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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: Panu Helistö

I confirm the absence of any conflict of interest	**Signature:** **Date: 21-09-2020**

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

The thesis of candidate Stepan Romanov concerns thermoacoustic sound generation with SWCNT based thermophones. The field of thermoacoustics, originally developed mostly by Arnold and Crandall in their pioneering work more than 100 years ago, was revived in 2008, when Xiao et al. showed that with carbon nanotube heaters, the heat capacity per unit area can be minimized and thus the efficiency of thermophones improved. They also extended the theory of Arnold and Crandall. In 2009 Niskanen et al. showed that sparse arrays of suspended Al nanowires can be used as thermoacoustic sound sources and in 2010 Vesterinen et al extended the theory of thermophones to include also finite size sources causing directivity effects. Especially, they derived the 'ultimate limit' of free-space thermophones, i.e. the maximum theoretical power efficiency, both for point-like and finite-sized sources and showed experimentally that a suspended Al nanowire reached 1/10'th of the ultimate limit, limited both by the substrate effect and the heat capacity of the nanowires. The finding that the ultimate efficiency turned out to quite low when compared to other existing (ultra)sound technology has not ended the interest in thermoacoustics. On the contrary, the field seems to be growing steadily, and perhaps in the near future we will see the first applications of thermophones.

The main outcome of this thesis work is the development of improved, carbon nanotube-based free-standing thermoacoustic sound generators, approaching and in some cases even exceeding the ultimate limit. The thesis consists of three papers published in high quality journals and of an approximately 100-page long summary.

I go next through the main results of the thesis in the order presented in the summary.

In Chapter 2 (sections 1.1 - 1.3), the principle of a thermophone is introduced, and a brief review of the literature is given. The chapter ends with a statement that the developed theory requires theoretical modifications for finite-sized sources. However, the theory of finite-sized thermophones was already developed in 2010 as mentioned above. Also, the ultimate limit of (also finite-sized) thermophones originates from that reference as explained above.

Chapter 3 (Secs. 1.4-1.7) introduces an impressive list of techniques, used by the candidate, related to SWCNT synthesis, and characterization and temperature control of the developed samples. Based on the obtained results, the candidate seems to master these techniques excellently. Also the acoustic measurements are done in a scientifically valid way. This clearly fulfils the methodological requirements of a doctoral thesis.

The beginning of the theory part (Sec 1.8 of Chapter 4) repeats the previous results of Xiao et al. and Vesterinen et. al. using a derivation based on Aliev et al (2013). In addition, useful equations are given to describe volume radiators, which according to the thesis can provide larger sound intensities than surface radiators. Theory and experiments were compared to COMSOL-based simulations.

In Sec 1.9 of Chapter 4, the power handling capability of SWCNT samples is studied based on thermal analysis and known sensitivity to oxidation in air. A limit of 1.5 - 2 W is obtained for the 1 cm^2 samples used in the thesis work.

Sec. 1.10 of Chapter 4 and Publication 1 describe some main results of the thesis. Especially, the output pressure of free-standing CNT thermophones with varying thickness, fabricated with 'dry-transfer' technique, is determined and compared to literature values. Maximum pressure at 3 cm distance is shown to exceed 100 dB at 100 kHz, a value larger than what has been reported earlier when projected to 1-W input power. The highest sound pressure is obtained with a purified extremely thin SWCNT sample. It is quite remarkable that free-standing samples only ~50 nm thick with an area of 1x1cm2 can be fabricated and used successfully in air. Comparable results are, however, obtained with a much thicker MWCNT sample having twice the HCPUA of a SWCNT sample with similar performance. The result is explained by the volumetric effect. This is an interesting effect and would deserve further studies.

The power efficiency is measured and at 100 kHz, the candidate reports an excellent value 35 % of the ultimate limit (of the order of 10^{-5}) for finite-sized thermophones. By suppressing further the sample heat capacity, this could be increased by a factor of 2-3. If still higher efficiencies are desired, the area of the sample should be reduced.

Sec. 1.11 of Chapter 4 describes several interesting methods to improve the sound generation performance. Purification of the CNT films from catalytic particles by localized Joule heating in vacuum is studied in detail here as well as in Publication 2. This work is convincingly done and clear improvement of the performance is obtained.

As oxidation of the CNT's in air limits the maximum input power density, in the second method the CNT samples were protected by thin (5 nm) Al2O3 layers using ALD technique. The effect of the increased maximum power density surpassed the effect of increased heat capacity, resulting in higher maximum sound pressures than obtained without the shielding.

Next, the transducers were encapsulated in an inert gas filled mechanical resonator, forming a device that the candidate calls the 'thermoacoustic sound projector' (see also Publication 3). Due to the small volume of the resonator, the transducer operates in a different mode than in free space. This very interesting part of the thesis is described quite briefly in the summary, but the results appear very remarkable. An increase of power efficiency by up to five orders of magnitude was obtained in such systems, greatly exceeding the fundamental efficiency limit in open space for sinusoidal modulation. Highest reported power efficiencies were approaching unity (Fig 11(a) of Publication 3). This remarkable improvement appears to be achieved by simultaneous exploitation of various very different phenomena. The main factor is to couple the thermoacoustic sound generator to a high-Q resonator. This provides an increase in the efficiency by Q^2 at resonance. Using the inert gas environment eliminates the oxidation and allows the use of much higher power densities than in air. In addition, pulsed power excitation is used instead of sinusoidal power. This facilitates the use of still higher power levels as the static heating of the transducer is suppressed. It is also stated in Publication 3 that thermal sound generation, being nonadiabatic, is more efficient than adiabatic in transferring the pressure waves to the nearby resonating plates. This part of the thesis could have been more thorough, describing in more detail the quite complex phenomenology. E.g., in the case of pulsed excitation, what is the effect of the thermal time constant (~10 ms?) of the transducer, when very short pulses are used, and how is the signal purity affected by pulsed excitation.

It is also demonstrated that pulsed heating provides a convenient means to determine the heat capacity of the transducers. This determination is based partly on careful IR measurements of the temperature of the transducer, not a trivial task for these highly transparent devices. As one minor detail, from Fig 1.11-9 it is not clear to the reader that why the HCPUA of the SWCNT is smaller than that of MWCNT. It looks more like the opposite, the MWCNT signal looks approximately twice as steep as the SWCNT signal, while the thermal conductances of both sensors seem to be almost the same (20 % difference in used power levels according to Publ. 3).

Sec 1.12 discusses the potential applications of the transducers. A patent search is made showing an astonishing amount of patents filed during the last 10 years. A calibration device is suggested for ultrasound equipment as the frequency response of a thermophone is flat at high frequencies. Especially, the candidate discusses the application of thermophones for positioning systems and presents an idea of a cylindrical thermophone operating around 40 kHz for this purpose. This section could have been somewhat more thorough.

Overall, the thesis shows a very good understanding of both the scientific theory and practice of thermophones. In addition, it shows that the candidate masters the challenging synthesis, characterization and manipulation of large nanometer-thin free-standing SWCNT films. The thesis contains several interesting original results which can possibly lead to some applications also.

There are some changes that would make the thesis easier read. Especially, the numbering of the chapters, subsections and equations in the summary are for some reason not synchronized, which complicates reader's task unnecessarily. Unless there is a good reason for such somewhat confusing convention, it would be nice if this could be corrected. The rather lengthy chapter 4 of the summary could be split to two according to the theoretical and experimental findings. Btw, should there be a description of the candidate's contribution to the work presented?

In addition, the candidate should make the following corrections

1. E.g. in *Chapter 1 Introduction* and in *Chapter 4 Results and discussions* it is, obviously accidentally, not mentioned that the theory of finite-sized thermophones including the directivity effects was developed and experimentally verified already by Vesterinen et al in their Nano Lett paper and its supplement in 2010. The candidate should refer to their work properly.
2. When introducing one of the basic concept of the thesis, the ultimate limit of a thermophone (either pointlike or finite-sized) for the first time, the candidate could also refer to the above-mentioned original reference.

With these minor changes, I strongly recommend that the candidate should defend the thesis.

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*