

Hierarchy of self-organization and self-assembly processes exemplified by the growth of films at the „hydrocarbon–graphene nanofluid“ interface

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A comprehensive study of the interaction of graphene nanoparticles and hydrocarbons is performed in order to examine the mechanisms affecting the formation of ordered nanocrystalline structures at the interface of n-octane and graphene-containing nanofluids. An experimental setup of a proprietary design and a method for growing a film from hydrocarbon molecules and graphene nanowafers are presented. X-ray diffraction analysis and molecular mechanical modeling methods are used to determine the structure of the crystalline film. It is demonstrated that the film growth mechanism is associated with the processes of self-organization and self-assembly of graphene nanoparticles at the nanofluid–hydrocarbon interface. It is found that the hierarchy of self-organization and self-assembly processes determines the final structure of the film. It is demonstrated that the self-organization and self-assembly processes may be controlled by adjusting the initial temperature of the system and the concentration of graphene particles in the nanofluid.

Keywords: graphene, graphene-based nanofluids, nanostructured film, self-organization, self-assembly.

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Introduction

The concept of emergence of order from chaos (self-organization of a large number of elements in an open system) has been developed back in the middle of the 20th century by I. Prigogine [1].

Self-organization is a phenomenon that is observed in open dissipative systems. Structural order emerges due to nonlinearity. Such systems are characterized by correlation lengths (uniform over large distances). The following self-organization processes are known: Benard cells, laser radiation, the Belousov–Zhabotinsky reaction, spiral waves [2,3]. Self-assembly is the effect of local self-organization at the molecular level. Such structures tend toward equilibrium. A combination of self-organization and self-assembly processes is actualized as self-organized criticality in the presence of medium motion. An example here is provided by peaking-type processes that assume an explosive nature near the critical point [4]. Self-organization is the result of nonlinearity. At large spatiotemporal scales, new structures form at the interface between different media as a result of self-assembly of nanoparticles [5,6]. These phenomena may be observed at the interface between different nanofluids. The transition from an unstable state to a stable one occurs under non-equilibrium conditions. The passage from non-equilibrium to a metastable state provides the conditions

for self-assembly [7]. Thus, a hierarchy is established: non-equilibrium–self-organization–metastability–self-assembly.

Self-assembly is a phenomenon that is observed under equilibrium or quasi-equilibrium conditions. Langmuir films are one of the most striking and thoroughly studied examples of self-assembly. The interest in this phenomenon has surged with the advent of nanofluids, since it is an inexpensive and relatively simple way to obtain a molecular layer. Langmuir–Blodgett films method are currently experiencing another revival of interest, as evidenced by a 2020 review [8]. Two-dimensional materials, such as graphene, graphene oxide, etc. [9,10], may be the most exciting new materials in the so-called Langmuir–Blodgett nanoarchitectonics. Thermodynamic equilibrium (lack of vibrations and fluid flows at the interface) is a condition necessary to avoid destruction in Langmuir monolayers; i.e., this is an equilibrium process. However, self-assembly of thin films by the Langmuir–Blodgett method on the surface of a fluid with fluid flows at interphase boundaries has been demonstrated in several studies. A simple method for synthesis of carbon nanofilms with an approximate thickness of 10 nm from carbon nanoparticles was proposed in [11]. In the present study, films were fabricated using a beaker rotating about its own axis. Thin films of carbon nanoparticles formed as a result of motion-induced assembly.

Table 1. Characteristics of nanoparticles used in the study

Parameter	Graphene nanoparticles
Density, g/cm ³	2.1
Number of layers	3–5
Thickness, nm	1–2
Average lateral size of nanoparticles, nm	2000

Carbon frameworks of various shapes, such as nanowhiskers, nanotubes, nanosheets, nanocubes, and their microscopic counterparts [12,13], are obtained by liquid deposition. The authors of [14] have demonstrated the production of highly oriented arrays of microtubes (with fullerene C₇₀ being their structural unit) with the use of liquid deposition and convective flows. Films with highly oriented C₇₀ microtubular frameworks featured enhanced photoluminescence compared to C₇₀ molecules in powder form. The method of convective vortices for carbon nanoparticle orientation was also used to prepare scaffolds for orienting cell growth with aligned C₆₀ nanowhiskers of different curvatures; cells were then cultured on these scaffolds [15].

As in the case of Benard cells, the emergence of self-organized convective vortices leads to self-assembly of graphene nanoparticles from graphene-containing nanofluids (GNFs) on a substrate [16]. The authors of this study have demonstrated the formation of a porous structure, which may alter the micromorphology, wettability, and roughness of the surface. The heat transfer coefficient increases by more than 80 % as a result. The self-organization of convective flows during boiling of an aqueous nanofluid and the self-assembly of reduced graphene oxide nanoparticles have also been used in [17] to demonstrate the formation of ordered structures on the substrate surface. The thermal conductivity coefficient and critical heat flux were increased by 340 % and 203 %, respectively. The authors of [18–21] associate the observation of van der Waals waves at the hydrocarbon–graphene nanofluid interface with a film formed as a result of self-organization of graphene nanoparticles. A film forming as a result of self-organization of graphene particles also alters the optical properties of nanofluids (e.g., induces quenching of photoluminescence [22]).

Making use of a certain hierarchy of non-equilibrium and equilibrium states, one may grow various films, including those with given parameters, with their properties differing from the properties of their counterparts obtained by either equilibrium (e.g., the Langmuir method) or non-equilibrium (e.g., the drying droplet method) synthesis techniques.

Thus, what is discussed here is a novel mechanism for the formation of nanostructured objects at interphase boundaries with the involvement of carbon nanoparticles. This mechanism is presumably associated with the establishment of hierarchy between self-organization and self-assembly. In the present study, we use the growth of films at GNF–octane

interphase boundaries as an example to find out how the processes of self-organization and self-assembly affect the structure.

1. Materials and methods

1.1. Materials

Chemically pure n-octane was chosen as the hydrocarbon. This choice (C₈H₁₈) was dictated by the experimental methodology for synthesis and analysis of the formation of a quasi-crystalline nanostructured film and the subsequent mathematical description of this phenomenon.

Graphene with a thickness of 3–5 layers (NanoTechCenter Ltd., Tambov, Russia) was used as graphene nanoparticles. The characteristics of these graphene-containing nanoparticles are presented in Table 1.

Graphene nanofluids were synthesized in two stages: at the first stage, the initial graphene powder was introduced into a container with distilled water and stirred mechanically with a magnetic stirrer for 2 h; after that, it was filtered through a filter with a maximum pore size of 500 nm to remove large nanoparticle agglomerates. At the second stage, the obtained solution was subjected to ultrasonic dispersion for 30 min. This was followed by vacuum filtration through a filter with a maximum pore size of 100 nm.

1.2. Methods

1.2.1. Experimental setup and experimental procedure

A setup of an original design (Fig. 1) was constructed in order to examine the growth of films at the octane–GNF interphase boundary. The process of film growth was studied in several stages. At the first stage, prepared GNFs of various concentrations were poured into heat-insulated bowl 1 connected to a liquid thermostat. The system was then thermostatted. The temperature at which film formation was monitored varied from 0 °C to 60 °C in 1 °C increments. The absolute error of the thermostat thermometer is $\Delta T \pm 0.01$ °C. A temperature sensor (platinum thermistor) with absolute error $\Delta T = \pm 0.001$ °C was positioned on the bowl surface. To reduce heat loss, the system was separated from the environment by heat-insulating box 4. Octane was also thermostatted in advance in a heat-insulated chamber at the same temperature. At the second stage, octane was poured

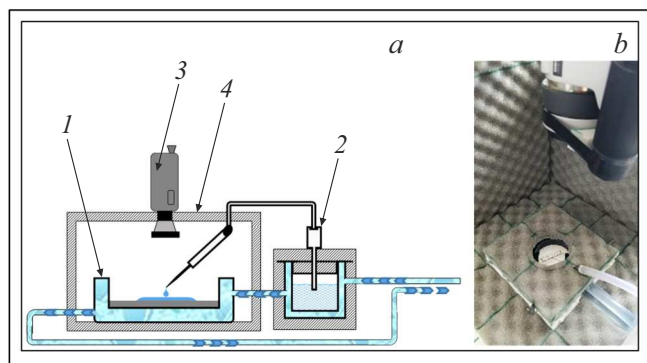


Figure 1. Experimental setup: *a* — diagram of the setup: 1 — heat-insulated bowl connected to a liquid thermostat, 2 — hydrocarbon supply and injection system, 3 — video microscope, and 4 — heat-insulating box; *b* — photographic image of the interior of the setup.

into bowl 1 via supply and injection system 2 and formed a thin layer on the GNF surface. Video microscope 3 was then used to record the process of film formation at the octane–GNF interphase boundary. The video from microscope 3 was processed, and the film growth process was studied.

1.2.2. Analysis of the film structure

The structure of films was examined by X-ray diffraction analysis using a DRON-7 X-ray diffractometer (OAO Burevestnik, St. Petersburg, Russia) ($\text{CuK}\alpha$ - radiation with $\lambda = 1.5406 \text{ \AA}$; scintillation detector). The interplanar distances in clusters were estimated using the least squares method in the PDWin [23] package.

The interaction of hydrocarbon molecules with graphene layers was modeled in several stages. At the initial stage, the structures of an *n*-octane molecule and a graphene sheet were modeled in the density functional approximation in the Siesta package using the B3LYP exchange-correlation functional and a two-exponential basis of Gaussian atomic functions (6-31G) supplemented by polarization functions at all atoms of functional groups (6-31G(d,p)) [24,25]. At the next stage, the obtained simulation results were used to specify the interaction of hydrocarbon molecules with graphene. The interaction calculations were performed using the atom–atom potential method. It was assumed that the interaction is mediated by van der Waals forces only and does not lead to distortion of hydrocarbon and graphene molecules. The Buckingham potential was chosen for the determination of energy of the van der Waals interaction between hydrocarbon molecules and graphene:

$$\varepsilon = \sum_{i=1}^{N_1} \sum_{j=1}^{N_2} (-A_{ij} \cdot r_{ij}^{-6} + B_{ij} \cdot \exp(-\alpha_{ij} \cdot r_{ij})), \quad (1)$$

where r_{ij} are the distances between each i -th graphene atom and each j -th atom of the hydrocarbon molecule; N_1

and N_2 are the numbers of atoms in graphene and the hydrocarbon molecule, respectively; and A_{ij} , B_{ij} , and α_{ij} are the coefficients determined from the experimentally measured van der Waals bond energies in various compounds for carbon–carbon, carbon–hydrogen, and hydrogen–hydrogen interactions [26]. The specific interaction energy per atom of the hydrocarbon molecule was calculated next: $E = \frac{\varepsilon}{N}$.

In all cases, it was assumed in modeling that the graphene layer had the shape of a circle with the molecule (or molecules) under study positioned in the center of it at a certain distance from the plane. The graphene layer diameter was chosen so that the specific energies of interaction between the molecule and the most distant carbon atoms of graphene differed by less than 0.01 %.

The energy of interaction of the hydrocarbon molecule and graphene was calculated for different positions relative to the graphene layer, which included linear shifts and rotation of the molecule about the longitudinal axis and the axis perpendicular to the graphene plane. Calculations were carried out both for a single molecule and for a group of 2–16 molecules. The results of calculations of specific energies were used to identify the most advantageous position of the molecule relative to the graphene layer, and the final geometry of the formed structure was then determined.

2. Results and discussion

2.1. GNF characteristics

A nanofluid with a mass fraction of particles of 0.1 % was obtained after ultrasonic dispersion of graphene particles in distilled water. The zeta potential measured with a NANOTRAC Wave II Zeta analyzer (Microtrac MRB) was 30 mV. The characteristic size of particles and their structure after ultrasonic dispersion are presented in Fig. 2. The inset in Fig. 2 shows the particle size distribution obtained using the dynamic light scattering method (NANOTRAC Wave II Zeta). The distribution reaches its maximum at the size of $\sim 1000 \text{ nm}$, which is consistent with the specified sizes of original particles (Table 1). The particle thickness also remained unchanged at $\sim 2 \text{ nm}$, which corresponds to 2–5 graphene layers (Fig. 2, *a*).

2.2. Self-organization and self-assembly of graphene particles at the octane–GNF interface

When octane is applied to the GNF surface, a droplet forms, and convective flows are formed along its perimeter (Fig. 3, *a*).

A convective flow entrains graphene particles, forming condensation sites. As a result of such self-organization, periodically distributed formation droplets (the so-called necklace with its „beads“ growing over time) emerge along the perimeter. This is illustrated by Fig. 3, *b*, where condensation sites formed at temperature $T_0 = 20^\circ \text{C}$ and initial particle mass concentration $C_0 = 0.0050$ in the GNF

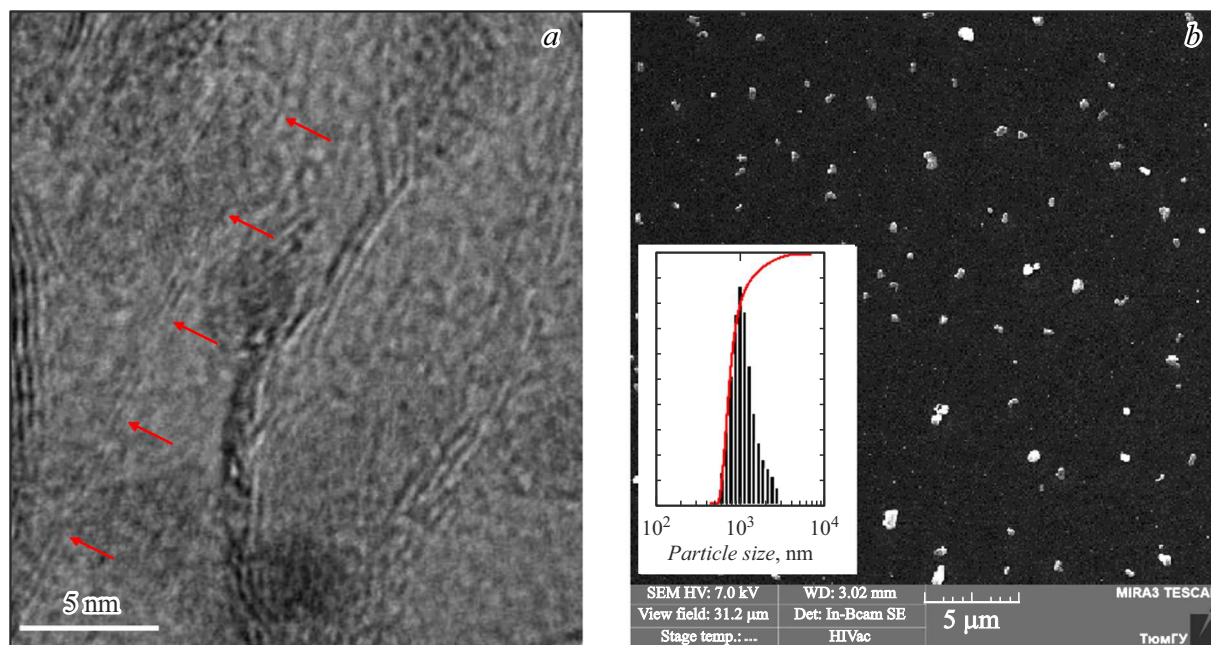


Figure 2. Characterization of graphene nanoparticles after the GNF preparation: *a* — TEM image of graphene particles obtained using a JEM-2010 electron microscope (JEOL, Tokyo, Japan) (a three-layer graphene particle is indicated with arrows); *b* — SEM image of particles obtained using a MIRA 3 scanning electron microscope (TESCAN) on a silicon wafer after water removal. The particle size distribution is shown in the inset.

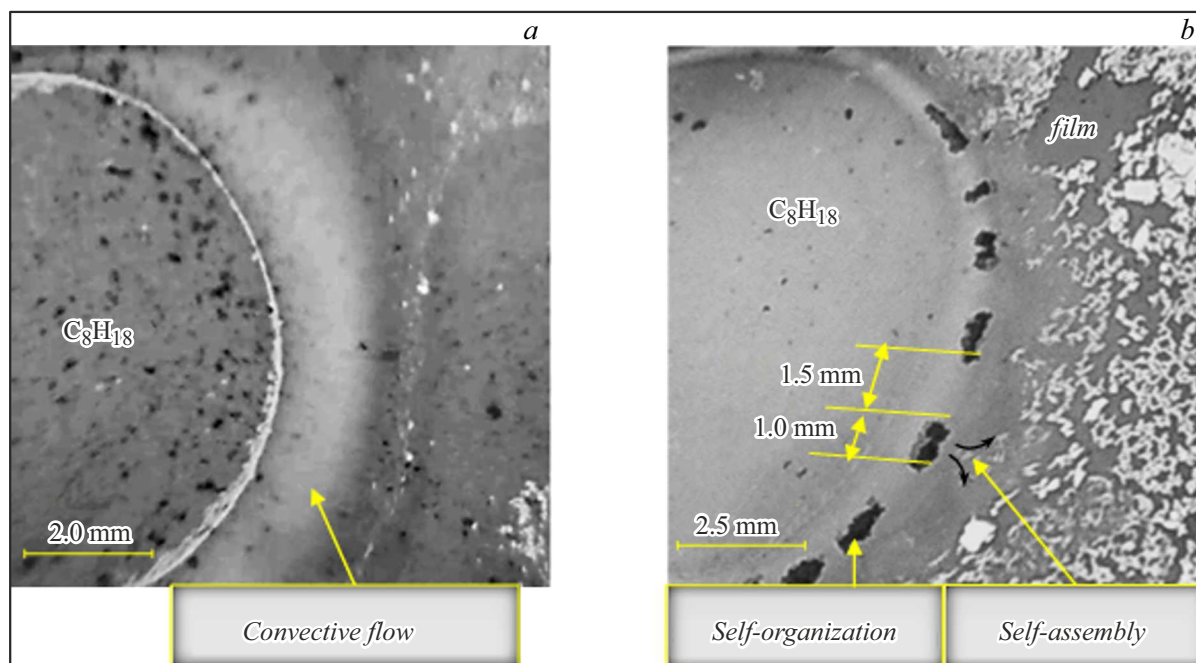


Figure 3. Self-organization and self-assembly in the process of film growth: *a* — the initial moment of formation of self-organized flows of graphene particles at the GNF-octane interface; *b* — self-organization and self-assembly (indicated by arrows) at the GNF-octane interface $\Delta t = 54$ s after the start of the process.

are imaged $\Delta t = 54$ s after the start of the process. Their length is $r_c = 1.0$ mm, and the distance between them is $\Delta l = 1.5$ mm. As can be seen (Fig. 3, *b*), graphene particles are ejected from these „beads“ by the flow and continue

moving along the interface with subsequent self-assembly. A film forms in the process of this self-assembly (Fig. 3, *b*).

Variations of initial concentration of particles C_0 and initial temperature T_0 of the system induce changes in the pro-

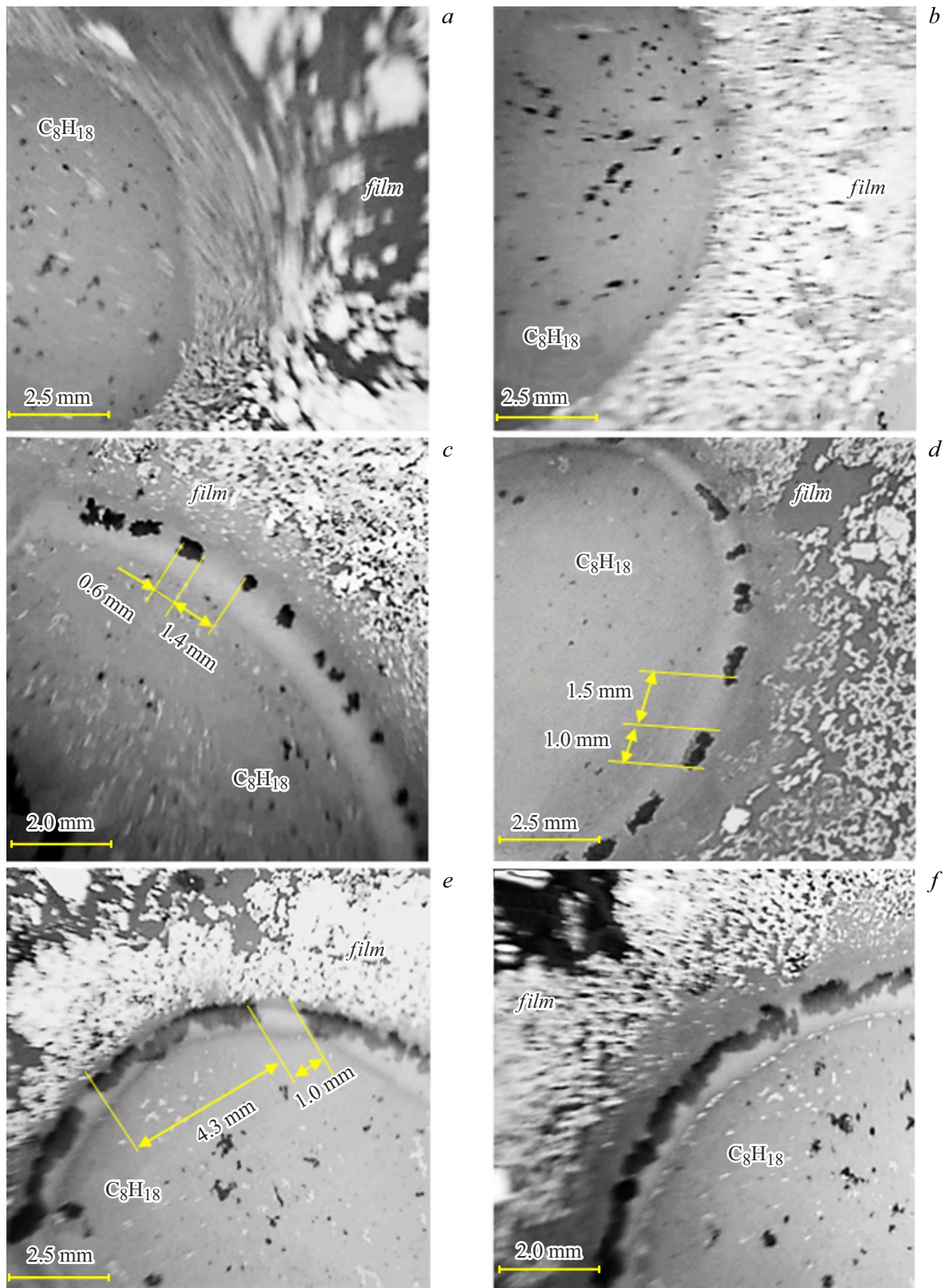


Figure 4. Self-organization and self-assembly in the process of film growth under various conditions: *a* — at temperature $T_0 = 10\text{ }^{\circ}\text{C}$ and concentration $C_0 = 0.0025$; *b* — at temperature $T_0 = 10\text{ }^{\circ}\text{C}$ and concentration $C_0 = 0.0050$; *c* — at temperature $T_0 = 20\text{ }^{\circ}\text{C}$ and concentration $C_0 = 0.0025$; *d* — at temperature $T_0 = 20\text{ }^{\circ}\text{C}$ and concentration $C_0 = 0.0050$; *e* — at temperature $T_0 = 30\text{ }^{\circ}\text{C}$ and concentration $C_0 = 0.0025$; and *f* — at temperature $T_0 = 30\text{ }^{\circ}\text{C}$ and concentration $C_0 = 0.0050$.

cesses of self-organization and self-assembly (Fig. 4). Specifically, necklaces do not form at temperature $T_0 = 10^\circ\text{C}$ and initial mass fraction of particles $C_0 = 0.0025$, and the resulting film has a fractal structure (Fig. 4, *a*). A two-fold increase in the initial concentration of particles ($C_0 = 0.0050$ at $T_0 = 10^\circ\text{C}$) does not lead to the emergence of necklaces (Fig. 4, *b*).

When the temperature increases to $T_0 = 20^\circ\text{C}$, necklaces with condensation sites with length $r_c = 0.6\text{ mm}$ and distance $\Delta l = 1.4\text{ mm}$ between them form at concentration $C_0 = 0.0025$ (Fig. 4, *c*). At concentration $C_0 = 0.0050$ and temperature $T_0 = 20^\circ\text{C}$, the necklace structure changes: $r_c = 1.0\text{ mm}$ and $\Delta l = 1.5\text{ mm}$ (Fig. 4, *d*). At temperature $T_0 = 20^\circ\text{C}$, the film structure for concentration $C_0 = 0.0050$ is denser than the one for $C_0 = 0.0025$.

A further increase in temperature also alters the structure of both the necklaces and the film; i.e., it affects the process of self-organization and self-assembly. Specifically, at temperature $T_0 = 30^\circ\text{C}$ and concentration $C_0 = 0.0025$, $r_c = 4.3\text{ mm}$ and $\Delta l = 1.0\text{ mm}$ (Fig. 4, *e*); at concentration $C_0 = 0.0050$, the condensation region becomes continuous (i.e., $\Delta l = 0\text{ mm}$), and $r_c = 2\pi R = 42.5\text{ mm}$ (Fig. 4, *f*).

2.3. Results of structural analysis of films

The results of X-ray diffraction analysis are presented in Fig. 5 and Table 2. Figure 5 shows the diffraction patterns of films obtained at different initial concentrations C_0 and temperatures T_0 . Comparing these results, one may identify common peak 002 inherent in all diffraction patterns that corresponds to the interplanar distance between graphene layers ($2\theta \approx 26^\circ$, $d_{002} = 3.4\text{ \AA}$; Fig. 5). It is evident that the films obtained at growth temperatures of 20°C and 30°C

Table 2. XRD analysis of the film obtained at a temperature of 20°C and concentration $C_{02} = 0.0050$ and the result of computer simulation

$2\theta_{\text{max}}$, deg	I_{max} , a.u.	d , $\text{\AA}$	$d_{\text{comp.sim}}$, $\text{\AA}$
14.2410	7725.3	6.21	—
16.4071	4414.8	5.39	—
16.7829	17408.9	5.28	—
17.1203	29639.4	5.18	5.18
20.5887	4255.8	4.31	4.39
20.918	6745.4	4.24	—
21.2138	11351.2	4.18	4.16
23.0071	14224.5	3.86	4.03
23.6339	5728	3.76	3.75
25.3157	1110	3.52	3.56
25.7378	3566	3.47	—
26.1227	1029.4	3.39	3.35

have a certain ordered structure, while the films obtained at 10°C and 60°C have a pronounced diffraction pattern of an amorphous material (the upper and lower curves in Fig. 5, respectively). However, films synthesized at the same temperature but different concentrations differ slightly. Specifically, the films obtained at a temperature of 20°C feature significant differences in the peaks corresponding to 23° , and the films formed at 30°C are characterized by slight differences in the peaks corresponding to 17° . All diffraction patterns are characterized by the presence of an amorphous halo, which is indicative of an amorphous phase in the structure.

The results of an in-depth analysis of the diffraction pattern of the film obtained at a temperature of 20°C and concentration $C_{02} = 0.0050$ are presented in Table 2 and Fig. 6, *a*.

The results of computer simulation are shown in Figs. 6, *b, c*. The XRD data (Table 2) agree well with the results of computer modeling (Figs. 6, *b, c*). It was found in computer modeling of the interaction between octane molecules and a graphene sheet that hydrocarbon molecules are capable of forming ordered structures in the form of crystalline clusters.

It was also established that the most energetically favorable orientation of octane molecules is their positioning at an angle of 72° to the graphene plane (Fig. 6, *b*). Thus, the crystalline structure in question is of triclinic symmetry with translation vectors of $4.16\text{ \AA}$, $4.39\text{ \AA}$, and $2.59\text{ \AA}$ (Fig. 6, *c*). The distance between the formed crystallite of octane molecules and the graphene sheet is $3.56\text{ \AA}$ (Fig. 6, *b*).

The results of calculation of the specific energy of interaction of hydrocarbon molecules and graphene are listed in Table 3. It can be seen that when a quasi-crystal is formed, a cluster of 32 molecules has the most favorable state with a specific energy of -10.746 kJ/mol . However, when a disordered structure (model of an amorphous state) is formed from 16 octane molecules, the specific energy is

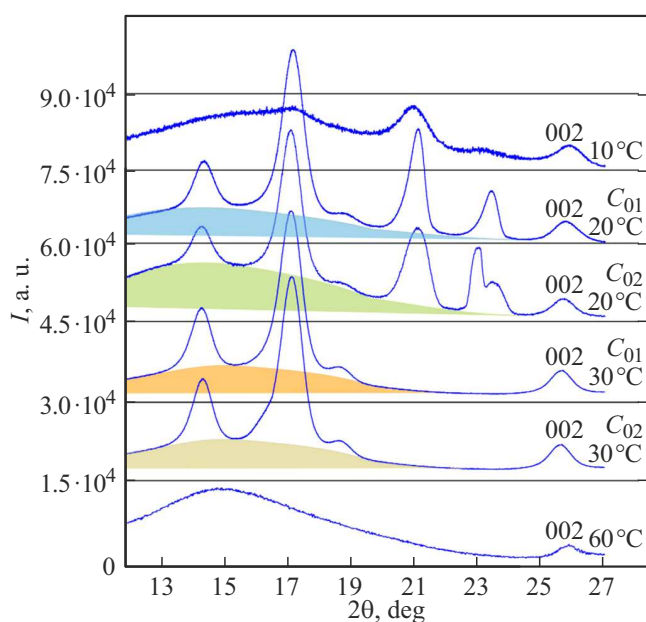


Figure 5. X-ray diffraction patterns of films obtained at temperatures of 10°C , 20°C , 30°C , and 60°C and mass concentrations $C_{01} = 0.0025$ and $C_{02} = 0.0050$.

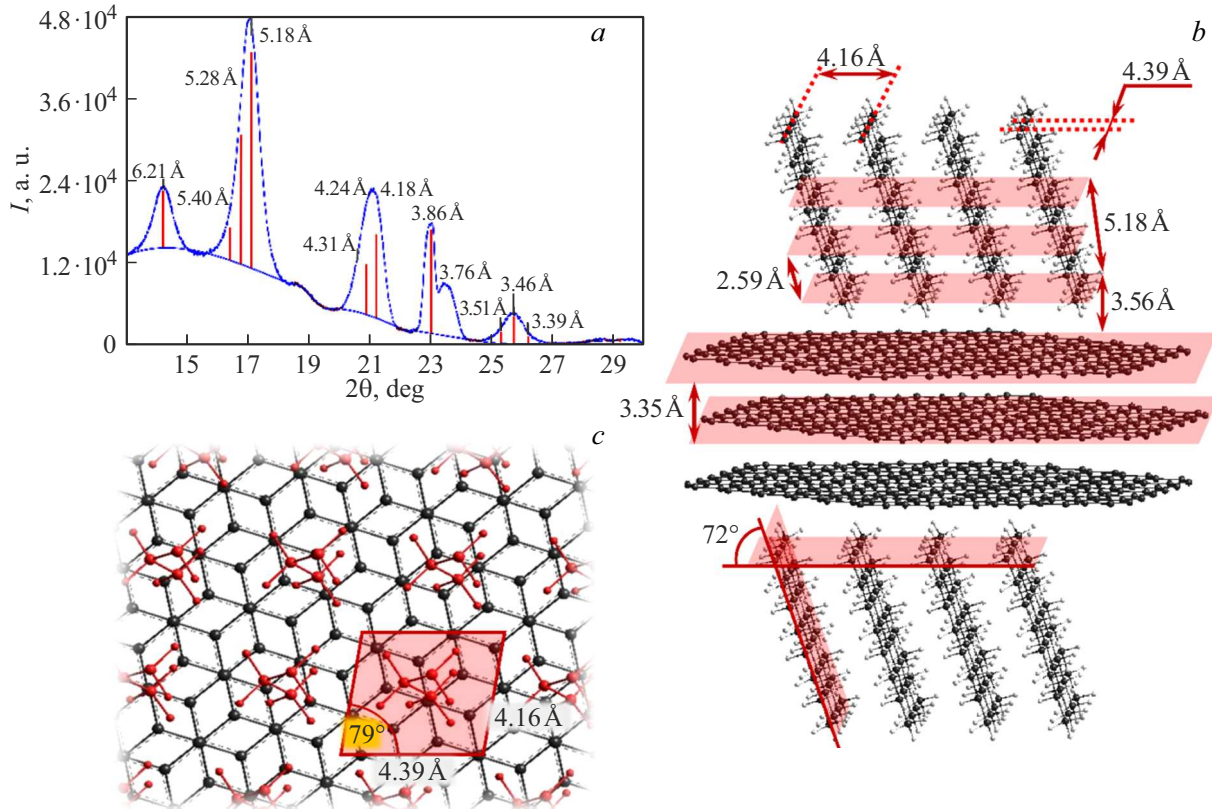


Figure 6. Structural analysis: *a* — XRD analysis of the film obtained at a temperature of 20 °C and concentration $C_{O_2} = 0.0050$; *b* — computer simulation of the formation of a cluster of 32 octane molecules on the surface of three-layer graphene; *c* — top view.

−9.878 kJ/mol, which differs by 8% from the crystalline state.

2.4. Hierarchical cosubordination of self-organization and self-assembly

Let us discuss in detail the process of film growth in the context of self-organization and self-assembly phenomena. Let us consider this process at the boundary of an octane droplet applied to the surface of GNF with a mass fraction of particles of 10^{-4} . Figure 3, *a* makes it clear that a convective flow of particles from the depth to the surface is established; thus, a region with a high concentration of particles emerges near the GNF–octane interface. This region is unstable, and a flow along the boundary forms within it. Spatially non-uniform concentration distribution $C(r)$ is established in this flow. The concentration is a function of the specific point coordinate with an average value of C_0 . Let us divide the area along the boundary into cells with volume $V_a = N_a \xi^{-3}$, where N_a is the number of nanoparticles in a cell and ξ is the cell size. Each cell has its own concentration C_a , where a is the cell index (Fig. 7). The concentration changes at the cell boundaries due to mass transfer. In this formulation of the problem, concentration fluctuations in transition from one cell to another may be considered Poissonian.

It is fair to assume that the flow of nanoparticles may be substituted with rearrangements of cells, since these cells differ from each other only in the number of particles contained in them. Rearrangements of cells translate into partitioning of the entire region into blocks with volume V_b and concentration C_b :

$$C_b = \frac{1}{V_b} \int C(r) dV = \frac{1}{n} \sum_{a=i}^{nb} C_a \approx C_0, \quad (2)$$

where $n = \frac{V_b}{V_a}$, $i = (b-1)n + 1$, $V_b > V_a$.

The set of $\{C_b\}$ values forms a certain conformation for which statistical weight $W(C)$ and energy $E(C)$ may be determined. Let us write statistical sum Z of the system for a certain conformation with concentration C_0 :

$$Z(C_0) = \prod_{a=i}^m \int \left\{ W(C) e^{-\frac{E(C)}{kT}} \delta \left[\frac{1}{m} \sum_{a=i}^m (C_a - C_0) \right] Q(C_0) \right\} dC_0, \quad (3)$$

$$Q(C_0) = \prod_{b=1}^{p-1} \delta(C_b - C_{b+1}),$$

where function $Q(C_0)$ corresponds to the selection of block configuration and $p = \frac{V_0}{V_b}$ is the number of consolidated blocks.

Table 3. Specific energies of the van der Waals interactions of octane molecules with graphene

Specific energy E , kJ/mol	n-octane C_8H_{18}
Single molecule, horizontal orientation	−6.446
32 molecules, horizontal orientation	−9.878
Single molecule, vertical orientation	−4.251
Domain of 32 molecules, vertical orientation	−10.746

Concentration C_b may be regarded as a continuous function of coordinates: $C_b \approx C(r)$.

Switching from discrete partitioning to a continuous one, we obtain $C = f(r)$. Let us write an expression for the free energy of the system. In the present formulation, this expression takes a simple form:

$$F(C) = \int [f(z) + K(\nabla C)^2 - h(C - C_0)^2] dV, \quad (4)$$

where K is the order parameter and h is the contribution of energy dissipation in the process of motion of nanoparticles.

Within this model, cell-to-cell concentration fluctuations manifest themselves as changes in concentration at the cell boundaries. Relying on the self-consistent field theory [27], one may determine the equilibrium value of concentration C (as a manifestation of self-organization) from the condition of the thermodynamic potential minimum. In accordance with Euler's variational equation, we obtain

$$\frac{\partial F(C)}{\partial C(r)} = -K\nabla^2 \delta C + \frac{d^2 f}{dC^2} \delta C - h\delta C = 0. \quad (5)$$

With contribution h being small, it may be assumed that $C = C_0 + \delta C$. The solution of Eq. (5) characterizes the δC distribution induced by a point external field source $h(r)$ and is defined by Green's function $G(r)$:

$$C(r) = (4\pi K r_c)^{-1} e^{-\frac{r}{r_c}}, \quad (6)$$

where r_c is the correlation radius.

A steady is observed at

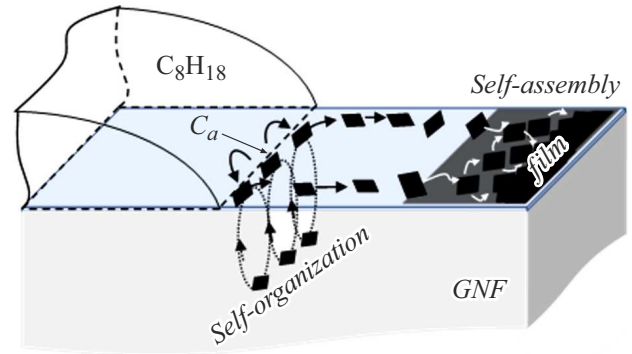
$$r_c = 2\pi \left[\frac{1}{2K} \left(h - \frac{d^2 f}{dC^2} \right) \right]^{-\frac{1}{2}}. \quad (7)$$

The $\langle \delta C(r) \cdot C(0) \rangle$ characteristic fluctuation size matches $G(r) = \frac{1}{T} \langle \delta C(r) \cdot \delta C(0) \rangle$. Therefore, $\delta C(r)$ may be regarded as an order parameter within the cellular model.

As a result, nanoparticles form clusters along the nanofluid-hydrocarbon interface (Fig. 7). This periodic distribution of nanoparticles is precisely the phenomenon of self-organization.

Let us estimate correlation length r_c based on tabular and experimental data. Order parameter K should be related to the interaction of a graphene sheet and octane. Let us use the expression proposed in [28] to estimate K :

$$K = nk_B T a^2, \quad (8)$$

**Figure 7.** Model illustrating the flows of self-organized particles with their subsequent self-assembly.

where a is the radius of interaction between a graphene sheet and an octane molecule, n is the concentration of molecules (m^{-3}), k_B is the Boltzmann constant, and T is the system temperature.

Let us rewrite expression (8):

$$K = a^2 R T \frac{\rho}{M}, \quad (9)$$

where R is the universal gas constant, ρ is the density of octane, and M is its molar mass. Transforming expressions (7) and (9) in tandem, we then obtain

$$r_c = 2\pi a \sqrt{\frac{2RT}{U - \Phi}}, \quad (10)$$

where $U = h \frac{M}{\rho}$ (J/mol) is the depth of the potential well of interaction of an octane molecule with a graphene plane, $\Phi = \frac{d^2 f}{dC^2} \frac{M}{\rho}$ (J/mol) — energy density of the system in a certain thermodynamic state.

Let us assume that $a \sim 10^{-9}$ (m) is the van der Waals interaction range, $T = 300$ K, and $U \approx 10^4$ J/mol; then, $r_c \approx 1 \cdot 10^{-6} \sqrt{\frac{1}{10^4 - \Phi}}$ (m). Thus, at $\Phi \neq U$, correlation radius $r_c \approx 1 \mu m$; at $\Phi \rightarrow U$ $r_c \approx 1$ mm (Fig. 8). This is close to the result obtained in the experiment (Fig. 3). At $\Phi = U$ $r_c \rightarrow \infty$; however, this state is unstable, and, as can be seen in Figs. 4, f, e, the r_c value increases.

To gain an understanding of the mechanisms of film growth as a result of self-assembly of formed nanoclusters, one needs to consider the features of first-order phase transitions in nanoobjects.

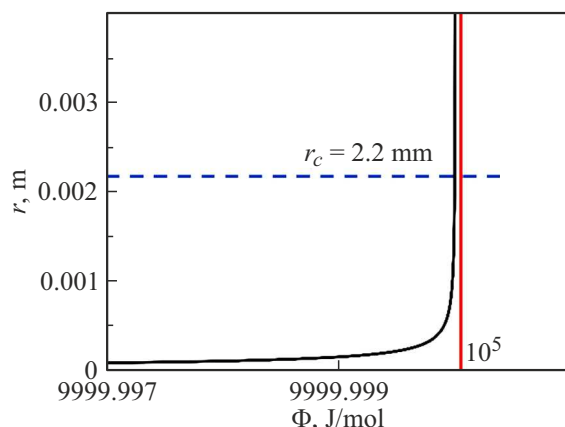


Figure 8. Analysis of the dependence of the correlation radius on the energy density of the system and the depth of the potential well of interaction of an octane molecule with a graphene plane (the line indicates the asymptote at $\Phi = U = 104 \text{ J/mol}$).

Such transitions in nanosystems are specific in that solid and liquid phases coexist within a certain temperature interval [29]. In the case at hand, this is manifested as the presence of octane molecules adsorbed on the surface of graphene sheets. When considering a molecular cluster as a system of bound atoms, one should separate configurational and thermal excitations. Thermal equilibrium is established within a time interval shorter than the time of transition between local minima of potential energy on the cluster surface. Only the configurational excitation remains at zero thermal excitation energy. The potential of interaction between neighboring atoms of different hydrocarbon molecules in a nanocrystallite is lower than the electron energy. According to the Born–Oppenheimer approximation, the entire system may be divided into atomic and electronic subsystems. Thermal relaxation occurs earlier in the atomic subsystem. Therefore, atoms (of neighboring molecules) tend to form a regular structure. This is seen in the results of both the XRD analysis and simulations (Figs. 5, 6). The crystallite surface is shaped by the pairwise interaction of atoms. The pairwise interaction is stronger than the collective one. The collective interaction is associated with thermal relaxation. If heat release is present, thermal relaxation becomes level with configurational relaxation, and the resulting continuous medium of octane molecules may be either crystalline or amorphous. With a further increase in heat release, thermal relaxation starts to lag behind configurational relaxation. This translates into dominance of the crystalline phase over the amorphous one. The diffraction patterns obtained at different temperatures and concentrations (Fig. 5) provide a clear illustration of this. Specifically, the amorphous phase is dominant at a temperature of 10°C . At temperatures of 20°C and 30°C , the crystalline phase is observed, but a pronounced amorphous halo is also seen (Fig. 5, colored region). With a further increase in temperature, the crystallization front velocity becomes greater than the phase transition time;

therefore, at a temperature of 60°C , only the amorphous phase is observed (Fig. 5, lower curve). Thus, cosubordination of self-organization of molecules, which pass (upon the establishment of local thermal equilibrium) into self-assembly with the subsequent formation of a crystalline phase, is observed. The self-assembly of molecules into crystallites (or the formation of amorphous states) is the result of emergence from a non-equilibrium state where the thermodynamic system was in self-assembly conditions.

Let us consider the hierarchical cosubordination of self-organization and self-assembly at the next stage of film formation. Growing in size due to the coalescence of small clusters into larger ones, clusters form self-organizing flows. A fraction of small clusters not involved in coalescence are ejected from the flow, which is illustrated in the model in Fig. 7 and is manifested as the formation of a film in Fig. 3, *b*. In the process of structure formation, edges and vertices have different energy values. The structure does not self-average (i.e., no spherical nuclei are observed). If heat release is present, thermal relaxation becomes level with configurational relaxation. With a further increase in heat release, thermal relaxation starts to lag behind configurational relaxation. This will take the system from a fractal state to an ordered one, which is illustrated in Fig. 3, *b*: a part of the film has an ordered structure, and the other part is fractal in nature. This behavior is the process of self-assembly of clusters. Hierarchical cosubordination of self-organization and self-assembly is also observed at this stage. The emergence of the system from a non-equilibrium state at the stage of self-organization (coalescence of self-organized flows of graphene particles at the nanofluid–octane interfaces) triggers the self-assembly scenario.

Conclusion

A nanostructured crystalline film forms due to the self-organization of graphene nanoparticles in a hydrocarbon. This was verified by the results of X-ray diffraction analysis. The molecular structure of films is set by the initial conditions of the system: the concentration of graphene particles in the GNF and the temperature.

The hierarchy of self-organization and self-assembly in these thermal processes plays a vital role. The emergence of a thermodynamic system from a non-equilibrium state in self-organization phenomena specifies the scenario for self-assembly, establishing the final structure of the nanostructured material (in the present case, a graphene film).

Another important result of the study is the possibility of controlling film growth. The effect of interface overheating provides an opportunity to control both the rate and the direction of growth of graphene films (e.g., through local heating). Therefore, the results of this study open up the possibility of developing a new method for application of graphene films with controlled geometry and structure at the molecular level.

Conflict of interest

The authors declare that they have no conflict of interest.

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