Skoltech
Skolkovo Institute of Science and Technology

Thesis Changes Log

Name of Candidate: Stepan Romanov

PhD Program: Physics

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

Supervisor: Professor Albert Nasibulin

The thesis document includes the following changes in answer to the external review process.

Name of the Reviewer: Prof. Esko I. Kauppinen

The abstract should be revised, in order to be more exact and scientific. It should accurately tell the main results and not use terms like huge, simple, resource efficient etc. non-scientific and not accurate terms, which can be understood in many ways. The first chapter does not tell reader anything more than what the thesis tittle already tells and could be removed.

The abstract was revised and confusing terms were removed.

I understand your concerns, but the first chapter was included for the non-specialist readers to provide an overview of the work and I decided to keep it.

Name of the Reviewer: Prof. Sergey D. Shandakov

1. In the work there are misprints, which, however, do not interfere with understanding the meaning of the text: 1) Abbreviation “AC alternating current” is presented twice in the abbreviation list (p. 11); 2) There is a misprint in the caption of Fig. 1.8-2, instead of “read” you need to write “red”; 3) Invalid reference to Figure 1.5-8 at bottom of p. 50; 4) Reference numbers in fig. 1.10-3 and in the Bibliography do not correspond to each other; 5) Symbols Pm and Pp in description after formula 1.11-1 are reversed; 6) The text lacks a description of the definition of the quantities presented in Table 1.11-1; 7) There is no description of the quantity V in formula 1.11-3.
2. On page 76, the author writes “At temperatures below 1200 °C, the process of carbon solubility is fast enough to increase the number of defects. Whereas, at higher temperature (>1200 °C) the evaporation process dominates resulting in a lower level of defects.” At the same time, no explanation of the influence of carbon solubility and iron evaporation on the number of defects is given.

1. Thank you! All the comments were taken into account and misprints were corrected.
2. To give a direct quantitative explanation, one should arrange additional experiments independently investigating rates of solubility and evaporation, which is a complex problem. In this thesis the analyses concerning the number of defects were performed by Raman spectroscopy and resistance measurements and revealed a technical result – larger evaporation rate lead to the smaller number of defects (Figure 4.4-4), which was followed by the suggestion that evaporation dominates on solubility at high temperatures. Without direct measurements, this note should be treated as a meaningful suggestion.

Name of the Reviewer: Prof. Panu Helistö

1. 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 readers’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 condidate’s contribution to the work presented?

2. 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 veified already by Vesterinen et al in the Nano Lett paper and its supplement in 2010. The candidate should refer to their work properly.
3. When introducing on of the basic concept of the thesis, the ultimate limit of the thermophone (either pointlike or finite-sized) for the first time, the candidate should also refer to the above mentioned original references.

1. The style of the numbering of the sections was changed to a more appropriate way. The splitting of Chapter 4 to theoretical and experimental parts will bring complications with numbering as far as they belong to the chapter Results and discussions. The contribution of the author is presented on page 2 and in acknowledgments, also I included a section Author’s contribution.
2. After detailed and careful studies of the paper by Vesterinen *et al.* I introduced 4 additional comments to the thesis:
    1. The numerical and experimental investigation of the finite size thermophones was included in Chapter 1. “The need to take into account the finite size of thermophones at high frequencies has been already demonstrated numerically and experimentally by Vesterinen *et al.*(reference 19)”.
    2. Theoretical analysis (Supporting information Section B: Suspended point source of sound) was performed for a point-sized thermophone and for the first time introduced the sound pressure for the thermophone over a gap. As far as this related to heat accumulation problem I included this fact in Chapter 4. “Also heat accumulation plays a stronger role in the case of suspended thermophone over a substrate with a small gap. A comprehensive analytical model which covers the point thermophone over such a gaped structure was developed in reference 19.”
    3. Also, the work verifies the directivity function of the rectangular source at a number of angles using measured on-axis sound pressure (figure 2 of original work), the fact was included in Chapter 4 “Experimentally the directivity function was verified for rectangular thermophone by Vesterinen *et al.*”
    4. The reference to the ultimate limit of efficiency (Equation 4.3-2) was added.
3. The ultimate limit of sound pressure by Xiao *et al.* was referred a couple of times. The reference to ultimate limit of efficiency defined in the work by Vesterinen *et al.* was added.

Name of the Reviewer: Prof. Oleg A. Sapozhnikov

1. 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.
2. 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 $q = \sqrt{i\frac{\omega\rho_g C_g}{\kappa}} = \pm\left(1+i\right)\sqrt{\frac{\omega\rho_g C_g}{2\kappa}}$. This clearly does not correspond to the expression $q = -\left(1-i\right)\sqrt{\frac{\omega\rho_g C_g}{2\kappa}}$ given in the text of the thesis.
3. 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.
4. 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.

5. p. 40: In Eq. (1.8-13) *u* should be a vector **u.** It is different from *u* in Eq. (1.8-14).
6. 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.
7. 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.
8. p.44: Eq. (1.8-22): The directivity does not depend on *r*.
9. 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.
10. p.47, Eq. (1.8-26), upper equation, after the comma: x should be $|x|$.
11. 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.
12. 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).
13. p.49, 1st and 3rd lines from the bottom, terminology: "Rectangular" is used for 2D case. In 3D, this is called a "cuboid region".
14. 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.
15. 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.
16. p.66, 1st and 3rd lines after the section 1.10.2 title: As mentioned above, the directivity does not depend on *r*.
17. 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.
18. 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 final 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".

19. 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.
20. 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.)

---

1. A one-dimensional approximation was used, assuming the negligible effect of convection and thermal conduction to contacts. Truly the approximation brakes if the convection effects and thermal conduction to contacts start to play an important role. To check the applicability of Eq. 1.8-2 the COMSOL numerical simulation was arranged and according to the results Figure 1.8-3. the theory and calculations are in a good agreement.
   In accordance to this comment, I have added the following text in the thesis: “Here, one-dimensional approximation was used to obtain the temperature oscillation, however, the full geometry has to be considered in the case of strong effects of convection and heat conduction to the contacts”.
2. Thank you. I have corrected this mistake, which did not affect the final result, because the wave number was substituted in other formulas in the correct form $q = \sqrt{\frac{i\omega\rho_g C_g}{\varkappa}}$. The form $q = (1+i)\sqrt{\frac{\omega\rho_g C_g}{\varkappa}}$, was used to demonstrate the attenuating part and introduce a thermal diffusion length *l(ω).*
3. Thank you. It is a typo, which appeared because of different thickness conventions in experimental and theoretical parts, where the thickness of the sample was named h and $2h$, correspondingly. The typo does not influence the result. To bring the variable names to the same style I have switched the thickness definition from $2h$ to h in the theoretical part.
4. I have corrected the limit and added corresponding notification in the text. “The result obtained in Eq. 1.8-12 agrees with the general concept of perturbation modes (links).”
5. Thank you, it was corrected.
6. This approximation was discussed in the beginning of section 1.8.4. To avoid misunderstanding the following text was introduced on pages 40: “To calculate the sound pressure near the sample surface we approximate our sample with a spherical transducer of the same surface area as discussed in section 4.1.4.”
   The section is called "Pressure oscillations near the sample surface” because of Eq. 1.8-17, where the boundary is taken on the sample surface.
7. I did not claim that the problem had not been considered before. As was mentioned in the beginning of the theoretical part, this work is an extension of Ali Aliev work of 2013, which in turn the extension of Arnolds and Crandall theory developed in 1917. To my knowledge the optoacoustic approaches are developed mainly for pulse signals, while here the derivation considered a sinus wave.
   The following note is added in the theoretical section: “One should note that the problem of thermophones is similar to photoacoustic transducers. The analogy may be successfully applied in description of thermophones, especially under pulse signals (links).”
8. Thank you, it was corrected.
9. Yes, this is correct that the derivation is valid for the gas of same properties as air, I have added corresponding notification in the text “Equation 4.1-24 assumes the same gas properties inside and outside the aerogel structure. In the case of dense aerogel structures (high volume fraction) and small pores size, the gas properties inside the pores of sample differ from those for free space (links).”.
10. Thank you, it was corrected.
11. According to Eq. 1.8 1. P(t) is a sinusoidal function.
12. Thank you, it was corrected.
13. Thank you, it was corrected.
14. In general you are right. However, this section considers only DC parts and the results were utilized to define the temperature during purification from catalyst and measurements of average temperature during the thermoacoustic experiments. To avoid misunderstanding, DC power application was mentioned explicitly.

15. To avoid poor words the “vacuum” was changed to “partial vacuum”. “In the case of the partial vacuum, the advection is absent and thermal conductivity depends on the surrounding pressure.”
16. To avoid misunderstanding the directivity gain was renamed to intensity gain all over the thesis.
17. Of course, you are right and the total power almost completely is spent to heat the medium. By the phrase I meant that no power goes to useless heat of the medium to some average temperature, and the time derivative of temperature increases. The phase was corrected to “Therefore, the applied power introduces higher time derivative of temperature, which results in the efficiency increase.”
18. It is the requirements of style.
19. Thank you, it was corrected.
20. As was mentioned in a previous sentence this attributes to other materials for thermophone application. “There is a number of advantages, which make SWCNT films attractive for thermophone applications compared to other materials. In terms of the sound generation, these advantages are: (i) the highest sound pressure…”.

Name of the Reviewer: Prof. Nikolay A. Gippius.

I have a minor question concerning the Fig.1.8-2:

What parameters control the average temperature, does it saturates at some level or grows slowly with time? How does the heating depend on the emitted power and geometry of the thermophone?

The average temperature is defined by the level of input power and heat-dissipating channels: conduction, convection, radiation, which discusses in section 4.2. The temperature saturates at the average temperature value, which in turn does not depend on time. The heating depends on the power. Figure 4.2.1b demonstrates the energy distribution between the heat dissipation channels for a fixed free-standing 1x1 cm^2 geometry. The geometry of thermophones can strongly influence the amount of power dissipated because of convection and heat conduction to the contacts. Speaking of 1x1 cm^2 thermophone, its transformation to 0.2x5.0 cm^2 thermophone will increase the level of energy dissipated because of convection, while heat conduction can both decrease or increase depending on the side where you introduce the electrical contacts.

Name of the Reviewer: Prof. Mikhail Skvortsov

1. It would be instructive to compare the thermoacoustic effects in free-standing SWCNT and freestanding graphene. Since the latter is the ultimately thin atomic monolayer, one could expect its performance could exceed that of SWCNT films.
2. The theoretical model developed in the first section of chapter 4 essentially assumes a 1D nature of air temperature/pressure modulation. In order for this model to be applicable one must require the length scale l be much smaller than the sample size a. How well this condition is satisfied in the relevant frequency range?
3. The rhs of Eq. 1.8-6 is complex, while the lhs is manifestly real. How can it happen?
4. How sensitive is the efficiency of heat conduction in the film (Section 1.9.2) on the area of contacts with the substrate?
5. Fig. 1.9-5 shows that T obtained under the assumption of 100% efficiency of radiation losses shows perfect agreement with experiment. It is not clear how it fits with Fig. 1.9-1.
6. Besides that, I'd like to suggest using a more appropriate section numeration changing with Chapters. For example, the first Section of Chapter 4 should be 4.1 rather than 1.8. This also refers to figures and equation numbering.

1. The performance of free-standing graphene theoretically should reach 94% of ultimate sound pressure limit (74% for SWCNTs) at 100 kHz due to the ultralow HCPUA of 6 10^{-4} J/m^2k (34 10^{-4} J/m^2k for SWCNTs).
   Also, I should note that the fabrication of free-standing monolayer of graphene of a large surface areas above a few mm^2 is a complex and unachievable technological task beyond the current state-of-the-art.
2. The characteristic radius a=0.28 cm was taken as an approximation to obtain the sound pressure near the surface of the thermophone as discusses in Sections 4.1.3-4.1.4. Also, the thermal diffusion length should be smaller than the sound wavelength. The conditions satisfy for the experimentally considered frequency range from 1 kHz to 100 kHz, $l(\omega) \in [81.9, 8.2]\ \mu m,\ \lambda \in [34.3, 0.3]\ cm$.
3. Thank you, there should be an absolute value of the expression, it was corrected.

4. The heat dissipation to the substrate by heat conduction is limited by the cross-section of the film and does not depend on the area of the contact.
5. Fig. 1.9-1 represents an estimation under the following assumptions: SWCNT film heat conductivity is 600 W/mK (as a maximum reported value) and substrate maintaining at room temperature. Most likely the value of our SWCNT films heat conductivity is smaller and in the experiments the substrate temperature was higher than room temperature, which led to theoretical overestimation of heat dissipation and mismatch.
6. The sections' numbering was corrected.