Optical methods for droplets evaporation on graphene nanocomposite surfaces

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Abstract. We study the evaporation of water droplets on the surface of graphene nanocomposites of different compositions. Methods for manufacturing samples of nanocomposites, optical methods for studying contact angles and evaporation dynamics are described. New experimental data are presented on the behavior of contact angles and evaporation rates at various temperatures for samples of nanocomposites 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

The paper presents research in the field of thermal physics of surfaces of functional thermal interface materials (TIM) based on graphene nanocomposites [1-4]. Contact angles and hysteresis angles were measured for various nanocomposite materials, including nanocomposites based on graphene flakes, boron oxide nanoparticles, nanodiamonds, aluminum nitride, as well as hybrid nanocomposites with the inclusion of polymers and microscopic metal microspheres. A study was carried out by optical methods, including optical observations of the nonstationary dynamics of the evaporation of droplets of various liquids on the surfaces of graphene nanocomposites. The processing of optical images made it possible to reveal the features of droplet evaporation on various surfaces in the modes of constant contact angle and constant contact line. These measurements are important for optimizing drip evaporative cooling processes in electronic and optoelectronic devices. New experimental data on the study and analysis of hydrodynamic and thermophysical properties of various thermal interface materials interacting with droplet flows, including the Leidenfrost effect, have also been obtained. One of the main objectives of the work is the study of the properties of thermal interface materials for the intensification of heat exchange and increasing the efficiency of cooling systems in microelectronics and high-current electronics. The physicochemical and thermohydrodynamic properties of such surfaces are important for a more efficient heat release in cooling systems using the droplet cooling method. Droplet evaporation is one of the most important phenomena and has various applications in spin-coating processes, cooling electronics, inkjet printing, Leidenfrost effect and other [5, 6]. For these reasons, the study of the evaporation of droplets on nanocomposite substrates at different temperatures is an important and promising task. Since graphene-based nanocomposites are being used increasingly actively in recent years, there are very few publications on this subject, our research seems to be relevant.
2. Experimental setup, materials and methods

Generation, observation, measurements of droplet evaporation time were carried out on a Kruss EasyDrop goniometer (the schematic of the current experimental setup is shown in figure 1). Kruss EasyDrop measuring system was used with special heater and temperature control system. This goniometer is equipped with a system for automatically dispensing drops with high accuracy. The volume of drops in all experiments was 5 μl. To change the temperature of the samples, the goniometer was equipped with a heater mounted on a standard holder. Heater power was controlled by changing the voltage on it. The surface temperature was measured with an Extech EA10 thermometer. The thermocouples of the instrument were located directly on the surface of the samples. The production of tablets was carried out with the help of an automatic machine for hot pressing the Buehler SimpliMet 1000 (figure 2). Samples of three types of graphene nanocomposites were manufactured: sample 1 (S1): graphene nanoflakes pressed into a tablet (p = 400 bar), sample 2 (S2): graphene nanoflakes (96%) + BN nanoparticles (4%) pressed into a tablet (p = 400 bar) and sample 3 (S3): graphene nanoflakes (96%) + AlN nanoparticles (4%) pressed into a tablet (p = 400 bar). In detail, methods for producing tablets have been described in [8-10].

Electron microscopy of the surface of nanocomposites is shown in figure 3 and figure 4: in figure 3 - graphene nanoflakes sample, in figure 4 - graphene nanoflakes (96%) + BN nanoparticles (4%) sample.

![Figure 1. Kruss EasyDrop goniometer.](image1)

![Figure 2. Automatic machine for hot pressing Buehler SimpliMet 1000.](image2)

Optical images of samples and optical microscopy are shown in figures 5-8. It is clearly seen that the surface of the nanocomposites is rather rough, therefore, it can be expected that there is a significant pinning of the contact line on such surfaces. This fact is indeed confirmed by experiments, the results of which are presented below.

![Figure 3. Graphene nanoflakes sample.](image3)

![Figure 4. Graphene nanoflakes (96%) + BN nanoparticles (4%) sample.](image4)
3. Drop Evaporation Experiments

The influence of surface properties on sessile drop evaporation has only recently been taken into account. The thermal conductivity of the substrate appears to be a key parameter in the evaporation process with respect to the internal flow and dynamics of evaporation. Previously proposed two modes of evaporation: constant contact angle (CCA) and constant contact radius (CCR) modes [5-7]. In the CCA mode, the contact area of the droplet on the surface decreases, whereas in the CCR mode, the contact angle shrinks. The evaporation rates of various samples of graphene nanocomposites were investigated. For this purpose, droplets of distilled water with a volume of 5 mkL were placed on nanocomposite surfaces from the top a dispenser. The evaporation rates for various nanocomposites are shown in figure 9. It is clearly seen that, qualitatively, the rate of evaporation from the surface of various nanocomposites is about the same.

![Figure 5](image1.png) **Figure 5.** Sample 1 (S1): GNF pressed into a tablet (p = 400 bar).

![Figure 6](image2.png) **Figure 6.** Optical microscopy of the sample surface GNF (S1).

![Figure 7](image3.png) **Figure 7.** Sample 2 (S2): graphene nanoflakes (96%)+BN nanoparticles (4%) pressed into a tablet (p = 400 bar).

![Figure 8](image4.png) **Figure 8.** Optical microscopy of the sample surface (S2).

![Figure 9](image5.png) **Figure 9.** Evaporation rates of various samples of graphene nanocomposites.
At the same time, a higher evaporation rate is observed for graphene nanoflakes (96%) + AlN nanoparticles (4%) nanocomposite. Apparently this is due to smaller contact wetting angles on a similar surface. This leads to the fact that near the contact line the mass evaporation flow is higher for smaller contact angles. At the beginning of the process, as can be seen from the figure 10 and figure 11, evaporation proceeds at an almost constant contact angle with an increase in the contact line. Upon reaching a certain critical value, the contact line remains constant, and the wetting angle decreases.

![Figure 10](image1.png)  ![Figure 11](image2.png)

**Figure 10.** Contact angle for the droplets evaporation on the surface GNF sample (S1) at different temperatures.

**Figure 11.** Contact angle for the droplets evaporation on the nanocomposite surface GNF (96%) + AlNNP (4%) at different temperatures.

It should be noted that the experimental data for a graphene sample (figure 10) at temperatures 70 °C and 80 °C clearly fall out of the overall picture of the dynamics of evaporation. It is possible that at such temperatures, bubbles of dissolved gas (air, for example) appear inside the drop, which affect the rate of evaporation. At the same time, this effect is not observed for nanocomposites GNF (96%) + AlNNP (4%) and GNF (96%) + BNNP (4%) the dependences of the contact angles on temperature have a clear character - as the temperature rises, the contact angles decrease.

![Figure 12](image3.png)

**Figure 12.** Contact angle for the droplets evaporation on the surface nanocomposite GNF (96%) + BNNP (4%) at different temperatures.
However, at a temperature 21 °C and 30 °C for nanocomposite GNF (96%) + BNNP (4%), an anomalous behavior of the contact angle is observed as a function of time. This effect has a high repeatability and we could not find an explanation for this phenomenon.

The study of the contact angle dynamics for a nanocomposite GNF (96%) + BNNP (4%) (T = 50 °C) is shown in the figure 13. It can be seen that in the first period of droplet evaporation, the contact line moves. At the next stages of evaporation, the contact line undergoes pinning and the contact angle decreases.

![Figure 13. Contact angle when droplets evaporate on the surface of nanocomposite GNF (96%) + BNNP (4%) (T = 50 °C).](image)

We also experimentally investigated the mass of vapor that is generated when the droplets evaporate on different surfaces of nanocomposites (figures 14 and 15). It is not difficult to see that the character of steam generation is monotonic with increasing temperature. It can also be noted that the evaporation rate is weakly dependent on the type of nanocomposite. In our opinion, the reason is the weak difference in the thermal properties of the nanocomposite surfaces GNF and GNF (96%) + BNNP (4%).

![Figure 14. The mass volume of steam during evaporation of a droplet on the surface GNF.](image)

4. Results and discussion

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 pressed into a tablet (p = 400 bar), sample 2 (S2): graphene nanoflakes (96%) + BN nanoparticles (4%) pressed into a tablet (p = 400 bar) and sample 3 (S3): graphene nanoflakes (96%) + AlN nanoparticles (4%) pressed into a tablet (p = 400 bar). By varying the roughness and surface energy of the substrate surfaces using various dynamics of the triple
line and a large range of wettability (contact angle from $10^\circ$ to $110^\circ$) are obtained. The influence of these parameters on the dynamics of evaporation is studied in order to highlight the separated and coupled roles of the triple line and the wettability of the drops on the sessile drop evaporation process. Strong dependences of the contact angles and evaporation rates were found for various temperatures for all types of nanocomposites. 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 materials for thermal stabilization and thermal management in electronics, optoelectronics, and power engineering\cite{9, 10}.

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