Thermocapillary waves formation at the interface of hydrocarbons and graphene-like nanofluids

Y V Paharukov¹,², F K Shabiev¹,², R F Safargaliev¹,², B S Ezdin³, A E Zarvin³ and V V Kalyada³

¹ Tyumen State University, 6 Volodarsky Street, Tyumen, 625003, Russia
² Tyumen Industrial University, 38 Volodarsky Street, Tyumen, 625000, Russia
³ Novosibirsk State University, 2 Pirogov Street, Novosibirsk, 630090, Russia

E-mail: pacharukovyu@yandex.ru

Abstract. The paper presents the study of supramolecular structuring forming a transition region at the hydrocarbon – nanofluid interface resulting from synergistic effect by the interaction of multilayer graphene planar nanoparticles and silicon carbide nanoparticles covered with graphene layers (Core-shell). During the film formation on the interphase, filamentous formations were obtained, which resulted from interaction with thermocapillary waves. It was found that the structure of the filamentous formation was influenced by the composition and concentration of nanofluids.

1. Introduction
To date, the interest of researchers in nanofluids is very profound, which is reflected in numerous literature reviews over the past ten years [1-7]. This increased interest is related to the unique physical and chemical properties of nanofluids, which depend on the species of the base fluid, as well as type, size, and nanoparticle concentration of the nanosuspension. Fluids based on graphene-like nanostructures (GLNS) such as single-layer graphene, graphene oxide, reduced graphene, multilayer graphene, and graphene with quantum dots are of particular interest. The thermal conductivity of graphene-like nanostructures (5300 W/(m K) for single-layer graphene [8]) exceeds the thermal conductivity of copper by an order of magnitude. The thermal conductivity of GLNS also exceeds that of nanofluids based on other materials [9]. Thus, in [10], an increase in the thermal conductivity of GLNS compared to the base liquid (distilled water) was shown, which amounted to 4.9 W/mK – for graphene oxide-based GLNS, and 6.8 W/mK – for graphene.

The thermophysical properties of GLNS, like all nanofluids, depend strongly on the concentration of nanoparticles. In most cases, regardless of the base fluid, the thermal conductivity increases linearly with increasing graphene-like nanoparticle concentrations. Thus, [11] shows an increase in the GLNS thermal conductivity based on graphene oxide by 97% when adding particles at a concentration of 0.02 wt.%. As for metal nanofluids, metal oxides, carbides, etc., the viscosity of GLNS also depends on the concentration of nanoparticles. For the viscosity of the nanofluids, the Batchelor formula is valid, \( N_B = 1 + 2.5 \phi + 6.2 \phi^2 \), where, \( N_B \) is the relative viscosity, \( \phi \) is the nanoparticle concentration. This change in rheological properties negatively affects the performance of nanofluids.

There are several approaches to solve this problem. The simplest solution is to reduce the concentration of nanoparticles. Then the thermal conductivity coefficient will decrease. Another
solution is to select the base fluid. However, here, several problems may appear. Another way is to use combinations of different nanostructures, i.e., using hybrid nanofluids. The review of periodicals [7] describes in detail hybrid GLNS with a combination of different nanostructures. Improved thermal properties in hybrid GLNS result from a synergistic effect when planar graphene nanoparticles interact with other nanostructures.

Creating a structured flow of nanoparticles also should lead to an increase in thermal conductivity. The combination of a synergistic approach and flow structuring should presumably lead to a significant increase in thermal conductivity. As known, the flow of a thin layer of liquid at the interface is characterized by the presence of structures that are formed under the influence of instability mechanisms [12]. In [13], thermocapillary waves were formed at the phase interface of the limiting hydrocarbon with an aqueous graphene suspension. At such a phase interface, a transition layer is formed in the form of a film about 50 nm thick, consisting of ordered graphene nanoparticles and hydrocarbon molecules [13].

The purpose of this work is to study the formation of a structured film on the phase interface of hydrocarbon-GLNS. Water-based fluids with multilayer graphene nanoparticles and Core-shell structures were used as GLNS. The paper considers variations of nanofluids with graphene and Core-shell nanoparticles separately, as well as hybrid GLNS, and graphene + Core-shell.

2. Materials and methods

Carbon nanoparticles and Core-shell structures were synthesized using a high-performance process – rapid cyclic compression in a chemical reactor [14-16]. Graphene nanofluid (GNF) was obtained as a result of the ultrasonic dispersion of polycrystalline graphite [17]. Nanofluid based on Core-shell nanoparticles (C-spf) was obtained by the same method.

Films of graphene and Core-shell nanoparticles were obtained at the phase interface of paraffin-graphene nanofluid. To do this, molten paraffin was placed on the surface of the nanofluid at a temperature of 60°C. Then, for 3 hours, the system was kept in the thermostat at the same temperature. After forming a transition region at the interface, the system was cooled to room temperature for 2 hours with a small temperature gradient (∇T=1K / mm).

3. Results and discussion

The size and shape of particles in GLNS were determined using the atomic force microscope Ntegra Aura (NT-MDT) and the scanning electron microscope MIRA 3 (TESCAN) (figures 1a, b). Particles from the fluids were deposited on a single silicon crystal. From the particle analysis, it can be concluded that graphene particles are predominantly cylindrical with a diameter D = 30 ±5 nm.

Core-shell structures formed by SIC crystals of 3-7 nm in size, which are covered with several layers of graphene, are shown in figure 2. Nanostructures were obtained with a significant excess of up to 50% of carbon relative to the stoichiometric balance 2SiH4 + C2H2 -> 2SiC + 5H2. The pressure in the adiabatic compression chamber reached 8 MPa in the cyclic compression-rarefaction process. The compression time of the precursors was less than 0.05 sec, which corresponds to a process periodicity of 10 Hz. The images were obtained by the HRTEM method using the JEM-2010 electron microscope (JEOL, Japan). Figure 3 shows images of particles at lower magnification. It can be seen that particles with a size of 40-50 nm form dendritic couplings-aggregates of many round-shaped particles.

Three nanofluids were obtained by ultrasonic dispersion: GNF with a concentration of 0.01 g/l; C-sNF with a concentration of 0.01 g/l; and hybrid nanofluid obtained by mixing GNF and C-sNF of the same concentrations. As a result of the experiment on the formation of ordered thermocapillary structures, a film was obtained on the surface of paraffin (figure 4).
Figure 1. Images of graphene nanoparticles on a silicon substrate obtained by (a) – SEM, (b) – AFM semi-contact method.

Figure 2. Nanoscale SIC crystallites, covered with 2-5 layers of graphene – (Core-shell structure).

Figure 3. Core-shell nanoparticles forming extended dendritic aggregates (resolution 100 nm).

The film results from graphene nanoparticles' self-organization and paraffin hydrocarbon molecules. A film of liquid paraffin on the surface of a graphene suspension passes into a solid state as a result of a first-order phase transition. The wax hardening front develops from the surface to the center. As a result, the phase transition heat is released at the front (Stefan's problem). With a slow heat removal at the front, a temperature gradient is created, which, as a result of the process nonlinearity, generates thermocapillary waves in a narrow surface layer. Besides, the edge effects associated with the meniscus create a slight tilt, which causes the film to move.

To understand the border area hardening mechanism, the film chip was studied using SEM. The SEM image shows a transition region of graphene nanoparticles on the paraffin surface of about 200 nm in size (Figure 5a). Upon a detailed examination of the film, it can be seen that the graphene film consists of ordered layers with a thickness of 10 to 50 nm (Figure 5b).
Figure 4. Filamentous structures at the interface: a – GNF-paraffin; b – C-sNF-paraffin; c – hybrid nanofluid-paraffin. d - 3D image of the filament structure formed on the crest of a capillary wave at the GNF-paraffin interface.

Figure 5. SEM image of a cleaved graphene film obtained at the GNF – paraffin interface: (a) a graphene film on the paraffin surface; (b) graphene film structure.

The formation of a structured region at the hydrocarbon-nanofluid interface may indicate a low surface tension. Therefore, it can be assumed that nanoparticles are directly involved in the structuring of the transition region. It is known that the thermocapillary wavelength depends on the interfacial
surface tension. Then, presumably, by controlling the film structure parameters, varying the concentrations and composition of nanofluids, it is possible to influence the structure of the filament, that is, to control its length and thickness. By controlling the threads structure and their directions, one can set the directed heat exchange at the phase interface. The reason that the displacing ability of nanofluids is reduced is the increase in viscosity of the base fluid. It is known that an increase in the concentration of nanoparticles in the base fluid leads to a quadratic increase in the viscosity of nanofluid [18].

Conclusions
The filamentous structures obtained on the crest of the thermocapillary wave formed at the GLNS-paraffin interface depend on the nanofluid composition. The filament formation is more intensive when using a hybrid nanofluid consisting of multilayer graphene and Core-shell nanoparticles. The research results can be used to create heat sink technologies.

Acknowledgments
The study was conducted using the shared equipment at the Applied Physics Center at NSU’s Physics Department with the financial support of the Ministry of Science and Higher Education of the Russian Federation, project No. FSUS-2020-0039.

References
[1] Saidur R, Leong K Y and Mohammad H A 2011 Renew. Sustain. Energy Rev. 15 1646–68
[2] Huminic G and Huminic A 2012 Renew. Sustain. Energy Rev. 16 5625–38
[3] Solangi K H, Kazi S N, Luhur M R, Badarudin A, Amiri A, Sadri R, Zubir M N M, Gharekhhani S and Teng K H 2015 Energy 89 1065–86
[4] Sadeghinezhad E, Mehrali M, Saidur R, Mehrali M, Tahan L S, Akhiani A R and Metselaar H S C 2016 Energy Convers. Manag. 111 466–87
[5] Devendaran D K and Amirtham V A 2016 Renew. Sustain. Energy Rev. 60 21–40
[6] Leong K Y, Ong H C, Amer N H, Norazrina M J, Risby M S and Ku A K Z 2016 Renew. Sustain. Energy Rev. 53 1092–105
[7] Babu J A R, Kumar K K and Rao S S 2017 Renew. Sustain. Energy Rev. 77 551–65
[8] Seol J H, Jo I, Moore A L, Lindsay L, Aitken Z H, Pettes M T, Li X, Yao Z, Huang R, Broido D, Mingo N, Ruoff R S and Shi L 2010 Science 328 213–6
[9] Bahiraei M and Heshmatian S 2019 Energy Conversion and Management 196 1222–56
[10] Yu W, Xiea H, Wang X and Wang X 2011 Phys Lett A 375 1323–8
[11] Chen L, Xu C, Liu J, Fang X and Zhang Z 2017 Sol Energy 148 17–24
[12] Shatskii E N, Chinnov E A, Zaitsev D V, Semenov A A and Kabov O A 2017 Tech. Phys. Lett. 43 1080–3
[13] Pakharukov Y V, Shabiev F K, Mavrinsski V V, Safargaliiev R F and Voronin V V 2019 JETP Let. 109 615–9
[14] Ezdin B S, Yatsenko D A, Kalyada V V, Ichshenko A B, Zarvin A E, Nikiforov A A, and Snytnikov P V 2020 Chem. Eng. J. 381 122642
[15] Ezdin B S, Yatsenko D A, Kalyada V V, Zarvin A A, Ichshenko A V, Nikiforov A A, and Snytnikov P V 2020 Data in Brief 28 104868
[16] Ezdin B S, Kalyada V V, Ischenko A V, Zarvin A E, Nikiforov A A and D A Yatsenko 2018 IOP Conf. Series: Journal of Physics 1115 042043
[17] Pakharukov Y V, Shabiev F K and Safargaliiev R F 2018 Tech. Phys. Let. 44 130–2
[18] Rudyak V Ya 2013 Adv. Nanoparticles 2 266–79