

Two-dimensional materials in energy technologies: thermophysical aspects

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Abstract. The prospects for the use of new two-dimensional nanomaterials, in particular graphene, for the heat and mass transfer enhancement in power and electronic equipment are considered. Examples of the influence of the properties of two-dimensional materials on the processes of wetting, evaporation, boiling, and crystallization are given in relation to energy technologies.

1 Two-dimensional materials in energy technologies

In recent years, interest in two-dimensional materials (2D materials) has increased significantly due to new possibilities and their unusual physical and chemical properties, including optical, magnetic and thermal. In this paper, we consider the prospects for the use of new two-dimensional nanomaterials, including graphene, hexagonal boron nitride, 2D heterostructures, two-dimensional oxides and chalcogenides, and MXenes as topical materials in energy technologies of the near future, in particular, for hydrogen energy, lithium-ion and other batteries, in supercapacitors, thermal energy storage systems, etc. [1-3].

Of particular interest are the problems the heat and mass transfer enhancement in power equipment using two-dimensional materials. The main types of 2D materials are presented, their physical and technological properties and unique characteristics are described. Separate technological methods for the manufacture of two-dimensional materials and films, composites, and nanofluids for various energy applications are presented. Special attention is paid to materials based on single-layer and multilayer graphene, characteristics of materials based on graphene components, their physicochemical and other parameters. The effects that are observed when using nanofluids as heat carriers and when applying coatings based on 2D materials on heat transfer surfaces during various heat transfer processes are described: single-phase convection, evaporation, boiling, condensation. It is shown that in all cases the heat transfer efficiency increases significantly. Specific examples of the use of 2D materials in heat pipes and thermosyphons are given, ways to improve the characteristics of these devices are described. Some mathematical and physical models of functioning of

two-dimensional materials in power engineering are considered. In particular, new mechanisms of nontrivial capillary thermohydrodynamics during evaporation from nanoporous materials, including laminated (ordered) graphene porous material or graphene and combined graphene foams, are considered in detail. It is shown that for certain sizes of long narrow pores between graphene sheets, evaporation from the surface can be observed with a mass flow exceeding the Hertz-Knudsen limit for evaporation into vacuum. A similar task is currently important for the new principles of operation of solar thermal power devices. Particular attention is paid to the peculiarities of the mechanisms of heat transfer, evaporation, boiling and condensation in processes associated with two-dimensional materials. In particular, the features of wetting and spreading of drops over the surface of two-dimensional materials, the temperature dependences of contact angles and hysteresis angles, and the influence of surface morphology (for example, the geometric structure of the surface) on these phenomena are described. The influence of the inside structure of nanoporous two-dimensional materials and their hybrid composites on the processes of evaporation, boiling, and condensation is described. It is shown that the inside structure (laminar or random) of nanoporous two-dimensional materials can significantly affect the thermal physics of evaporation, boiling, and condensation. Experimental and calculated results on the evaporation and boiling of liquid and nanofluid droplets from two-dimensional materials on morphologically different substrates are presented.

The importance of two-dimensional materials in recent years has been the processes of their interaction with radiation, for example, the solar Planck spectrum, which is important for new problems of thermal solar energy (solar-driven interfacial steam generation).

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The development of energy technologies has always been associated with the emergence of new materials. In recent years new problems have arisen in traditional and alternative (carbon-free) energy due to stringent requirements for the physicochemical and mechanical properties of functional materials [1–4]. Large-scale research on the development of such materials has been launched. The main feature of 2D materials is their thickness, which does not exceed the thickness of an atomic layer (no more than 1 nm). All atoms of such a “sheet” material are located in the surface layer, which determines the uniqueness of its properties (extremely high thermal and electrical conductivity, tensile strength at break). It is important to note that the free bonds of atoms make it possible to modify the properties of a material by doping with atoms of other elements. Figure 1 shows the families of developed 2D materials.

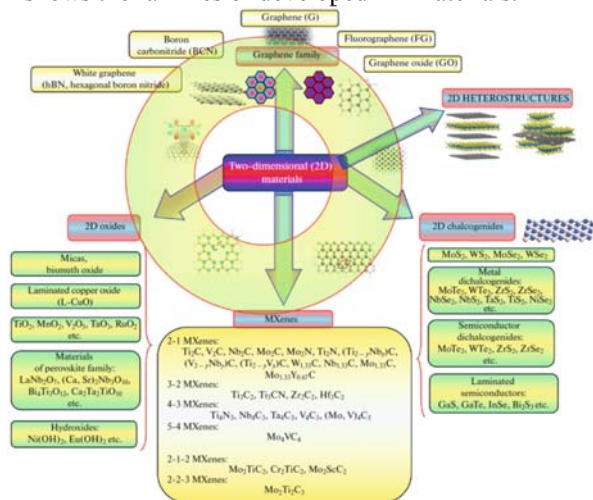


Fig. 1. 2D material families.

2 Application of 2D materials in the thermal power industry

At the same time, 2D materials have properties that can radically change the attitude towards some technologies in existing energy sectors:

- in thermal and nuclear power engineering—creation of effective heat and mass transfer surfaces using 2D materials used in the evaporation, boiling, and condensation of liquids, in water purification and desalination systems, etc. [1–7];
- in hydropower—improvement of the mechanical characteristics of structures, including concrete structures;
- in installations based on renewable energy sources—increasing the mechanical strength of the blades of wind power plants and reducing the noise they emit, improving the erosion characteristics.

The properties of most 2D materials are described in [5–11]. In this article, attention is mainly paid to graphene and its derivatives in relation to heat-transfer processes. Graphene materials include not only graphene itself but also its oxide (GO), reduced graphene oxide (rGO), and heteroatomic, functionalized, and three-dimensional (3D) graphene. The properties of graphene of monatomic thickness — single-layer graphene (single graphene layer (SGL)) —

are also preserved in multilayer graphene (few graphene layers (FGL)) with the number of layers N not exceeding 10. At $N > 10$, multilayer graphene acquires the properties of conventional graphite. In addition, there are so-called graphene foam and other analogues of three-dimensional graphene structures. Graphene-based materials exhibit unique physical and chemical properties, such as a large specific surface area, excellent electrical and thermal conductivity, high mechanical strength, and good chemical stability. Graphene has a significant theoretical surface area (up to 2630 m²/g), which is approximately two orders of magnitude greater than that of graphite powder (approximately 10 m²/g) [1]. Two-dimensional graphene-based materials with a large surface area can have an increased adsorption capacity for reagents due to strong interaction with π -electrons, which allows them to be used as catalysts [1]. Graphene is a zero bandgap semiconductor with high carrier mobility (approximately 10000 cm²/(V·s)) and electron speed (approximately 10⁶ m/s) due to the overlap of the valence and conduction bands. The mobility of carriers in graphene is less affected by temperature, so their ultrahigh mobility is achieved already at room temperature.

2.1 Wetting on the surface of two-dimensional materials

Wettability has a strong influence on the heat transfer between the working fluid and the working surface. Various materials and more diverse methods of surface modification can be used for this purpose. The wettability of two-dimensional materials by various liquids has many features, in particular, related to the liquid phase itself. In addition, the wettability radically depends on the number of monatomic layers of the material, which is especially characteristic of the water wettability of single-layer and multilayer graphene [1–3]. Since the modes of wetting and spreading of drops on the surfaces of two-dimensional materials at different temperatures are important in energy technologies, we note some important results of the interaction of drops, for example, water, with graphene materials (similar phenomena also occur for other 2D materials, for example, hexagonal boron nitride). As an example, in figure 2 experimental results on the study of the dependence of the contact angle for water drops on the surface of 2D materials are presented. Four samples were made: a) graphene nanoflakes under a pressure of 300 bar; b) graphene nanoflakes with a copper mesh up to 300 bar; c) graphene nanoflakes with a copper mesh under 180 bar; d) graphite microparticles with a copper mesh up to 300 bar.

The data obtained show that materials based on two-dimensional components change the contact angle quite strongly with temperature changes, which is an important feature of such materials. Adding a regular copper grid to a graphene pellet results in an increase in the contact angle from a few degrees to 20 degrees at various surface temperatures. This must be taken into

account when developing new effective surfaces for power equipment.

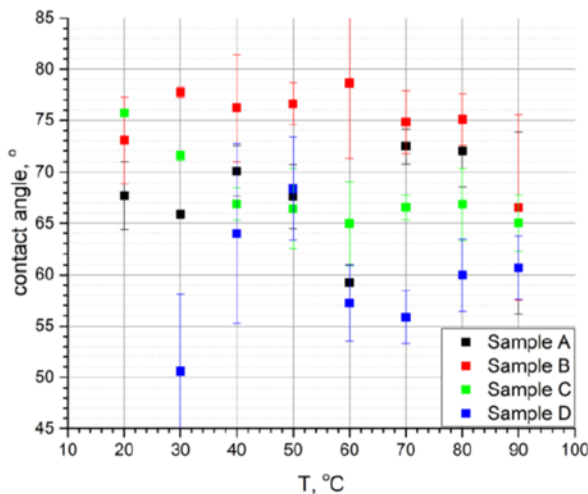


Fig. 2. Contact angle versus temperature for some materials with 2D components.

2.2 Evaporation of droplets and the Leidenfrost effect

The processes of droplet evaporation on graphene surfaces over a wide temperature range (up to film boiling temperature and above) and the effect the Leidenfrost effect are considered in the series of publications [3,12]. Unlike other researchers, the authors of [12,13] worked with pure graphene nanoflakes obtained by the method of their supercapacity vitational exfoliation in distilled water, so the nanoflakes were not oxidized. In the process of studying heat and mass transfer during evaporation droplets of various liquids (water, alcohol, ethylene glycol, etc.) flakes somewhat oxidized but, as shown by Raman spectroscopy, only along the boundaries, which left them actually not oxidized. Typical samples of graphene materials (9), as well as graphene + boron nitride (10) and graphene + aluminum nitride (11) materials are shown in the figure 3.

Figure 4 shows the experimental dependences of the evaporation time of droplets on graphene substrates on the surface temperature: 9 – aluminum; 10 – graphene coating; 11 – graphene coating with mesh.

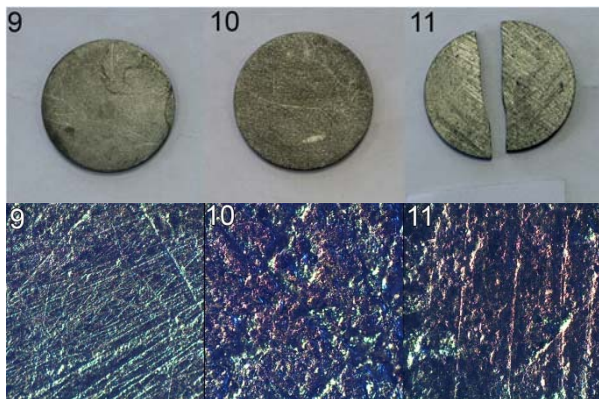


Fig. 3. Graphene materials (9), as well as graphene + boron nitride (10) and graphene + aluminum nitride (11) materials.

The evaporation rates of pure water from the surface of

graphene coating and graphene coating on a mesoporous aluminum substrate were measured. Figure 5 shows the indicated types of grapheme structures (at the initial moment, all the water was inside the graphene layer). It is noted that the rate of evaporation from the free surface of water is several times lower than from the surface of the graphene layer.

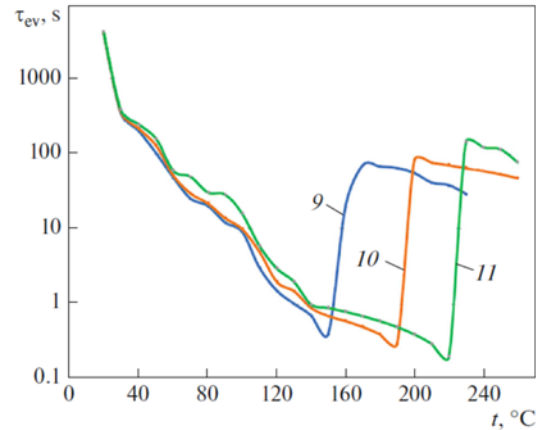


Fig. 4. Evaporation of droplets on graphene substrates embedded in copper grids with an initial droplet diameter of 3 mm: time dependence change of droplet evaporation from the surface temperature; 9 - pure aluminum; 10 - graphene coating; 11 - graphene coating with mesh.

The difference can be from 2.5 to 8 times with heat fluxes in the range from 50 to 180 kW/m² (water enters the layer due to strong absorption by capillaries through the lower part of the graphene layer) [14].

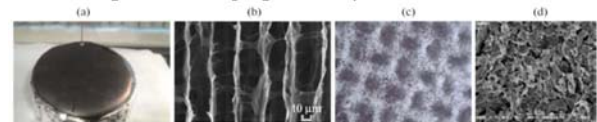


Fig. 5. Graphene structures for the study of evaporation rates. (a) Graphene layer saturated with water; (b) mesostructure of the graphene layer; (c) graphene on mesoporous aluminum pores 0.2–5.0 μm ; (d) structure of the graphene layer (pores 25–150 nm).

2.3 Model chip cooling using an active thermal interface

The use of nanoporous two-dimensional materials as active thermal interfaces for cooling electronic devices is an extremely important task. The modes of cooling of electronic chips were studied using nanoporous graphene obtained by the formation of laminated graphene structures (similarly shown in Fig. 5b).

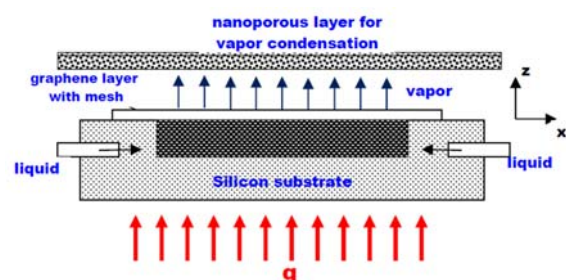


Fig. 6. Schematic of an experimental nanoporous graphene evaporation cell.

The layout of the experimental nanoporous cell for studying chip cooling is shown in figure 6. For studying the cooling rate of the model chip, in addition to non-contact thermometry, a set of thermocouples and a high-speed high-resolution infrared camera Artcam-320 were used. The results of the experiments showed that from the initial temperature of 55°C, due to the evaporative cooling of the nanoporous graphene structure, the substrate is cooled down to 28°C in about 40-55 seconds. The cooling rate in this case is about 0.675 degrees per second. This means that the removal of steam to the external environment or to the receiver makes it possible to remove a heat flux of more than 120 W/m², which is comparable and even higher than when boiling in microchannels.

Mathematical models of evaporative cooling of the microchip were developed, the calculation results were compared with experimental data. Such a comparison is shown in the figure 7.

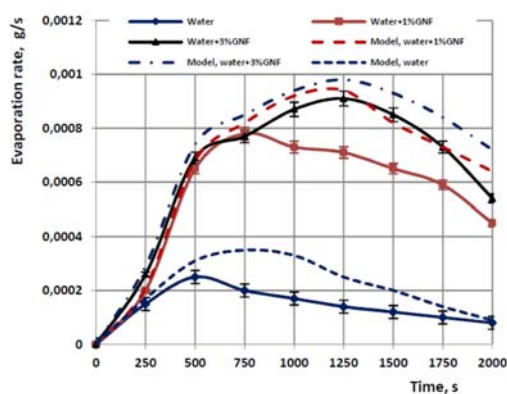


Fig. 7. Evaporation rates of various liquids using graphene nanochannels and nanopores.

2.4 Heat and mass transfer enhancement using two-dimensional materials

The mechanism of heat and mass transfer enhancement during nucleate boiling using graphene nanofluids or graphene substrates (in the form of graphene microfilms or special graphene inserts) is now fully mastered. The main thing that affects growth of the critical heat flow (CHF) and heat-transfer coefficient is the high thermal conductivity of graphene and the formation of a nanoporous layer on the surface itself or near it, which contributes to the generation of vapor inside nanopores. This leads to increased bubble generation during boiling, liquid movement to the base of the bubble, and efficient evaporation near “dry” spots, as shown in figure 8 [3]. Here is a picture of the deposition of graphene nanoflakes on the heat-exchange surface, which leads to the formation of places with efficient generation of microbubbles and their rapid growth due to the nanoporosity of the layer and its high thermal conductivity.

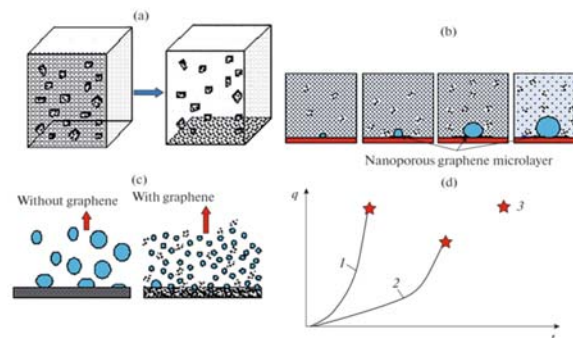


Fig. 8. Formation of a layer of graphene deposits from the heating surface, (b) the formation of a nanoporous graphene microlayer, (c) generation of microbubbles inside the nanoporous layer on the heating surface, and (d) the dependence of the heat flux q temperature t (boiling curve). (1) Graphene substrate or graphene nanofluid; (2) without graphene; (3) critical heat flow.

2.5 Freezing of nanofluid droplets with inclusions of two-dimensional materials

Of particular interest are two-dimensional materials for freezing and crystallization processes, since nanocomponents affect the crystallization rate and the morphology of the resulting structures. This is especially well observed for nanofluid droplets with nanocomponents of two-dimensional materials. Some examples of such processes using graphene nanoflakes (GNF) are presented below.

The freezing of water + graphene nanofluid droplets (graphene nanoflakes), as well as water + TiO₂ + graphene hybrid nanofluids on a cooled substrate, were studied. A thermoelectric cooler was used as a cooling system, which made it possible to have a substrate temperature in the range of -40 - -5 °C. The studies were carried out with a concentrated nanofluid, in which the mass concentration of graphene varied from 1% to 15%. Droplet morphology and freezing and crystallization rates were studied using the Kruss system.



Fig. 9. Water + GNF (5%), $t_{\text{freeze}} = 1\text{min } 35\text{s} \pm 3\text{s}$.

The figure 9 clearly shows, when a solution of water with GNF freezes, the phenomenon of purification of water from impurities occurs, GNF is collected from above.

The influence of an external magnetic field on the crystallization of graphene liquids was studied, since graphene nanoflakes acquire a certain orientation in a magnetic field. In all experiments on the freezing of nanofluid droplets, 30 μl drops were used. The temperature is maintained constant -45 °C or -70 °C. It was assumed that due to the magnetic properties of graphene, the freezing morphology of the drop would change. Unfortunately, due to the dark color of graphene

and the high concentration of graphene nanoflakes, it was not possible to observe the movement of the crystallization front, however, high-speed video recording showed the chaotic movement of graphene particles under the influence of thermal microcurrents. As a result, after crystallization, a cone-shaped peak was formed at the top (Figure 10); full crystallization time - 70 sec.

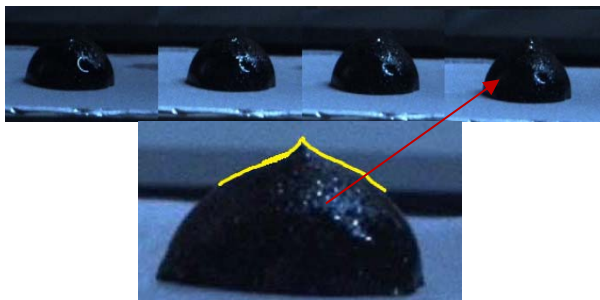


Fig. 10. Formation of a cone on the surface of a frozen drop (Graphene (3%) + water).

Preliminary data were also obtained on the effect of a constant magnetic field on the morphology and crystallization rate of graphene nanofluid droplets. The influence of magnetic fields on the shape and morphology of graphene nanocolloid freezing has not been revealed, because due to the rapid freezing of the droplet, graphene nanoflakes do not have time to line up along the magnetic lines.

As a result of studies of the freezing of droplets of graphene liquids, it was noted that the crystallization front velocity and the morphology of frozen droplets change compared to the case of pure water. The picture of the formation of heterogeneous nuclei of the crystalline phase on graphene nanoflakes is shown in the figure 11. Graphene flakes actively become centers of nucleation (crystallization) of water, leading to a faster number of centers and the formation of crystallization zones. Since the crystallization front moves from the cold substrate to the top of the hardening drop, it passes through the region of active crystallization centers at a higher speed.

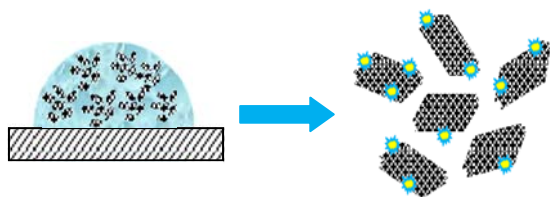


Fig. 11. Formation of heterogeneous nuclei of the crystalline phase on graphene nanoflakes.

The above analysis shows that for energy technologies the use of two-dimensional materials can be of great interest, since it opens up new opportunities for improving many processes and technological solutions.

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