The Photoacoustic Effect of Multilayered Graphene Films

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Abstract. This paper presents a theoretical model of the photoacoustic effect for multilayered graphene films based on the photoacoustic theory of solids and the thermoacoustic theory of graphene films. The expression of sound pressure of the photoacoustic signal from a multilayered graphene film is therefore derived according to the theoretical formula. An acoustic platform is built to measure the output sound pressure generated by graphene film on a polyethylene terephthalate (PET) substrate, and the experimental values are compared with the corresponding theoretical values. The results show that the trends of the two in the frequency domain are identical, thereby validating the proposed theoretical model. The graphene film speaker has a wide range of frequency response, and the output sound pressure of the film varies linearly with the input optical power. In the far-field region below 17000 Hz, the output sound pressure of the film gradually rises with an increase of the incident light frequency under constant incident light power. The frequency response of the film is relatively stable in the near-field region by comparison.

1. Introduction

When periodic modulated light is incident on a solid, the solid surface is heated periodically. Then, temperature variations cause oscillations in the surrounding air, thereby generating sound waves. This phenomenon is called the photoacoustic (PTA) effect of solids.

In 1880, Alexander Graham Bell first discovered the PTA effect of solids in long-distance acoustic transmission experiments. When chopped sunlight periodically shines on an enclosed cell of a solid, an audible sound is produced. He then performed experiments and proved the existence of PTA effects in gases and liquids. The discovery of the PTA effect led to a widespread discussion in the academic community. The theoretical model of PTA effects has since been continuously improved. In 1975, Rosenwaiag and Gersho[1] proposed a theoretical model of PTA effects in solids. On this basis, Mcdonald et al[2] proposed generalized theory of PTA effect.

To improve the PTA efficiency, selecting a material with low heat capacity per unit area (HCPUA) and good thermal conductivity is necessary. Research on PTA effects was revived with the recent advancement of nanotechnology[3-11]. As a new type of nanomaterial, graphene has the characteristics of light weight, low HCPUA and high thermal conductivity, and is an ideal material for experimental researches on PTA effects. Tian et al[12,13] studied the coherent generation of photo-thermo-acoustic wave from graphene sheets and demonstrated the ability to control the phase of sound waves by utilizing ultrafast optical pulses. Giorgianni et al[14] studied the PTA effect of 3D graphene sponges and proposed the application of graphene sponges to PTA speaker fabrication. Yi et al[15] established a theoretical model of PTA effect of graphene sponges, which was in good agreement with the experimental results, and provided a useful reference for the application of graphene materials to PTA devices.
However, compared with the multilayered graphene film, the graphene sponge is bulky, thereby limiting its applicability in the creation of micro devices. The sponge itself has good sound absorption performance, which can reduce the efficiency of the PTA speaker. To investigate the PTA effect of multilayered graphene films, a theoretical model of PTA effect of multilayered graphene films is established. The PTA experiments of graphene films on PET are conducted to verify the validity of this model and the acoustic properties of the films are initially studied.

This study lays the foundation for the research on the PTA efficiency, influencing factors and optimal design of PTA loudspeakers, and has important guiding relevance for its application to PTA loudspeakers. Compared with the widely used conventional speakers, PTA speakers have a wider frequency response range and a lighter weight structure, and have broader application prospects in fields, such as aerospace and electronic equipment.

2. PTA model

The theoretical model of the PTA effect is shown in Figure 1. The graphene film is heated by a modulated light periodically. Heat is conducted between the film and its surface gas medium, which also leads to periodic temperature oscillations, thus creating sounds. The mechanical vibration of the film barely contributes to the sound signal.

![Theoretical model of PTA effect of graphene film](image)

**Figure 1.** Theoretical model of PTA effect of graphene film

The gas around the film is assumed to be a non-viscous ideal gas. The thermal boundary layer of the gas is thin and the acoustic vibration is fast; thus, the influence of gas natural convection can be ignored, with only the thermal coupling in the gas and the thermal conduction between substrate and graphene are considered. Taking the surface of the graphene film as the coordinate origin, the thermal-mechanical coupling equations are as follows:

\[
\begin{align*}
\frac{\partial^2 T_g}{\partial x^2} &= \frac{1}{\alpha_g} \frac{\partial T_g}{\partial t} - \frac{1}{\kappa_g} \frac{\partial p_g}{\partial t} \\
\frac{\partial^2 p_g}{\partial x^2} &= \frac{\rho_g}{P_0} \frac{\partial^2 p_g}{\partial t^2} - \frac{\rho_g}{T_0} \frac{\partial^2 T_g}{\partial t^2} \\
\frac{\partial^2 T_s}{\partial x^2} &= \frac{1}{\alpha_s} \frac{\partial T_s}{\partial t} \\
\frac{\partial^2 T_0}{\partial x^2} &= \frac{1}{\alpha_0} \frac{\partial T_0}{\partial t}
\end{align*}
\]

where \( T_g \) and \( p_g \) are the gas temperature and gas pressure that need to be solved, respectively; \( P_0 \) is the ambient pressure; and \( T_0 \) is the ambient average temperature. Based on TA model established by
Xing et al\textsuperscript{[16]}, we have changed the model input into optical input. \( I_o \) is the incident light intensity. The sound pressure of PTA effect in the near-field is denoted as:

\[
p_{g,nu} = \frac{\gamma_g - 1}{\sqrt{2\nu_g}} \cdot \frac{e_g}{M\epsilon_g + e_g} \cdot I_0 \cdot \beta_{MLG} \quad (r < R_0)
\]

In the far-field, assuming the acoustic wave is a spherical distribution, the amplitude of the spherical wave needs to be multiplied by the \( \frac{R_0}{r_0} \), compared with the plane wave in the near-field. The sound pressure expression of the PTA effect in the far-field is:

\[
p_{g,nu} = \frac{\gamma_g - 1}{\sqrt{2\nu_g}} \cdot \frac{e_g}{M\epsilon_g + e_g} \cdot \frac{R_0}{r_0} \cdot I_0 \cdot \beta_{MLG} \quad (r > R_0)
\]

where

\[
M = \frac{(e_g + e_o) \cdot \text{exp}\left(\frac{\sqrt{\omega\epsilon_g d_g}}{\kappa_G}\right) + (e_g - e_o) \cdot \text{exp}\left(-\frac{\sqrt{\omega\epsilon_g d_g}}{\kappa_G}\right)}{(e_g + e_o) \cdot \text{exp}\left(\frac{\sqrt{\omega\epsilon_g d_g}}{\kappa_G}\right) - (e_g - e_o) \cdot \text{exp}\left(-\frac{\sqrt{\omega\epsilon_g d_g}}{\kappa_G}\right)}
\]

\( d_g \) represents the thickness of the graphene film, \( \nu_g \) represents the sound velocity in the surrounding gas, and \( \gamma_g \) represents the heat capacity ratio of the gas. In an ideal gas, \( \gamma_g = \kappa_g \epsilon_g / (\kappa_g \epsilon_g - \alpha_g \rho_g) \), and \( \alpha_g = \kappa_g / \rho_g c_{g,p} \) is the thermal diffusivity of the gas. \( \epsilon_i = \sqrt{\kappa_i \rho_i c_{i,p}} \) is the thermal effusivity (the heat exchange rate between the material and the surrounding environment) of material \( i \), where \( \rho_i \) represents density, \( \kappa_i = \alpha_i \rho_i c_{i,p} \) is the thermal conductivity, \( \alpha_i \) is the thermal diffusivity, and \( c_{i,p} \) is the specific heat. The subscripts correspond to gas (\( g \)), graphene film (\( G \)) and substrate (\( s \)), respectively. Considering the high transmittance of graphene film, the absorption coefficient \( \beta_{MLG} (\beta_{MLG} \approx 0.05)\textsuperscript{[17]} \) of the multilayered graphene film is introduced. The incident light intensity is \( I_0 = q_o / A_o \), where \( q_o \) is the input optical power and \( A_o \) is the area of the film that is irradiated with incident light.

When the ambient temperature is 300 K, the air related constants are listed in Table 1.

\begin{tabular}{|l|l|l|l|l|l|}
\hline
Density \( \rho_s \) (kg / m\(^3\)) & Specific heat \( c_{g,p} \) (J / (K \cdot m\(^3\))) & Thermal conductivity \( \kappa_g \) (W / (K \cdot m)) & Sound velocity \( v_g \) (m / s) & Thermal diffusivity \( \alpha_g \) (m\(^2\) / s) & Heat capacity ratio \( \gamma_g \) \\
\hline
1.16 & 1006 & 0.0262 & 347 & 2.25 \times 10\(^5\) & 1.4 \\
\hline
\end{tabular}

\textbf{3. Experimental preparation}

To verify the accuracy of the PTA model of graphene film, we built an acoustic experimental platform to measure the PTA performance of the graphene film and compared it with the theoretical model. The schematic diagram of the experimental system is shown in Figure 2. PTA experiments were conducted in a 5.4 \( \times \) 3.6 \( \times \) 2.7 m\(^3\) semi-anechoic chamber, and the background noise in the semi-anechoic chamber was less than 20 dB, as shown in Figure 3.

The acoustic device in the experiment was a multilayered graphene film with an area of 2\( \times \)2 cm\(^2\) produced by Shenzhen Six Carbon Technology Co., Ltd. Graphene was grown on the surface of a copper foil via chemical vapour deposition, and then the copper substrate was etched by using \( \text{FeCl}_3 \) solution. When the film floated in the solution, the film was transferred to a transparent substrate via a PMMA-assisted method. The average thickness of the film was 10 nm. The graph of the graphene film
is shown in Figure 4. The physical parameters of the materials required for theoretical calculations are shown in Table 2.

![Schematic diagram of the experimental system](image1)

**Figure 2.** Schematic diagram of the experimental system

![Graph of background noise](image2)

**Figure 3.** Background noise of semi-anechoic chamber

![Graphene film on PET](image3)

**Figure 4.** Graphene film on PET
Table 2. Physical parameters of graphene film

| Materials | Thermal conductivity $\kappa$ (W/(m·K)) | Density $\rho$ (kg/m$^3$) | Thermal effusivity $e$ (W/(K·m$^2$)) | Specific heat $c$ (J/(kg·K)) | Area $A$ (cm$^2$) |
|-----------|----------------------------------------|---------------------------|--------------------------------------|----------------------------|------------------|
| PET       | 0.15                                   | 1390                       | 494.33                               | 1172                       | 3.5×3.5          |
| Graphene  | 130                                    | 2100                       | 13922.28                             | 710                        | 2×2              |

The laser used in the experiments was a Poplar-355-5A ultraviolet laser produced by Wuhan Huaray Precision Laser Co., Ltd., with a laser frequency range of 20Hz-20 kHz and a laser pulse width of 15 ns. The PTA signals generated by the graphene film were obtained by the microphone (BSWA MA231) and then input into the DASP signal analysis software through a data collecting instrument for analysis and processing. The layout of the field test is shown in Figure 5, and the test points are arranged on the central axis of the film.

Figure 5. Field test of graphene film

4. Experimental results and discussion

The frequencies of incident light we selected in our experiments were 5000, 8000 and 10000 Hz. The Rayleigh distances at three different frequencies were all less than 1.15 cm. The position of the measuring point was located at 2 cm from the film; thus, the measured sound pressure values fell in the far-field. The experimental results are shown in Figure 6; sound in the low frequency band is the background noise of the semi-anechoic chamber.

The theoretical values of the PTA sound pressure of the film were obtained by substituting the corresponding parameters required for the theoretical calculation into Formula (3). As shown in Figure 7, the experimental and theoretical values are rather consistent. A linear relationship was observed between the input optical power and the output sound pressure of the graphene film. However, when the incident optical power is higher, the error becomes larger, which may have been caused by the performance degradation of graphene film due to excessive input optical power.
According to Formula (3), in the far-field, the relationship between the sound pressure emitted by the film and the distance from the measuring point to the film is \[ P_{s, rms} \propto \frac{1}{r_0} \]. The experiments were conducted at 3000 Hz, whereas the input optical power was \( q_0 = 500 \text{ mW} \), and the Rayleigh distance was about 0.35 cm. The sound pressures were recorded at a distance of 1-9 cm in the far-field.

The relationship between the output sound pressures and distance is shown in Figure 8. Experimental results agreed with the theoretical values, and the discrepancy may be due to a measurement error.
The PTA response of graphene film on PET at frequencies ranging from 1500 Hz to 20 kHz was studied in air. Figure 9 shows the SPLs measured at different frequencies when the optical input power \( q_0 = 250 \, \text{mW} \) and the distance \( r_0 = 2 \, \text{cm} \). The SPLs measured multiple times at the same position were stable. Thus, the experimental values shown in Figure 9 were the average values of the multiple measurements. The theoretical values of the SPL were obtained by substituting the corresponding parameters required for the theoretical calculation into Formula (3). The theoretical values of SPL of graphene film on PET are shown in Figure 9.

Figure 9 shows that the graphene film loudspeaker has a wide frequency response. The PTA signal gradually increases with the increasing incident light frequency in the far-field (below 17000 Hz). In the near-field, the frequency response of the film is relatively flat.

5. Conclusion
   (1) On the basis of the PTA effect of solids and the thermoacoustic theory of graphene film, the theoretical model of PTA effect for graphene film is established, and the sound pressure expression of PTA effect of graphene film is derived.
   (2) The PTA experiment was performed on a graphene film on PET, and the experimental values of the output sound pressure are compared with the theoretical values. The two trends are rather consistent in the frequency domain, thereby verifying the accuracy of the theoretical model of PTA effect.
   (3) The graphene film loudspeaker has a wide range of frequency response, and the output sound pressure of the film is linear with the input optical power. In the far-field below 17000 Hz, when the
incident light power is constant, the output sound pressure of the film gradually increases with the increase in incident light frequency, and the frequency response of the film is relatively stable in the near-field.

Formula (3) shows that the film thickness, thermal effusivity of substrates and the parameters of different ambient gases affect the PTA efficiency of graphene film. Substrates with low thermal effusivity, such as PET and polydimethylsiloxane (PDMS), can have a significant influence on improving the PTA effect of graphene films. Encapsulating the graphene film in an ambient gas with high density, high thermal conductivity and low specific heat is expected to enhance the PTA efficiency. These inferences all require further exploration.

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