Study on Changes in Spatial Self-Phase Modulation Pattern of Graphene Dispersion

Lingyue Ma*
School of Automotive Studies, Tongji University, Shanghai 201804, P. R. China
*Corresponding author email: 1751457@tongji.edu.cn

Abstract. Changes in spatial self-phase modulation (SSPM) patterns have been studied when a laser beam passes through graphene dispersions and graphene dispersed gel. Interference rings are formed due to spatial self-phase modulation, which is induced by the change of the intensity dependent refractive index of graphene dispersions. The interference pattern of SSPM is found to be distorted rapidly for the graphene dispersions, while no distortion for the graphene dispersed gel. Experimental results show that thermal convection effect plays a dominant role for the distortion of the SSPM pattern. The distorted extent and area of the SSPM pattern depend on the speed and direction of convection in the graphene dispersions. Theoretical analyses have been given for the reason of the SSPM pattern distortion. Convection can effectively change the spatial symmetry distribution of polarized graphene sheets and non-linear refractive index in the beam cross section, thus making the interference rings distortion based on the spatial self-phase modulation.

1. Introduction
SSPM is a third-order nonlinear optical effect, which was investigated in liquid crystals decades ago [1], [2]. Thereafter, the effect of SSPM has been observed in several systems, especially the recently discovered two-dimensional (2D) quantum materials such as graphene [3] and MoS$_2$ [4]. These layered electronic materials have relatively high photo-carrier mobility, leading to relatively higher nonlinear optical response $\chi^{(3)}$ values, which are fundamentally determined by their band structures.

When a laser beam traverses a nonlinear optical medium, the refractive index is a function of the intensity distribution. In terms of the third order nonlinearity, the refractive index can be expressed as $n = n_0 + n_2 I$, where $n_0$ and $n_2$ are the linear and nonlinear refractive indexes, respectively, $I$ is the light intensity. This leads to a local refractive-index change $\Delta n(\rho, z)$ in the medium and a corresponding phase shift $\Delta\psi$ of the beam traversing the medium of thickness $l$ [1]:

$$\Delta\psi(\rho) = \frac{2\pi}{\lambda} \int_0^l \Delta n(\rho, z) dz,$$

where $\rho$ is the transverse position in the beam, $\lambda$ the laser wavelength in vacuum, $z$ is normal to the sample surface. For a Gaussian laser beam, we expect that $\Delta\psi(\rho)$ is cylindrically symmetric in the form of a bump peaked at $\rho = 0$. We assume that $\Delta\psi(\rho) \approx \Delta\psi_0 \exp (-2\rho^2/a^2)$, where $a$ is the $1/e^2$ beam radius. For each point, say $\rho_1$, on the $\Delta\psi(\rho) - \rho$ curve, there always exists another point $\rho_2$ with the same slope. Since the $\frac{d\Delta\psi}{d\rho} = k_1$, the radiation waves from the regions around $\rho_1$ and $\rho_2$ have the same wave vector and can interfere. Maximum constructive or destructive interference occurs when $\Delta\psi(\rho_1) - \Delta\psi(\rho_2) = m\pi$, $m$ being an even or odd integer, respectively, leading to the appearance of interference rings. The interference rings are concentric circles of bright and dark in the far field of the beam. The total number of rings $N$ can be estimated from the relation $N \approx \Delta\psi_0/2\pi$ for a given laser intensity. $\Delta\psi_0$ is the maximum phase difference in the beam section. The concentric rings are the interference pattern caused by spatial self-phase modulation due to the Gaussian
distribution of laser intensity, so they are called SSPM patterns.

When a Gaussian laser beam passes through graphene dispersions, it is found that the SSPM pattern of the graphene dispersion is not stable, being distorted from symmetric patterns to asymmetric ones with the upper part squeezed in a short time. The distortion phenomenon of SSPM has been reported in several nonlinear materials [5,6]. It is only ambiguously attributed to the thermal convection induced by the traversing laser beam. However, it is still not very clear how the thermal convection affects the dynamic process of the SSPM pattern distortion.

In this work, the changes in the SSPM patterns of the samples with and without convection have been investigated. It is found that the distortion of the SSPM pattern actually originates from the asymmetrical changes in the spatial distribution of polarized graphene sheets and the nonlinear refractive index caused by convection in the graphene dispersions. The distorted extent and area of the SSPM pattern are determined by the speed and direction of the convection in the beam cross section. A physical model is proposed to analyze the experimental results. This study will provide a great help to understand the nonlinear optical properties of graphene and to explore its application in optical and optoelectronic fields.

2. Experiment
The graphene dispersion with a concentration of 0.15 mg/ml in N-methyl-2-pyrrolidone (NMP) was prepared by ultrasonic method. Graphene powder and NMP solvent were commercially available. Quartz cuvettes with different optical path lengths (thickness) were used to keep the graphene dispersions.

A graphene dispersed gel was prepared to study the SSPM patterns of the colloid state sample. Agar was used as a coagulant to prepare the gel. Agar is a polymer, its structure is full of micro-pores, and the size of the pores can be controlled by the gel concentration. We prepared an agar solution with a concentration of 0.05 mg/ml at 100 °C, dropped the agar solution (3-5 drops) into the graphene dispersion at temperature above 50 °C, mixed the agar solution and graphene dispersion uniformly. After one hour at room temperature, the mixture solidified into a gel.

Figure 1 shows the schematic diagram of setup for studying the SSPM pattern of the graphene samples.

![Figure 1. Schematic diagram of setup to study the SSPM pattern of the graphene](image)

3. Results and Discussion
Figures 2 and 3 show changes in the SSPM patterns of a graphene dispersion and a graphene dispersed gel, respectively. It can be seen that the dynamic processes for the two samples are different. For the graphene dispersion, the SSPM pattern quickly expanded from a bright spot into symmetrical concentric rings until it reached its maximum at about 0.5 s (Figures 2a-c). Then, the upper part of the rings quickly collapsed, the pattern changed from a circular symmetry to an asymmetric one with a
vertical distortion (Figures 2d and e). The distorted pattern maintained stable after about 1 s (Figure 2e). For the graphene dispersed gel sample, the SSPM patterns kept circular symmetry and no distortion occurred with time. The outermost diameter of the SSPM pattern of the gel gradually increased with the increase of the time. The SSPM patterns of the gel sample took about 3 seconds to reach the maximum (Figure 3d), while this process in liquid sample is about 0.5 s.

When a laser beam passes through graphene dispersion and graphene dispersed gel samples, the two biggest difference is that there is convection in the graphene liquid sample, while there is no convection in the graphene gel sample. In the absence of convection in the gel, the SSPM patterns exhibit good circular symmetry, no distortion appears with time. This result verifies that the convection in the liquid sample plays a dominant role to make the SSPM pattern distortion.

The graphene sheets in the agar meshes of the colloid can’t form convection current, but they can be slightly rotated by electric field in their own position. Because the resistance of graphene sheets reorientation in colloid is greater than that in liquid, resulting in the graphene sheets reoriented parallel to the electric field direction takes longer time. This result proves that the SSPM pattern comes from the polarized graphene sheets, which is in good agreement with the wind chime model [3].

Figure 4. (a) The distorted SSPM pattern due to convection, (b) schematic diagram for convection in the graphene dispersion, (c) the variation of the refractive index profile, (d) the distribution of polarized and unpolarized graphene sheets in the beam.

Figure 5. The model for changes of polarized and reoriented graphene sheets with time in the beam cross section of the graphene dispersion.
sheets are replaced by cool parts, causing changes in the distribution of the temperature and polarized graphene sheets. A schematic diagram for the convection of the graphene dispersion in the laser beam cross section is shown in Figure 4 (b). The graphene sheets in the bottom portion of the beam are those flowing into the beam from the external laser beam by convection process. They are cool and non-polarized. The non-polarized graphene sheets are represented by “black dots”, as shown in Figure 4 (d). They are in random orientation, and have no contribution to the SSPM. After a period of time, they will be polarized and reoriented by the electronic field when they approach the area near the beam center. The polarized and aligned graphene sheets are represented by “white dots”. Most of the graphene sheets in the upper half of the beam section are polarized and aligned along the external electric field because they have been in the beam for enough time (the polarized time is about 0.1 s [3]). The distribution of the polarized and aligned graphene sheets becomes asymmetric due to the influence of thermal convection in the beam section, as shown in Figure 4 (d). According to Reference 3, the total third-order nonlinear susceptibility $\chi^{(3)}_{total} \approx M_{ef}^{2} \chi^{(3)}_{monolayer}$. $M_{ef}$ is the number of polarized graphene sheets in the optical path. As $\chi^{(3)}_{total}$ is proportional to the effective nonlinear refractive index $n_2$, and $n_2 = (1.2 \times 10^4 \times \pi^2/n_2^2c)\chi^{(3)}_{total}$ can then be tuned by the change of polarized graphene distribution caused by the thermal convection. The polarized graphene sheets in the lower half part of the beam become less when convections occur, resulting in a decrease of the effective nonlinear refractive index $n_2$ in this region, as shown in Figure 4 (c). The asymmetrical distribution of the non-linear refractive index lead to the distortion of the SSPM patterns, as shown in Figure 4 (a). The distortion area of the SSPM pattern is opposite to that of the refractive index distribution because of the self-focusing effect of the graphene dispersion.

In the absence of convection for the gel sample, because of the Gaussian distribution of the laser intensity, the temperature and irradiance fields in the sample are radially symmetric about the axis of the beam, the temperature dependent refractive index profile of the sample is circular and symmetrical, too. So the SSPM pattern is circularly symmetric, no distortion of SSPM pattern occurs with time.

Using this model, the changes in the SSPM patterns of the graphene dispersion with time can be understood easily. Figure 5 shows the corresponding relationship between the SSPM pattern and the distribution of polarized graphene and non-polarized graphene sheets in the beam section at different times when a laser horizontally passes through the dispersion. When the laser irradiates the dispersion at the initial moment, the graphene sheets are cool and not polarized. “Black dots” randomly distributed in the beam section, and the nonlinear refractive index is too small to occur the SSPM, so the pattern on the screen is a bright spot ( Figure 5a). After a period of time (about 0.1 s), the graphene sheets can be polarized and reoriented by the electronic field of laser, the SSPM pattern appears. Absorption of laser energy is little at the initial time, thermal conduction is the only heat transfer mechanism. The diameter of the temperature gradient distribution is smaller, it increases with the increase of the irradiation time and the energy absorbed by graphene sheets, then the distribution diameter of the temperature-dependent refractive index gradually increases and reaches its maximum at about 0.5 s. Therefore, the maximum phase difference also gradually increases, resulting in the number and diameter of the interference rings increase gradually over time, as shown in Figures 5 (b) and (c). No convection presents in the beam section before 0.5 s, so the SSPM patterns are concentric rings. When the laser irradiation time is more than 0.5 s, the dispersions can be effectively heated by the laser energy, and the temperature gradient between the center and the surrounding in the beam section further increases, resulting in a thermal convection in the dispersions. In the presence of an upward convection, the reason for the distortion of the SSPM pattern has been discussed with the above model shown in Figure 4. Because the heating effect due to a laser beam is instantaneous, the system rapidly reaches a stable state. The change of the SSPM pattern with time corresponding to the process of the heating effect in the graphene dispersion is also instantaneous.

From above experimental and theoretical results, it can be seen that the essential reason for the distortion of the SSPM pattern is the asymmetric distribution of the polarized graphene sheets in the beam section caused by convection. If the direction of convection in the beam section changes, the distortion area of the SSPM pattern will also change accordingly. The influence of different convection directions on the distorted area of the SSPM pattern can be simulated by shifting the sample up and
down or left and right in the beam cross section. The experimental results are shown in Figures 6 and 7.

When the liquid graphene sample was shifted downwards at different speeds, an interesting result was observed. The SSPM image of the liquid sample showed a circular symmetry and almost no distortion at a downward speed of about 1 mm/s, as shown in Figure 6 (a). This situation is like no convection in the liquid dispersion, and means that the upward convection should be eliminated or modulated by the downward movement of the sample at the same speed. When the downward speed of the sample is greater than 1 mm/s, the distorted area of the SSPM pattern changes from the top to the bottom part, as shown in Figure 6 (b). This is similar to the existence of a downward convection in a liquid. This result reveals that the speed and direction of convection in the beam section determine the distorted extent and area of the SSPM patterns. This conclusion can be further proved by shifting the sample left and right in the horizontal direction, as shown in Figure 7.

When the convection direction is different, the area of the unpolarized graphene sheets newly entered into the beam cross section is different. For the sample moved down at a speed higher than 1 mm/s, the convection direction becomes downward. The non-polarized graphene sheets are located at the top portion of the beam cross section, according to above model, the bottom part of the SSPM pattern was squeezed. When the sample was moved horizontally to the left or the right, meaning that the convection direction was to the left or right, the unpolarized graphene sheets newly entered in the laser beam were located on the right or left side of the beam, respectively. The asymmetric distribution of polarized graphene sheets in the horizontal direction caused the distortion of the SSPM pattern in the horizontal direction, as shown in Figure 7(a) and (b).

The gel sample is characterized by the fact that the graphene sheets can’t be moved in a wide range but can be slightly rotated in their own position. When the gel sample was shifted up or down perpendicular to the laser beam, the graphene sheets in the sample shifted up or down relative to the beam, which could be used to simulate the upward or downward convection of the liquid sample. The shifted speed of the gel sample is corresponding to the convection speed in the liquid dispersion. The effect of the convection direction and speed on the distortion area and extent of the SSPM pattern can be studied by this method.
Figures 8 and 9 are the SSPM patterns as the gel sample was shifted up and down, respectively. It can be seen that the top part of the rings squeezed for upward moved sample, which is the same as the distortion of the SSPM pattern in the liquid sample, indicating that this experimental simulation method is correct and feasible. The bottom part of the rings was distorted for the downward moved sample. The extent of the distortion increased with the increase of the shifted speed.

Figures 10 and 11 show the variations in the SSPM patterns as the gel sample was shifted horizontally to the left and right, respectively. This simulates the convection in the horizontal direction in the beam cross section of the liquid sample. As it is expected, the distortion of the SSPM pattern appeared in the horizontal direction for the horizontally moved sample. The distortion extent and area of the SSPM patterns increase with the increase of the movement speed. The same result was observed in the liquid sample, too. These experimental results further illustrate that the distortion extent and area of the SSPM patterns are governed by the speed and direction of convection in the beam cross section of the graphene dispersions.

The convection speed in the graphene dispersion increases with the increase of the laser power. The faster the convection speed, the larger proportion of the number of the unpolarized graphene sheets entering into the beam, and the larger magnitude the distortion of the nonlinear refractive index profile. Finally, the larger magnitude the distortion of the SSPM pattern.

4. Conclusion
In this paper, it is demonstrated that the SSPM pattern distortion of the graphene dispersion is originated from the convection in the beam cross section by a series of designed experiments. The convection produces a spatial asymmetric distribution of the polarized graphene sheets and the refractive index, further lead to the asymmetric distribution of the phase shift, resulting the distortion of the SSPM pattern. The distortion extent and area of the SSPM patterns in the graphene dispersion depend on the speed and direction of convection in the graphene dispersions. We expect that our experimental study will facilitate graphene new potentials in nonlinear optical applications.

5. Acknowledgement
We gratefully acknowledge the support of Dongrun-Yau Science Award. We would like to thank the Experimental Physics Teaching Center of Tsinghua University to provide experimental devices and Chen Yibao for his helpful guidance.

6. References
[1] Durbin S D, Arakelian S M, Shen Y R. 1981 Opt. Lett. 6 pp 411-3.
[2] Satamato E, Shen Y R 1984 Opt. Lett. 9 pp564-6.
[3] Wu R, Zhang Y L, Yan S C, Bian F, Wang W L, Bai X D, Lu X H, Zhao J M and Wang E G 2011 Nano letters 11 pp 5159 - 64.
[4] Wu Y L, Zhu L L, Wu Q, Sun F, Wei J K, Tian Y C, Wang W L, Bai X D, Zuo Xu and Zhao Jimin 2016 Appl. Phys. Lett. 108 241110.
[5] Wang G Z, Zhang S F, et al. 2014 Appl. Phys. Lett. 104 141909.
[6] Ji W, Chen W, Lim S, Lin J and Guo Z 2006 Opt. Express 14 8958.