Skoltech
Skolkovo Institute of Science and Technology

Jury Member Report – Doctor of Philosophy thesis.

Name of Candidate: Stepan Romanov

PhD Program: Physics

Title of Thesis: Single-walled carbon nanotubes as a source of ultrasound

Supervisor: Professor Albert Nasibulin

Name of the Reviewer: Oleg A. Sapozhnikov

I confirm the absence of any conflict of interest (Alternatively, Reviewer can formulate a possible conflict)	**Signature:** **Date: 23-09-2020**

The purpose of this report is to obtain an independent review from the members of PhD defense Jury before the thesis defense. The members of PhD defense Jury are asked to submit signed copy of the report at least 30 days prior the thesis defense. The Reviewers are asked to bring a copy of the completed report to the thesis defense and to discuss the contents of each report with each other before the thesis defense.

If the reviewers have any queries about the thesis which they wish to raise in advance, please contact the Chair of the Jury.

Reviewer's Report

Reviewers report should contain the following items:

- Brief evaluation of the thesis quality and overall structure of the dissertation.
- The relevance of the topic of dissertation work to its actual content
- The relevance of the methods used in the dissertation
- The scientific significance of the results obtained and their compliance with the international level and current state of the art
- The relevance of the obtained results to applications (if applicable)
- The quality of publications

The summary of issues to be addressed before/during the thesis defense

REVIEWER'S REPORT

Brief evaluation of the thesis quality and overall structure of the dissertation.

The thesis is devoted to the study of the physical processes associated with the operation of thermophones – thermoacoustic devices, in which sound is generated by heating a thin layer of an electrically conductive material when an electric current is passed through it. The heated layer leads to heating and thermal expansion of the near-surface layers of the medium, which leads to the generation of sound. Unlike previous studies on this topic, single-walled carbon nanotubes are considered as the material of the heating layer, due to which a low heat capacity per unit area is achieved and, as a consequence, the efficiency of sound generation is increased.

The dissertation work is a complete study combining theoretical and experimental research. Its scientific quality is high and corresponds to the level of typical PhD theses in physics. The structure of the thesis is standard, it consists of 5 chapters, the first of which is a short introduction, the second reviews the literature and describes the current state of research on the development of thermophones, the third describes the research methods, the fourth presents the results and discussion, and in the fifth chapter briefly summarizes the results obtained. It should be noted that the first and last chapters are relatively short (2-3 pages), i.e., the main presentation is contained in three central chapters.

The relevance of the topic of dissertation work to its actual content

The declared topic of the dissertation work is reflected in the title and in the abstract. The title "Single-walled carbon nanotubes as a source of ultrasound" reflects the actual content, although I would recommend using the term thermophone in the title, since, strictly speaking, it is not the nanotubes themselves that emit sound (they do not vibrate at all during the thermophone operation), but the thermal expansion of the medium that they heat up. However, this is just a soft recommendation. The abstract of the dissertation correctly presents its content.

The relevance of the methods used in the dissertation

Several modern research methods were used that made the results obtained convincing and interesting. Experimental methods are especially impressive. The method of producing nanotubes is described – by synthesized in a flow reactor by aerosol floating catalyst CVD method. To characterize the number of defects in the samples after Joule assisted purification in a vacuum, Raman spectroscopy was employed. In addition, UV-vis-NIR spectroscopy was used to characterize the nanotube films after Joule-assisted purification. Sound detection was performed using a B&K 4138-A-015 microphone. Temperature was controlled by the non-contact method based on measurements of radiation from the heated sample. As for the theoretical part, both the use of analytical formulas for analysis and finite-element modeling in the Comsol package were employed.

The scientific significance of the results obtained and their compliance with the international level and current state of the art

The results obtained are certainly of scientific value and correspond to the international level of research in this area of physics and technology. As noted in the dissertation work, despite a rather long history of research, effective thermophones have been made only in recent years, with the advent of new materials, including those based on nanotechnology. The fact that about a hundred patents on this topic have been issued in the last decade indicates the importance and timeliness of the research carried out. In addition to investigating the operation of the thermophone as such, the findings and new techniques presented in the dissertation are attractive. For example, I really liked the proposed encapsulation of nanotube films into atmosphere of inert gas, as well as covering the films with nanometric layer of Al_2O_3 to overcome oxidization problem at high temperature.

The relevance of the obtained results to applications (if applicable)

The dissertation work has direct path to applications. The proposed thermophones have unique properties, primarily in terms of frequency response – broadband nature and uniformity of the response, which allows undistorted radiation of signals of various waveform. In addition, nanotube films are flexible, which is often convenient for the manufacture of acoustic sources with adjustable directivity.

The quality of publications

The quality of publications is high. They include 7 journal paper, with the main results published in the high-ranked journals.

The summary of issues to be addressed before/during the thesis defense

I have several critical remarks:

p. 37, Eq. (1.8-2). Temperature should be a function of *x, y*, *z*, not just *x*, because the author claims to be studying thermophones of finite dimensions. Here, obviously, a one-dimensional approximation is considered. If so, this should be stated explicitly.

p. 37: The expression for the wave number q of the temperature wave seems to be incorrect. Indeed, if the representation (1.8-3) is substituted into the formula (1.8-2), then we get a dispersion relation of the form $-i\omega\rho_g C_g = -\kappa q^2$, whence it follows that $q = \sqrt{i\frac{\omega\rho_g C_g}{\kappa}} = \pm(1+i)\sqrt{\frac{\omega\rho_g C_g}{2\kappa}}$.
This clearly does not correspond to the expression $q = -(1-i)\sqrt{\frac{\omega\rho_g C_g}{2\kappa}}$ given in the text of the thesis.

p. 37: The definition $C_s = \rho_h h C_h$ contradicts the earlier statement that the thickness of the layer is equal to $2h$ (not h).

It is difficult to verify whether the indicated errors on p. 37 are just typos and whether they influenced the calculation results.

p. 39: Although the main idea of the estimate is clear, in formula (1.8-12) the upper limit of the integral is not infinity, but some finite distance, which is much larger than the temperature scale *l*, but much smaller than the acoustic wavelength. Note also that the corresponding conclusion can be made less vague and approximate if the process is considered in accordance with the concept of perturbation modes, namely, entropy and acoustic modes. The perturbation modes approach is discussed in Pierce, Allan D. Acoustics: an introduction to its physical principles and applications. Springer, 2019. See also: Sapozhnikov, O. A. "High-intensity ultrasonic waves in fluids: nonlinear propagation and effects." In Power Ultrasonics, pp. 9-35. Woodhead Publishing, 2015.

p. 40: In Eq. (1.8-13) *u* should be a vector **u.** It is different from *u* in Eq. (1.8-14).

p. 40–41: Going to a spherical surface and choosing the radius of the sphere *a* sounds incomprehensible. The same can be said for representing a pressure wave as a spherical wave. This would be reasonable for a point source, but the thermophone under consideration has finite dimensions. If the point source (i.e., low-frequency) approximation is considered, this must be mentioned. If the author means that the pressure wave is viewed in the far field, then the directivity factor should be included. Another remark relates to this: the subsection is called "Pressure oscillations near the sample surface", but the equations given refer to a zone far from the sample, i.e., not near it.

p. 42 and around it – a general remark to this theoretical part. The author conducts a theoretical analysis using qualitative reasoning and approximations as if this problem had not been considered before. In fact, the problem of a thermophone is equivalent to the problem of optoacoustic excitation of sound upon absorption of light at the interface between media. Much has been done in this field of photoacoustics, and the theory has been sufficiently developed. A good source, for example, would be the following book: Gusev, V.E. and Karabutov, A.A., 1991. Laser optoacoustics. In particular, the problem of sound generation upon absorption of light in a strongly absorbing medium covered by a rigid transparent medium from the side of incidence of the light beam fully corresponds to a thermophone with zero surface heat capacity. This book contains a careful and detailed analysis of all factors, including diffraction effects. Incidentally, the analogy with photoacoustics can also be used to analyze a thermophone of finite thickness, i.e., with finite surface heat capacity, if a suitable value of the light absorption coefficient is chosen.

p.44: Eq. (1.8-22): The directivity does not depend on *r*.

p.45, Eq. (1.8-24): It is not clear why the medium inside the layer is considered to be a pure gas with the same properties as the external gas. Isn't this a porous material made of nanotubes? Isn't this the thermal conductivity somewhat higher there? It would be nice to have some discussion of the related effects.

p.47, Eq. (1.8-26), upper equation, after the comma: x should be $|x|$.

p.47, Eq. (1.8-27), upper equation: This equation is true only if *P*(*t*) is a sinusoidal function. In the above notation it is written so that this is an arbitrary function of time.

p.47, after Eq. (1.8-27): it seems the incorrect expressions for $q_1, q_2 \sim -(1-i)$ instead of $(1+i)$ are used (see my note above).

p.49, 1st and 3rd lines from the bottom, terminology: "Rectangular" is used for 2D case. In 3D, this is called a "cuboid region".

p.51, 2nd and 3rd line from the bottom: It is written “At ambient conditions, the heat dissipation by convection dominates (Figure 1.9-1b) and at low input power takes over 80% of total power.” Aren't the AC and DC parts of the temperature change related to different parts of the heat dissipation mechanisms? Convection seems to be too slow to affect AC part so much. It would be helpful to discuss this.

p.52, 2nd and 3rd line from the bottom: It is written “In the case of the vacuum, the advection is absent and thermal conductivity depends on the surrounding pressure.” Pressure in a vacuum? This seems to be poorly worded.

p.66, 1st and 3rd lines after the section 1.10.2 title: As mentioned above, the directivity does not depend on *r*.

p.84, 3rd line from the bottom: Discussing impulse excitation, it is written: “Therefore, the total power is directed to the sound generation”. In my opinion, this is a false statement. The total power during the operation of the thermophone goes almost completely to heating the medium, only a small part of it is converted into acoustic energy. Pulsed excitation is characterized by a larger “fraction of a small fraction” of the applied power. The author himself admits this low efficiency later, on p.87 (bottom line). By the way, it would be useful to compare continuous and pulsed excitation in terms of efficiency. Note that in terms of the entropy and acoustic modes mentioned above, heating only generates an entropy mode in the bulk of the medium, and this entropy mode couples with the acoustic mode due to the immobility of the interface (central plane of the layer), converting a small part of its energy into acoustic mode.

p.91 and 92. Chapter 5 is only 2 pages long. This can hardly be called a "chapter". I understand that it is recommended that Chapter 5 be the “Conclusions” chapter, but then it is better to move some of the discussion from the previous chapters into this last one so that it is at least 3–5 pages. It would also be good to name it in the plural, i.e., "Conclusions".

p.91, 2nd paragraph: It is written “sound pressure anisotropy”. This is a strange sounding term. By definition, pressure is a local (point) value; it cannot be isotropic or anisotropic. I suspect that the author had in mind the anisotropy of the acoustic *field* (not just pressure) in terms of its directionality.

p.92, 3rd line in the 3rd paragraph: It is written “(i) the highest sound pressure.” It is not clear what is meant here. Of course, there are sources of much higher pressures (e.g. explosions, sparks, sirens, etc.)

MISPRINTS:
p.24, 3rd line from the bottom: Socks should be Stocks
p.39, 1st line after Eq. (1.8-8). “In Equation 1.8-7” should be “In Equation 1.8-8”
p.44, the line before Eq. (1.8-22): “than” should be “then”

Provisional Recommendation
☐ *I recommend that the candidate should defend the thesis by means of a formal thesis defense*
☑ *I recommend that the candidate should defend the thesis by means of a formal thesis defense only after appropriate changes would be introduced in candidate's thesis according to the recommendations of the present report*
☐ *The thesis is not acceptable and I recommend that the candidate be exempt from the formal thesis defense*