Active thermal interface graphene nanocomposites for thermal control of electronic and power devices

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Abstract. New experimental and calculated data are presented for active thermal interface materials, in which heat is removed not only due to high thermal conductivity, but also due to the evaporation of liquids, for example, water, inside a nanoporous graphene structure. It is shown that such active thermal interfaces may be new systems of active thermal control.

1. Introduction
The development of modern and promising electronic and energy devices requires ever more efficient thermal control systems for thermal stabilization and management of thermal conditions [1,2]. Until now, thermal control systems have been divided into two broad categories. The first is thermal interface materials (TIM), i.e., passive materials to reduce the thermal boundary resistance between different blocks of devices, for example, a processor and a heat sink (e.g., a radiator). The second is active cooling systems (based on convective or evaporative cooling, for example, evaporative heat pipes). However, recent developments of new nanomaterials, including graphene, graphene nanocomposites and other two-dimensional materials (boron nitride, aluminum nitride, molybdenum disulfide, etc.) allow developing and creating active thermal interface materials (active TIM), which simultaneously reduce thermal boundary resistance (Kapitza resistance at interfaces of various materials), and cool such interfaces due to either microchannel or evaporative cooling [1]. A significant step towards the creation of active TIM was the discovery of non-trivial capillary hydrodynamics of working fluids, in particular, water, inside porous graphene nanocomposites, which enables their quick delivery to the evaporation surface through the quasi-laminar structure of graphene nanoclaps [2-6].

In this work, we experimentally and theoretically investigate the main processes in active TIM, including thermohydrodynamics of flow and heat transfer inside quasi-laminar structures of graphene nanoflakes with different numbers of monoatomic thickness of graphene plates and study the processes of surface evaporation from graphene nanocomposites in a wide range of temperatures from room temperature up to Leidenfrost temperature and above. It is shown that the fast flow of water and other working fluids is associated with nontrivial capillary hydrodynamics of the non-Poiseuille type, and heat transfer inside such structures is associated with efficient heat transfer (low boundary thermal resistance between graphene nanoflatter and fluid flows due to a sharp increase in the velocity of fluid sliding along the surface - the Navier effect in the hydrodynamics of nanostructures [1]). The processes of wetting and evaporation of droplets of working fluids are investigated in different temperature ranges, and the dependences of the droplet evaporation rates on
the heterogeneity and roughness of the surface are shown, which is important for the correct choice of technologies for the manufacture of new materials for active TIM.

2. Materials and method

The experimental cell consisted of a silicon heated substrate, a container inside which an evaporating liquid was supplied (this work presents data only for water and aqueous graphene nanofluids), a graphene structure block placed inside steel meshes of copper or stainless steel, and consisting of a nanoporous structure steam condensation unit. The condenser could force condensed liquid into the cooling unit (or similar to heat pipes) (Figure 1).

Graphene nanoflakes with an average size of 10-30 μm (thickness of 1.5-3.5 nm) were received from Graphene Institute Ltd (Russia). Chemically clean graphite microparticles of ~300 μm were used. Cooper M1(Cu>99.6%) or stainless-steel mesh with cell side size of 0.3 mm and wire diameter of 0.1 mm supplied by TDMC, Russia, were used as a mesh. A nanoporous oriented layer of graphene nanoflakes before its placement inside the experimental cell is shown in Figure 2. Graphene nanoporous oriented structures were fabricated by the original "domino method" - the stacking of graphene flakes with a flow of rotating liquid through a narrow slit with a gap of about 1 mm.[7] Graphene nanoflakes had a thickness of 1.5-3.5 nm and lateral size from 20 to 100 microns, and a substrate was made of these nanoflakes for active thermal control (high thermal conductivity and highly efficient evaporative cooling through nanopores). Photo and electron microscopy of the samples is shown in Figure 3. The temperature of the silicon substrate varied from 25 to 65 °C. It is clear that the evaporation rates and cooling efficiency increased with an increase in the substrate temperature. The substrate temperature was measured with thermocouples and heat flux sensors. The temperature was measured with an accuracy of about 0.5 °C. The evaporation rate was measured by an accurate electronic balance inside the nanoporous capacitor, as well as by the liquid flow rate through the heating unit.

![Figure 1. Schematic of an experimental nanoporous graphene evaporation cell](image1)

![Figure 2. Graphene structure (wick) with mesh for placement inside the evaporation unit](image2)
3. Cooling the model chip using active thermal interface material

In our work, to observe the cooling rate of the model chip, in addition to contactless thermometry and a set of thermocouples, a high-speed high-resolution infrared camera Artcam-320 is used. An infrared thermogram is shown in figure 4. It is clearly seen that from an initial temperature of 55 °C due to evaporative cooling of the nanoporous graphene structure after about 40 seconds, the substrate is cooled to 28 °C. The cooling rate is thus about 0.675 degrees per second. This means that due to the removal of steam to the external environment or to the receiver, a heat flux of more than 120 W/m² can be removed.

4. Evaporation rate data

In addition to pure liquids, we were the first to study the evaporation of graphene nanofluids inside nanoporous structures. We investigated both the evaporation of pure liquids, in particular distilled water, and nanofluids based on graphene nanoflakes of various lateral sizes (from 10 μm to 60 μm). Naturally, the evaporation of graphene nanofluids occurred inside structures with large pores (from 10 to 100 μm). It was quite surprising that graphene nanofluids penetrated through the graphene structure with negligible resistance, practically forming a denser layer in the upper part. As a result of the experiments, it was found that when the concentration of graphene in the nanofluid was no more than 1%, there was practically no decrease in the evaporation rate. Preliminary data demonstrated that such fluids heat up and evaporate more efficiently, as shown by the empirical data in Figure 5.
Figure 5. Evaporation rates of various liquids using graphene nanochannels and nanopores

The physical mechanisms of the increased evaporation rate are not yet completely clear and require additional study. At the same time, the use of graphene nanofluids together with graphene nanoporous structures allow creating an active system of evaporative cooling of a continuous cycle, which is extremely important for a large number of applications. The obtained experimental data on the evaporation of water and aqueous graphene nanosuspensions with mass concentrations of 1% and 3% are shown in Figure 5.

5. Mathematical models

A feature of evaporation from oriented graphene nanostructures is nontrivial capillary hydrodynamics - a strong influence of the boundary conditions on the liquid - graphene plate surface on the movement of the meniscus of the interface (almost complete water sliding without tangential resistance - (Navier boundary condition and significant slip length) [4]. In this work, we used models close to those developed in the [5].

5.1 Capillary-driven flow

The imbibition of liquid into a nanoporous structure occurs when the solid–vapor specific surface energy ($\sigma_{sv}$) is greater than the solid–liquid specific surface energy ($\sigma_{sl}$). This usually occurs when the contact angle is less than 90°. The driving force for imbibition is characterized by the Young–Laplace equation

$$\Delta p = p_l - p_v = 2\sigma_{lv}\Gamma$$

where $\Delta p$ is the local capillary pressure, $p_l$ is the local liquid pressure at the liquid–vapor interface, $p_v$ is the pressure of the vapor phase, $\sigma_{lv}$ is the liquid–vapor surface tension, and $\Gamma$ is the local mean curvature of the liquid surface.

In contrast to work [5], where the Brinkman equation (or an analogue, the Darcy equation) was used for the flow of a liquid inside a porous structure, in this study we describe the flow of a liquid inside a graphene structure based on non-slip flow. In this case, the slip length significantly exceeded the characteristic scale of nanopores $L_s>>\delta$ ($L_s~50$ nm, $\delta~3-5$ nm).

5.2 Heat transfer

Heat in thermal control devices is generated due to Joule heating and is transferred to the liquid vapor interface through the combined solid-liquid matrix by the heat conduction mechanism. Further, heat is dissipated by convection, heat conduction and thermal radiation.
into the environment. Typically, thermal control systems use a heat transfer coefficient
\( \alpha = q(T_s - T_\infty) \), where \( q \) is the steady state heat flux dissipated by the graphene nanostructures (wick), \( T_s \) is the temperature at the solid interface, and \( T_\infty \) is the temperature of the far ambient field. The effective thermal conductivity of graphene nanostructures is dependent on the working fluid, the solid material and nanostructures and operating conditions. In the simplest case, the following model can be adopted (the study shows that the complication of the model insignificantly affects the final result)

\[
\lambda_{\text{eff}} = \lambda_s \frac{2 + \lambda_s / \lambda_l}{2 + \phi(1 - \lambda_s / \lambda_l)} - 2\phi(1 - \lambda_s / \lambda_l)
\]

where \( \lambda_s, \lambda_l \) are the thermal conductivities of the solid and liquid, and \( \phi \) is the porosity. When using nanofluids, the quantity is replaced by the effective thermal conductivity of the nanofluid (\( \lambda_l \rightarrow \lambda_{l, \text{eff}} \)).

5.3 Vapor flow
The mass flow of vapor during evaporation can be determined by the following relationship

\[
\dot{j}_v = \rho_m \phi \dot{u}_v - \rho_m D_v \nabla \phi
\]

where \( \dot{j}_v \) is the vapor mass flux vector, \( \rho_m \) is the mixture (air + vapor) density, \( \phi \) is the vapor mass fraction, and \( D_v \) is the diffusivity of vapor in the gas (or mixture of gases). The evaporative mass flux is related to the evaporative heat flux by \( q_v = j_v \alpha_v \), equivalent thermal resistance is \( R_v = (T_s - T_\infty) / j_v \alpha_v S \).

Using the above model, the rates of evaporation of various liquids (water and water suspensions of graphene) have been calculated. These calculated data are presented in Figure 5, which also shows experimental data in the study of evaporation from graphene oriented nanostructures.

Unfortunately, within the framework of the used model, there is no good agreement between theoretical and experimental data, which, first of all, indicates the shortcomings of the existing models of evaporation from nanostructures. Note that the results of the calculations give data exceeding the evaporation rate found experimentally. It should be especially emphasized that for the case of liquid sliding inside graphene nanochannels and evaporation from the surface of the meniscus inside the channel, an interesting situation may arise - the liquid inside the channels can move much faster (slip boundary condition) than the liquid-vapor interface. As far as we know, such cases have not been previously considered within the framework of mathematical models.

In our opinion, it is precisely in these processes that the nontrivial capillary hydrodynamics of liquids inside the nanochannels manifests itself. Therefore, in addition to the importance of further constructing models of vapor transport in the external environment, it is necessary to more consistently consider capillary nanohydrodynamics inside channels, especially when it concerns two-dimensional materials such as graphene and its structure.

5.4. Cooling
The fraction of heat dissipated by evaporation was determined by subtracting the perceptible cooling and parasitic heat loss from the heating source. The heat flux used for cooling was calculated from the ratio of the energy balance

\[
q_c = \frac{[\dot{j}_s + \dot{j}_l]C_p(T_\text{sat} - T_\infty)}{S_{\text{Cool}}}
\]
where $q_c$ is the heat flux for cooling, $j_v$ is the vapor mass flux, $j_L$ is the evaporation loss, $C_p$ is the specific heat capacity of the working fluid, and $S_{Cool}$ is the cooling surface area. The table 1 shows the calculation results and experimental data on the dependence of heat fluxes during cooling on the type of working fluids and the heat transfer coefficient.

Table 1. The dependence of heat fluxes

| Working fluids | $\alpha$, W/cm$^2$K | Maximum heat flux, W/cm$^2$ | Publication |
|----------------|----------------------|----------------------------|-------------|
| Water          | 9.6                  | 140                        | [6,8]       |
| Water          | 14.8                 | 180                        | [6,8]       |
| Water          | 38                   | 390                        | [6,8]       |
| R-245fa        | 39.7                 | 550                        | [6,8]       |
| Pentane        | 18.4 (th – 20.2)     | 230 (theory – 244)         | [this work]|
| Water          | 24.7 (th – 20.2)     | 297 (th – 316)             | [this work]|
| Water+GNF1%    | 31.2(th – 34.8)      | 340 (th – 369)             | [this work]|
| Water+GNF3%    | 34.7(th – 34.8)      | 365 (th – 369)             | [this work]|

6. Conclusions
As a result of experimental studies and on the basis of the developed mathematical models we have revealed active thermal interfaces, in which, in addition to high thermal conductivity, heat removal is carried out by evaporative cooling of graphene nanoporous structures. In addition to ordinary liquids (for example, water), nanofluids, including graphene nanocolloids, can also be used. It has been established that in the future such active TIMs can replace passive TIMs and provide the necessary thermal control of energy and electronic devices.

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