or no effect on both the wetting properties of the substrate and heat transfer in the substrate. Further work is needed to study the effect of the single walled carbon nanotube coating on the droplet evaporation at the very last stage of the droplet life when the contact line is moving fast and the size of the droplet is comparable to the thickness of the carbon nanotube coating. For this, a measurement optical system with high spatial and time resolution is needed.

Acknowledgments
The work was supported by the Russian Science Foundation, Project No. 18-19-00538.

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