**Supporting Information**

**Experimental Characterization of Three-Dimensional Graphene’s Thermoacoustic Response and its Theoretical Modelling**

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# A. DERIVATIONS

## Physical parameters of each layer

An equation for all physical parameters in each layer is to be derived. From Eq. (5) of the main text, the pressure is

. (A.1)

Hence the normal surface tension is then written as

. (A.2)

Eq. (A.1) is then substituted into Eqs.(6) and (7) of the main text, leading to

, (A.3)

. (A.4)

Using the relation between specific heat at constant pressure and volume

, (A.5)

Eq. (A.4) becomes

. (A.6)

By substituting Eq. (A.6) into Eq. (A.3) we find as a function of

. (A.7)

Finally, by deriving Eq. (A.7) and injecting it in Eq. (A.4) while using the relation in Eq. (A.5), a pure differential equation for is discovered as

.

(A.8)

leading to

. (A.9)

with unknown constants to be determined in each layer. Assuming weak viscosity and weak thermal conduction, asymptotic solutions of the associated fourth order differential equation of Eq. (A.8) are found to be

, (A.10)

, (A.11)

with the speed of sound in the medium and .

Similarly, the temperature in the solid is also easily solved through Eq. (8) of the main text as

, (A.12)

with unknown constants and

, (A.13)

. (A.14)

## Finding constants

In this sub-section the formulation of the system of equations used to computationally find the constants is detailed with the subscript of the considered layer. For simplicity, the notation and will be used to refer to the associated vectors of unknown constants in the layer . Similarly, the subscript will refer to position of the boundary as defined in Fig. 3 of the main text.

Knowing that layers 0 and N+1 are semi-infinite no reflection is assumed, hence . Furthermore, in those layers the solid is not present so . The boundary conditions written in Eqs. (9) to (14) are now rewritten using the matrix form introduced in Eqs. (21) and (23) of the main text. The continuity of between layers are easily respectively written as

, (A.15)

, (A.16)

, (A.17)

. (A.18)

Lastly, the heat flux interactions are respectively written as

, (A.19)

. (A.20)

The line/column notation is here adopted and the symbol “:” is used to refer to a whole section. Hence, means that all columns of line 2 of matrix H are considered.

We have boundary condition equations for the continuity of in Eqs. (A.15, A.16, A.17, A.19) and (A.20) respectively. Then we have equations for continuity in Eq. (A.18) (no continuity at and since does not exist at the edges). To this we add the 8 conditions defined for the semi-infinite layers at the edges and the non-existence of the solid in those layers. In conclusion, we clearly defined equations for a system with 6 unknowns in each layers. A sparse matrix can then be created to numerically determine all unknown constants thus determining all parameters in at any position and at any frequency. It can be proved that the system of equations giving all the unknown coefficient is always non-singular, and it can be therefore solved by classical numerical methods.

# B. EXPERIMENTAL

## Fabrication of 3D-C

3D-C was synthesized following Ngoh et al.’s thermal chemical vapor deposition (TCVD) method [1]. A nickel foam template (Latech Scientific Supply Pte Ltd) was inserted into the middle of a split tube furnace before the system is ramped up to 1000°C under argon and hydrogen gas flow. After achieving the required temperature, the graphene precursor, methane gas, is flown into the system. After graphene growth is achieved, methane gas is switched off and the lid of the furnace is lifted for rapid air cooling. The graphene coated nickel template is then soaked in hydrochloric acid (HCl) at 85°C to chemically remove the sacrificial nickel template and obtain the final free-standing 3D-C.

## Material characterization

The microstructures of 3D-C were captured with the use of SEM (JEOL JSM-IT100). The crystallinity of 3D-C was determined using a Raman spectroscope (WITec CRM200 Raman, utilizing Nd:YAG 532 nm laser as excitation source).

The direct current (DC) resistance of 3D-C mounted to the backing was measured

by probing the ends of the samples using a multimeter (Fluke 83 III).

## Configuration of 3D-C samples

The synthesized 3D-C samples were adhered to the middle of the microscope glass slides (76.2×25.4×1.1mm, Sail brand) and customised acrylic holders with a 25×25×4mm hole in the middle (60×35×4mm, Dama Trading Pte Ltd, Singapore) using conductive silver paint (Leitsilber 200 Silver Paint, Ted Pella, USA) as depicted in Table B.1.

Table B.1. Schematics of how the various configurations of 3D-C are mounted on their respective backings.

|  |  |  |
| --- | --- | --- |
| **Sample type** | **Front view** | **Back view** |
| 3D-C on microscope glass slide with **point** connection |  |  |
| 3D-C on microscope glass slide with **line** connection |  |  |
| 3D-C on microscope glass slide with **volume** connection |  |  |
| 3D-C on microscope glass slide with **4** connection paths |  |  |
| 3D-C on customised acrylic holder slide with **point** connection |  |  |

## Acoustic, power and thermal characterization set-up

The acoustic performances of the mounted 3D-C samples were measured using the set-up in a non-anechoic room as seen in Fig. B.1. The lap-top used for data logging and parameter entry **1** is connected to the output generator module (Type 3160-A-022, Brüel & Kjær) **2**. The AC signal generated by the output generator is amplified by a power amplifier (Type 2735, Brüel & Kjær) **3**, and applied to the mounted 3D-C sample **4** via crocodile clips. The microphone (Type 4138, Brüel & Kjær) **5**, which is 3cm from the mounted 3D-C sample, receives the signal. This signal is amplified by the pre-amplifier (Type 2670, Brüel & Kjær) **6** and the conditioning amplifier (Type 2690, Brüel & Kjær) **7**. The amplified signal is feedbacked into the output generator to be relayed to the lap-top for data logging. The real-time power and temperature measurements when the system is in operation are captured by a power meter (PW335, Hioki) **8** and infrared thermal camera (Ti480, Fluke) **9**. The background noise of the room was captured to be ~25 dB, except two broad peaks at 28 kHz and 32kHz with sound pressure levels between 27 and 32 dB (Fig. B.2). All acoustic measurements made were significantly above background noise, indicating sufficient signal-to-noise ratio for it to be considered acoustic signals from the samples instead of background noise. The raw SPL of the 50 × 20 × 2mm 3D-C mounted on a microscope glass slide with acoustic power of 10kHz and input power of 3W is as seen in Fig. B.3.

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Fig. B.1. Set-up for measurement of 3D-C’s acoustic performance. (a) Schematic diagram of set-up. Lap-top (1), output generator module (2), power amplifier (3), mounted 3D-C (4), microphone (5), microphone preamplifier (6), conditioning amplifier (7), power meter (8) and infrared thermal camera (9); (b) Visual images of circuitry set-up and; (c) Visual image of 3D-C mounted in set-up.

*A screenshot of a cell phone

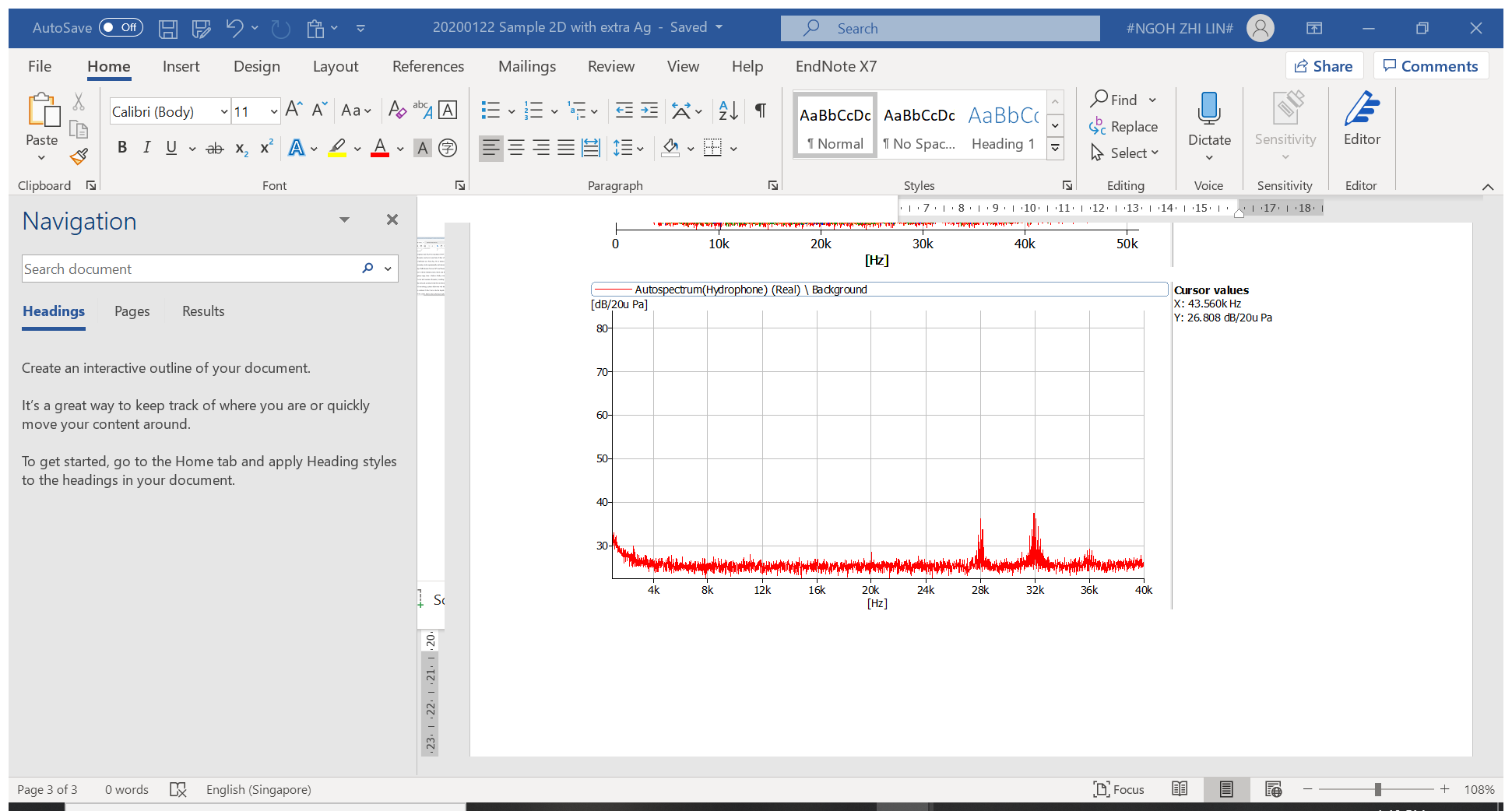
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Fig. B.2. Captured background noise of non-anechoic chamber.

Fig. B.3. Background noise and raw SPL of 50 × 20 × 2mm 3D-C mounted on a microscope glass slide with acoustic power of 10kHz and input power of 3W in black and yellow respectively.

## Sample Parameters

The geometries of the samples used and the physical parameters of the medium (air and 3D-C) are found in Table B.2 and Table B.3 respectively. The number *N* of discretized, regularly-spaced layers used in simulations is found in Table B.2. The number of layers used in simulations is approximately three times larger than the estimated one simply obtained by multiplying the thickness of the samples with the ppi data. As our model is one-dimensional and since the synthesized 3D-C has a very complex geometry with hollow branches, it is assumed that more energy is provided from 3D-C to the surrounding medium than that generated by the branches simply aligned in the propagation axis. This is indicated in our model by the additions of effective layers.

Table B.2. Parameters of the samples used in the experiment with their equivalent number of layers N used in the simulations.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Figure** | **4/5/6/14/S4** | **4/11/12** | **4** | **5/6** | **5/6** | **8** | **8** | **8** |
| *Lx* (mm) | 20 | 30 | 50 | 20 | 20 | 20 | 20 | 20 |
| *Ly* (mm) | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 |
| *Lz* (mm) | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
| N (simulations) | 28 | 28 | 28 | x | x | x | x | x |
| Ppi | 110 | 110 | 110 | 110 | 110 | 110 | 110 | 110 |
| Connection (see Table 1) | Point | Point | Point | Line | Volume | Across | Diagonal | Same Side |
| DC Resistance (Ohm) | 2.9 | 3.7 | 5.1 | 2.1 | 1.7 | 2.2 | 2.5 | 2 |

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Figure** | **8** | **10** | **10** | **13** | **14** |
| *Lx* (mm) | 20 | 30 | 30 | 30 | 20 |
| *Ly* (mm) | 20 | 20 | 20 | 20 | 20 |
| *Lz* (mm) | 2 | 5 | 2 | 1 | 1 |
| N (simulations) | x | 70 | x | X | 28 |
| Ppi | 110 | 130 | 110 | 110 | 110 |
| Connection (see Table 1) | All through | Point | Point | Point | Point |
| DC Resistance (Ohm) | 1.7 | 1.8 | 1.1 | 3.8 | 3.7 |

Table B.3. Medium parameters used in the simulations.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | **(kg/m-3)** | **(J.kg-1.K-1)** | **(J.kg-1.K-1)** | **(Pa)** |
| **Air** | 1.20 | 9.96 × 102 | 7.17 × 102 | 1.01 × 105 |
| **3D-C** | 3.0 | 660 | 660 | 1.44 × 108 |
|  |  |  |  |  |
|  | **(K-1)** | **(W.K-1.m-1)** | **(N.s.m-2)** | **(N.s.m-2)** |
| **Air** | 3.33 × 10-3 | 26.2 × 10-3 | 16.82 × 10-6 | 5.61 × 10-6 |
| **3D-C** | 2.6 × 10-6 | 160 | 0 | 0 |

# A close up of a map Description automatically generatedC. COMPARISON WITH OTHER CARBON NANOSTRUCTURED MATERIALS

Fig. C.1. (a) Acoustic frequency, (b) power input and (c) temperature spectra comparison of uncompressed 3D-C used in sub-section 3.2.4.2 with reported literature values.

In Fig. C.1, the uncompressed 3D-C used in sub-section 3.2.4.2 in the main text is compared with thermophones tested by Aliev et al. 2015 [2]. In Fig. C.1a, 3D-C performs similarly as Indium Tin Oxide coated PolyAcrylonitrile Nanofibers (ITO PAN), Multi Walled Carbon Nanotube (MWNT) forest and MWNT sponge, but is 10 to 20dB below the performances of gold coated PAN, Graphene sponge (GS) and Carbon Nanotube (CNT) Sheet, commonly agreed to be one of the most efficient thermophones currently available. This is confirmed by the proximity of the CNT sheet curve with the theoretical optimal pressure of Eq. (31) in the main text.

Similar observations are drawn from Fig. C.1b, where the power spectrum are plotted, with the information provided by Aliev et al. 2015 [2] adapted to be compared with our measurements based on our frequency spectra results. It is interesting to realize that the two temperature model also has been positively confronted to Aliev’s data in Guiraud et al. 2019 [3]. The data used in the model for 3D-C and GS are very similar, with the main difference being that the theoretical specific surface area of 3D-C is 10 times higher than GS, resulting in a proportionally higher power density in GS. This is corroborated by Fig. C.1c in which the temperatures of the samples are investigated. The temperature of Aliev’s sample are 10° to 40°C hotter than the 3D-C. The very high porosity of 3D-C improves the cooling properties of the sample making it less likely to break down due to high temperature induced by high input power.

Comparing 3D-C with GS at the same temperature, there is a ratio of two between the input powers. This difference would only explain a difference of 6dB between the frequency spectra curves and is not equal to the ratio of 10 in the simulation. This difference could be attributed to thermal losses in the 3D-C packaging, inherent sample properties’ differences wrongly defined in the model, or the different 3D geometries. A more thorough analysis should be conducted to define an optimal geometry for a thermophone to further improve the efficiency of such devices.

For instance, the acoustical efficiency for a spherical radiation can be written as

. (C.1)

The presented frequency spectrum plots being normalized at 1m and 1W, a 10dB difference is equivalent to a loss in efficiency by a factor of 10. At 5kHz our 3D-C efficiency is %, while a regular loudspeaker has an efficiency ranging from 0.5% to 4%. Even CNT sheets which are among the most efficient thermophones have efficiency of only % [2]. Thermophones still must be improved before being able to compete in the market with commercial loudspeakers for audio purposes.

# REFERENCES

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