Thermohydrodynamic processes of droplet evaporation and boiling on functional nanomaterials surfaces

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Abstract. We study the evaporation and boiling of water droplets on functional nanomaterial surfaces. Methods for manufacturing samples of nanocomposites, methods for studying contact angles, and evaporation dynamics are described. New experimental data on the behavior of contact angles and evaporation rates at various temperatures for samples of nanocomposites are presented in both the constant contact line mode and the constant contact angle mode. The features of evaporation for nanocomposites with inclusions of boron nitride and aluminum nitride nanoparticles inside graphene samples are noted.

1. Introduction
In recent years, graphene structures, films, and composites, including hybrid nanocomposites, have attracted great attention as new promising functional materials for power engineering and electronics [1-3]. The use of such materials is very promising in various applications when heat and mass transfer occurs on their surfaces [4-7]. Drop evaporation is one of the most important phenomena and has various applications in the coating processes, inkjet printing, cooling electronics, Leidenfrost effect and others [6-13]. For these reasons, the study of droplet evaporation on nanocomposite substrates at various temperatures is an important and promising task. Since graphene-based nanocomposites have been increasingly used in recent years, but there are very few publications on this subject, and our study seems relevant.

The parameters of droplet evaporation on a heated substrate are determined by thermal conductivity, wettability (contact angle of the droplet with the substrate), and roughness. In this case, the roughness dimension (micro-, meso- or nanoroughness) and their morphology are important for the evaporation rate. Previously, the parameters during evaporation of a water drop on various substrates (hydrophilic, hydrophobic, and mixed wetted surfaces) were experimentally studied [14-18]. The placement of droplets on a surface overheated above a certain temperature led to the rapid formation of vapor bubbles. It should be noted that this temperature depends on various factors, including surface morphology and contact angle, thermal properties of the surface. The parameters of the droplets, such as the contact angle and the evolution of the volume during the evaporation time, were measured experimentally. The results showed that surface wettability plays a critical role not only in the dynamics of vapor bubbles, but also in evaporation.

2. Experimental setup, materials and methods
We studied the preparation, observation, and measurement of droplet evaporation rate using the Kruss EasyDrop goniometer. This goniometer is equipped with an automatic dropping system with high precision. The droplet volume in all experiments was 5 µl. The Kruss EasyDrop measuring system was used with a special heater and temperature control system. The power of the heater was controlled by changing the voltage on it. Surface temperature was measured using an Extech EA10 thermometer. The thermocouples of the device were located directly on the surface of the samples. Samples were made in the form of tablets, the production of which was carried out using a Buehler SimpliMet 1000 hot-pressing machine. Samples of three types of graphene nanocomposites were made: sample 1 (S1): nanoparticles of graphene compressed into a tablet (p = 400 bar), sample 2 (S2): nanoscale graphene particles (96%) + BN nanoparticles (4%) compressed into a tablet (p = 400 bar) and sample 3 (S3): graphene nanoflakes (96%) + AlN nanoparticles (4%) pressed into tablet (p = 400 bar). The methods for producing tablets are described in detail in [14-16]. Electron microscopy of the surface of nanocomposites is shown in figure 1. It is easy to see that the surface of the materials has different morphology and roughness.

![Graphene nanocomposite surfaces](image1.png)

**Figure 1.** Graphene nanocomposite surfaces: (a) – GNF (100%), (b) - GNF (96%) + BN (4%), (c) - GNF (96%) + AlN (4%).

3. **Droplets evaporation and boiling on graphene nanocomposite surfaces**

The experimental results are shown in figures 2-10 for various surfaces of graphene composites. Photos of the evaporation of water droplets (diameter of 4 mm) on the surfaces of graphene composites in a wide temperature range from 20°C to 120°C are presented.

**Case 1 (sample S1, GNF - 100%)**

![Drop evaporation](image2.png)

**Figure 2.** Drop evaporation on a graphene substrate (a - 0 sec, b - 300 s, c - 700 s, g - 1200 s); substrate temperature 20°C

![Drop evaporation](image3.png)

**Figure 3.** Drop evaporation on a graphene substrate (a - 0 s, b - 50 s, c - 100 s); substrate temperature 50°C.
Figures 2 and 3 show that the evaporation of droplets on the surface of graphene nanoflakes occurs in a constant contact line mode. Figure 4 clearly shows that even at a temperature close to 120°C, nucleation and growth of vapor bubbles are observed. The nature of such bubbles can be associated with both water-soluble air and their heterogeneous nucleation on separate graphene nanoflakes on the surface of the composite. Individual bubbles grow very stably to large sizes, which corresponds to a stable three-phase contact line, which has a boundary that coincides with the boundary of the droplet. Over time, the size of the bubble decreases along with a decrease in the radius of the drop below it.

Case 2 (sample S2, GNF (96%) + BN (4%))

Figures 5 and 6 show the evaporation of droplets on the surface of GNF (96%) + BN (4%) nanoflakes at different substrate temperatures. Figure 7 shows the evaporation of droplets on the same substrate at a temperature close to 120°C.
On substrates GNF (96%) + BN (4%) (figures 5 and 6), evaporation occurs in an intermediate mode: both the contact angle and the contact line change. At a substrate temperature of about 100°C, bubble boiling is observed, but the size of the bubbles is much smaller than the diameter of the droplet; there is no three-phase contact line. This behavior differs from the modes observed on a clean graphene surface.

Case 3 (sample S3, GNF (96%) + AlN (4%))

On the surfaces GNF (96%) + AlN (4%) with increasing surface temperature, a change in the wetting modes is observed: from hydrophobicity to hydrophilicity. We were not able to explain this effect, since no visible changes in the material occurred in this temperature range, but the frequency of occurrence of this phenomenon is very high. At a substrate temperature of about 100°C, bubble boiling is not observed. The evaporation rates for various nanocomposites are shown in figure 11. It is clearly seen that, qualitatively, the rate of evaporation from the surface of various nanocomposites is about the same. At the same time, on substrates, the evaporation rate at all temperatures is higher. In addition, from approximately 90°C, the influence of microbubbles arising inside the water droplets is noticeable, which leads to faster evaporation.
A very surprising effect that can be observed in the figures is a noticeable difference in the behavior of water droplets on the surfaces of various nanocomposites. Given that these materials differ in composition insignificantly (the second and third only by the addition of BN (4%) and AlN (4%) nanoparticles to graphene nanoflakes), the differences in wettability by water droplets, evaporation rate, and bubble structure nucleate boiling are very different.

It should be noted that the surface morphologies of the materials are different; the initial contact angles also differ. In addition, as shown by estimates of effective thermal conductivity, a material based on graphene flakes has thermal conductivity 6–11% higher than that of composites with the addition of BN (4%) and AlN (4%). The latter circumstance is related to the contributions of the boundary thermal resistance at the GNF - BN and GNF - AlN boundaries.

4. The evaporation rate and boiling mechanism on micro- and nano-rough graphene surface

During the evaporation process on the substrate, the droplet volume decreases continuously, this leads to a decrease in the contact angle, radius of the base, or both of them. However, there is an obvious correlation between the volume of the droplet, the contact angle, and the main radius of the droplet, only two of which are independent. If we assume that the droplet shape above the substrate is a spherical segment, with height $h$, then the dependence of the droplet volume on the contact angle and the main radius of the droplet can be written as:

$$V = \pi R^3 \left(\frac{2-3\cos \theta + \cos^3 \theta}{3\sin^3 \theta}\right) + \pi R^2 (1-f)h$$

where $V$ is the droplet volume, $R$ is the main radius of the droplet, $\theta$ is the contact angle, $f$ is the solid contact fraction with the droplet, $h$ is the height of the micro- or nano-irregularities wetted by the droplet. For the Cassie-Baxter state, the value $h$ is zero, and for the Wenzel state $h = h_0$. To calculate the evaporation rate, we used a modified model [17-19]

$$-\frac{dV}{dt} = 4\pi \rho RD (c_0 - c_m) f(\theta) = 4\pi \rho R D c_v (1-H) f(\theta)$$

where $c_0 - c_m = c_v (1-H)$ is the difference in vapor concentration between the drop surface (the saturated vapor concentration) and a point far from the drop, $\rho$ is the fluid density $H$ is relative humidity of the ambient air, $f(\theta)$ is the contact angle function [8, 9], $D$ is the diffusivity of the vapor
in air. The figure 11 shows the results of calculating the evaporation rate by the model. It can be seen that the theoretical evaporation rates are higher than those obtained in the experiments. This may mean that there is an influence of the boundary thermal resistance between the droplet and the substrate, which affects the mass flow in the evaporating droplet.

To explain the high heat flux during boiling and explosion of liquid droplets on the surface of a graphene nano-rough coating, it is necessary to take into account that there is a large temperature difference between the droplet and the surface, which should transfer the liquid phase due to evaporation into vapor. The nano-roughness of the graphene surface has characteristic dimensions of several nanometers (the thickness of graphene nanoflakes is about 3-5 nm), and their lateral dimensions are 10-30 nm. In addition, graphene flakes on the surface, as shown by scanning electron microscopy, are in the form of steps, which leads to another scale of meso- and nano-inhomogeneities. When the surface temperature is higher than the saturation temperature, active generation of bubbles is observed. Estimates of the surface overheating for all types of surfaces are in the range of 2–3°C. Analysis of the rate of generation of bubbles by the standard methods shows that with such overheating above the saturation temperature, the time of formation of bubbles of the critical diameter is 20-25 µs. This value is consistent with the times of emergence of supercritical bubble size inside the droplets.

5. Results and discussions
The influence of the surface properties of various substrates on the evaporation of sessile drops is studied. Three types of nanocomposite substrates were used to study the evaporation of distilled water droplets: sample 1 (S1): graphene nanoflakes (GNF) pressed into a tablet (p = 400 bar), sample 2 (S2): GNF (96%)+BN nanoparticles (4%) and sample 3 (S3): GNF (96%)+AlN nanoparticles (4%). As a result of the research, the following conclusions can be made:
1. It has been established that despite the small difference in the properties of the samples of graphene composite materials, the evaporation rate on their surfaces is noticeably different.
2. Evaporation modes (constant contact angle, constant contact line and transition) also differ for different samples.
3. Small overheating of the surface of the composites relative to the saturation temperature leads to different mechanisms of nucleation of bubbles inside the droplets. It remains unclear why boiling behaves so differently on the samples of similar types.

These data clearly show the importance and the effect of surface properties on sessile drop evaporation. They can be used for new functional materials, including thermal interface materials, as well as thermal management materials in power engineering, electronics and optoelectronics.

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