On thermal problems of the solar thermal multigeneration: new nanomaterials and working fluids

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Abstract: The study considers various thermophysical problems, including the processes of heating new nanomaterials and nanofluids, as applied to solar thermal multigeneration (steam generation and turbine and turbineless conversion into electrical energy), as well as thermoelectric generation (solar thermoelectric generation) using new nanomaterials, including graphene and its composites. The main unsolved problems of thermohydrodynamics and heat transfer in such systems are noted.

1. Introduction
The powerful turbine conversion power plants have known disadvantages, primarily associated with a large number of optical concentrators, the need for precise positioning of concentrated radiation on a container with a working fluid. Failure to meet one of these conditions known to lead to serious accidents, as happened at the power unit mentioned in [1-4].
Along with the purely thermal turbine conversion of solar radiation of the Planck spectrum, other types of conversion have been discussed in recent years, including those associated with multigeneration - the simultaneous use of not only a steam turbine, but also, for example, thermoelectric conversion [1,2].

2. The main thermophysical problems of solar multiconversion
In recent years, interest in solar thermal power engineering based on new materials and technologies has sharply increased [1-6]. The efficiency of various types of generation due to the conversion of solar radiation of the Planck spectrum is largely related to both the use of conversion technologies (steam generation - volumetric and surface with subsequent conversion of steam through machine (turbine) and electric generator conversion), and the thermoelectric generation, i.e., conversion of solar radiation heat with a high degree of its absorption in nanomaterials due to the use of modern and promising materials with high quality factor, as well as with hybrid conversion of solar radiation (part - photoelectric conversion, part - steam generation due to heating by Planck spectrum radiation, followed by thermoelectric or steam generation). Finally, the use of materials with phase transitions (for example, paraffin-graphene composites and their analogs), followed by the use of the heat of phase transitions in energy-efficient converters of low-grade heat or according to a thermo-electrical scheme. However, all the noted transformation methods can be combined and used as mult-
generation, the efficiency of which is related to the calculation of the efficiency of each of the channels. Studies have shown that in such a scheme there may be a synergistic effect, in which the total efficiency is not additive in terms of contributions from certain types of solar radiation conversion [7] (Figure 1).

**Figure 1.** Solar thermal multigeneration

2.1. Solar steam generation
In such problem statement, thermophysical problems play a decisive role, since the indicated efficiency largely depends on the mechanisms of absorption, distribution and transfer of heat [1]. At present, not enough attention is paid to works devoted to both the calculation of individual processes and model experiments on solar multigeneration. At the same time, it is well known that the first stage of considering such problems is directly related to the choice of materials that should have a number of important parameters. These parameters primarily include: high absorption coefficient of solar radiation, high heat capacity and thermal conductivity, low thermal boundary resistance, etc. Among such materials, in recent years, close attention has been paid to nanomaterials, in particular two-dimensional ones, including graphene and its nanocomposites, as well as nanofluids.

Solar thermal multigeneration can include several channels for using the solar radiation spectrum: from the optical absorption of photons with energy greater than the band gap – PV cells, to the almost complete absorption of the entire Planck radiation spectrum – thermoelectric (STEG) and machine (turbine or turbineless) conversion (Figure 2).

Numerous works on the selection of new nanomaterials and nanocomponents for intensifying the evaporation of water and generating steam with high efficiency have appeared recently [1-4]. In
particular, research is being actively carried out on graphene nanoporous structures, which show an extremely high degree of absorption of solar radiation, rapid heat transfer into the material, and a high evaporation rate (Figure 3).

![Figure 2. Steam generation processes using nanoplasmonics and nanophotonics](image-url)

This work formulates the main criteria for solar multigeneration, and some problems related to the mechanisms of radiation absorption in nanomaterials, heat transfer mechanisms and boundary thermal resistance, which significantly expand the class of heat transfer mechanisms in nanostructures [1]. In addition, the main advantages of using new thermoelectric materials in multigeneration at various temperature levels are indicated. For the first time, calculations of the conversion efficiency of solar radiation to the Planck spectrum in generation systems are carried out, the synergistic effects of such conversion are noted, and a map of the conversion modes of solar radiation based on new nanomaterials and nanofluids is presented. In addition, it has is shown that solar multigeneration of electrical and thermal energy can be very effectively combined with methods of desalination and obtaining clean drinking water based on the use of solar radiation concentrators.

![Figure 3. Nanoporous graphene structure [2] (left) and general view of a graphene coating for intense evaporation under the influence of solar radiation (on right)](image-url)

Figure 4 shows the data of our experiments on the propagation of solar radiation inside containers with various nanofluids. It is easy to see that the most effective absorption is observed in water with graphene nanoflakes (2–3 atomic layers, lateral size of 30–50 μm) [1]. The key mechanism associated with volumetric solar receivers for generating steam is nanoplasmonics - a strong improvement in the absorption of solar radiation, thanks to the mechanism of plasmon resonance. Localized surface plasmon resonance is an optical phenomenon where collective oscillations of free
conduction electrons in metal nanoparticles excite radiation with a wavelength comparable to or
greater than the particle size [3]. Materials with high conductivity, in particular, metal nanoparticles
such as gold, silver, and platinum, are highly efficient centers of absorption and scattering, although
they are very expensive for practical use [4].

Figure 4. Steam generation processes using nanoplasmonics and nanophotonics [1, 6]

The plasmon resonance wavelength can be controlled depending on the composition, size, geometry,
the width of the gap between the nanoparticles and the type of environment.

The generation of vapor upon heating of nanocomponents by solar radiation (nanoparticles of noble
metals, nanodiamonds, graphene flakes, etc.), as shown by numerous studies, cannot be fully
explained within the framework of the classical mechanisms of bubble nucleation [1,7]. First of all, it
should be borne in mind that the local plasmon heating is, as a rule, unsteady; therefore, the
temperature of the nanoparticles increases all the time. Second, the nanoparticles are so small that
their size is much smaller than the critical diameter of the heterogeneous nucleation of the vapor
phase; therefore, the equilibrium mechanism is unlikely. Third, the role of the boundary (interfacial)
thermal resistance between a nanoparticle and a liquid, as well as between a nanoparticle and the
resulting vapor phase, is completely unclear.

In this regard, it can be argued, based on modern research, that:
1. The mechanism of generation of photothermal bubbles around plasmonic nanoparticles differs
from the mechanism of generation of bubbles around microscopic and macroscopic absorbers
(including conventional heating surfaces):
   • the threshold value of bubble generation under solar irradiation significantly depends on the particle
     size and duration;
   • the mechanism of vapor phase generation during localized heating can be completely different from
     the mechanism of thermal conductivity during heat transfer from nanoparticles to the environment; at
     the same time, it may turn out that the heating of the liquid occurs under the influence of a near
     fluctuating electromagnetic field, the heat flux from which at ultra-small distances from the
     nanoparticle can be hundreds of times higher than the heat flux, according to the Stefan-Boltzmann
     relation; this mechanism has not been investigated at all, but the first results have shown its high
     efficiency;
   • an increase in the size of particles and their clustering, in some cases lead to a decrease in the
     threshold density and initial temperature for steam generation; this fact remains a mystery;
• localized heating of graphene flakes and other highly anisotropic heat sources depends both on the presence of doped nanoparticles inside such nanocomponents (the plasmon frequency and heating efficiency dependence) and on the characteristic dimensions (recall that graphene flakes have a thickness of 3 to 5 nm, and their longitudinal dimensions are tens of microns); the mechanism of the boundary thermal resistance between liquid and graphene flakes and its contribution to the mechanism of vapor generation are still unclear;
• bubbles generated by nanoparticles and nanocomponents can temporarily and spatially localize the thermal field induced by solar radiation and prevent additional heating of working fluids; these collective effects have not been studied experimentally or theoretically, although they play an important role for the efficiency of solar thermal power engineering;
• The mechanisms of floating vapor bubbles - thermal flotation, convective mechanism and their contribution to the efficiency of steam generation - have not been studied at all.
2. Optimization of the conditions for the generation of vapor bubbles can provide a minimum solar heat flux and, consequently, the maximum efficiency and selectivity of plasmon interactions through:
• optimization of the size of nanoparticles and their overall ionic state, in particular, the use of clusters of nanoparticles instead of single particles;
• optimal choice of the size and geometry of the container with the working fluid, if bubbles are generated in closed volumes.
3. The properties of optical scattering of photothermal bubbles provide the possibility of their detection with high sensitivity and time resolution.
Bubbles enhance optical scattering compared to plasmonic nanoparticles. At the same time, this leads to very strong additional scattering of the incident radiation, which requires an optimal choice of the optical thickness of the volume with the liquid.
The problems posed and methods for their solution allow us to take a fresh look at the problems of solar multigeneration, to determine materials, processes and technologies for efficient conversion of solar radiation of the entire Planck spectrum, which will determine further ways of implementing such technologies in engineering and industrial solutions.

2.2. Solar thermoelectric generation
Thermoelectric materials represent a unique opportunity in the field of converting solar radiation into electrical energy without the use of machines. The development of thermoelectric materials over the past decades has taken place in huge leaps, using the latest advances in nanotechnology and nanomaterials: growing semiconductor crystals, controlled doping, nanostructuring and two-dimensional confinement, as well as wave effects in phonon transfer, correlated electronic physics and unconventional transport in organic materials. In addition, the use of 2D materials can be called a promising direction. The search for new nanomaterials for solar thermoelectric conversion is associated with the fact that the figure of merit for them significantly increases due to a sharp decrease in the phonon and electronic thermal conductivity, since they are included in the denominator of the ratio for the figure of merit [8]. In addition, the temperature difference between hot and cold surfaces is essential [9-11].
Since it is the high absorption coefficient of nanomaterials, for example, graphene, that makes it allows obtaining high temperatures of the hot surface, a high temperature difference, up to several hundred degrees may be ensured.
The Seebeck coefficient of the sample increases substantially when that of the grain boundary is high and the thermal conductivity of the grain boundary is low. This can be understood with a simple 1D model

$$S = \frac{S_F (1 - \delta_{FB})/\lambda_F + S_{FB} (\delta_{FB}/\lambda_{FB})}{(1 - \delta_{FB})/\lambda_F + (\delta_{FB}/\lambda_{FB})}$$

Where $S_F$ is the Seebeck coefficient of the grain, $S_{FB}$ is for the grain boundary, $\delta_{FB}$ is the thickness of the grain boundary, and $\lambda_F$ and $\lambda_{FB}$ are the thermal conductivities of the grain and the grain boundary.
3. Results and conclusions
Today, a new approach to the selection of materials for solar thermal multigeneration has been formed. Efficient evaporation and vapor generation during surface and volumetric absorption, requires two-dimensional materials, among which the most accessible are graphene and graphene-based composites. This is primarily due to the high nanoporosity (in this case, almost all the pores are open), which forms long open channels of very small diameter - 1–2 nm). The nontrivial hydrodynamics of water in such channels leads to extremely fast movement inside them, the formation of a two-phase liquid-vapor interface with high curvature, and active evaporative heat and mass transfer. This makes allows actively generating steam with a high temperature (in a number of experiments with concentrators, solar radiation reaches a power density of 20 kW / m²), and the temperature can reach 650 °C. At the same time, capillary boiling is much more efficient than usual surface boiling, since overheating and steam generation occur inside nanoporous structures.

It has been established for thermoelectric generation that it is very efficient to use high-temperature thermodynamic cycles with a temperature difference between hot and cold surfaces above 200 °C (better, up to 400 °C). In this case, it is possible to use both silicon-germanium nanocomposites and nanostructures based on bismuth telluride, as well as graphene nanocomposites. To increase the efficiency of thermoelectric conversion, it is necessary to use materials with very low electronic and phonon thermal conductivity. The latter is possible, for example, in new nanomaterials with hydrodynamic electron flow regimes (electron drift motion). In this case, for a sharp decrease in phonon thermal conductivity, it is necessary to use nanomaterials with a small free path (for example, nanopolyycrystalline structures with a phonon path length of 3-5 nm). The Seebeck coefficient, power factor, and efficiency, ZT, can be increased by nanostructuring when energy barriers exist around the grain boundaries or embedded nanoparticles.

Acknowledgments
The work is supported by the Russian Science Foundation (Grant No. 17-19-01757).

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