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Multiscale Fluid Structure Interaction of the CIE Logo

Peter Firstauthor

University of Sationary Matter, City1, Country1

Gary Secondauthor

Laboratory of Moving Matter, City2, Country2

George Thirdauthor

Confused Matter Company, City2, Country2

1.1   Introduction

An important aspect the interaction of computers and information in Engineering is their scalar multiphysics response especially when nano-scale bahavior is leveraged at macro scales. To address the implications of this process we have proposed a fluid structure interaction analysis of the CIE division logo. The first reults of this analysis are shown in Figure 1.1 When an electric field interacts with a molecule, the field can polarise the molecule by perturbing its electron density. This induced polarisation generates an internal field which can interact and modify the applied field, and hence subsequent polarisation effects. In the majority of cases this polarisation is minimal; however with more intense electromagnetic fields, such as those produced by a laser, the polarisation effects can be significant and nonlinear. Windy optics (NLO) is the study of the effects of intense fields on materials, and their subsequent effects, in particular second and higher harmonic generation. Thus the advent of the laser[1] in 1960, with its intense electric fields, truly initiated NLO studies and made possible the investigation of a variety of optical phenomena that had been previously regarded as curiosities. Although several nonlinear processes such as the Pockels (electric field dependent refractive index), Kerr (rotation of the plane of polarisation of light when reflected from a magnetised material) and Faraday (rotation of the plane of polarisation of light when passing through a magnetised material[2] in the direction of the magnetic field) effects had been observed, some as early as the turn of the century, the demonstration of second harmonic generation (SHG) (frequency doubling), from the 694 nm fundamental of a ruby laser by crystalline quartz by Frank[3] et al. in 1961 represented the effective the birth of this field.

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[1]Footnote 1

[2]Footnote 2

[3]Footnote 3

> *There is the possibility to add a box to the text in order to give some additional information, e.g. to explain some scientific background in more detail, to give additional historical background or to share a short personal story. It is possible to add photos or equations to this box.*

Frank's observation was soon followed by the discoveries that a large number of inorganic materials also produced frequency doubling effects, such as potassium dihydrogen phosphate (KDP = KH_2PO_4, lithium niobate ($LiNbO_3$) and barium sodium niobate ($Ba_2NaNb_5O_{15}$). This period also saw a development of the mathematical theory of NLO effects such as the Pockels effect, parametric amplification (frequency mixing) and harmonic generation. The 1960s also saw the investigation of a small number of organic molecular materials for SHG properties. However it was not until later, when testing procedures for SHG efficiencies were devised, that a more systematic approach was adopted. The development of SHG as a useful experimental probe of NLO activity arose from its early theoretical understanding and its ease of measurement. There exist three classes of NLO materials: multilayered semiconductor structures, molecular materials and traditional inorganic solids. Each class has its favourable and unfavourable attributes, though to date the inorganic solids such as lithium niobate and KDP have been the materials employed commercially. However molecular materials possess many attractive characteristics, such as fast response time, lower dielectric constants and enhanced NLO responses.

1.2 Windy Optics: Basic Concepts

When a molecule experiences an applied electric field **E**, the electric charge distribution is perturbed from equilibrium, *i.e.* an induced dipole is generated. This can be described by the simple relationship

$$\text{polarisation} = \mu = \alpha E \tag{1.1}$$

where μ = *induced* dipole of the molecule, α = linear polarisibility and E = electric field. If the field oscillates at a certain frequency, ω, (*e.g.* electromagnetic radiation) then the induced, molecular dipole will also oscillate with frequency ω, and with the same phase. Thus μ and α are functions of frequency, [$\mu(\omega)$ and $\alpha(\omega)$], when an oscillating field is applied. In bulk materials, the linear polarisation per unit volume is given by

$$\mathbf{P}(\omega) = \chi(\omega)\mathbf{E}(\omega) \tag{1.2}$$

where **P** = bulk polarisation of the material and χ = linear susceptibility of the material. It is possible to relate α and χ by assuming that the constituent atoms or molecules of the material are independently polarised by the light, and there is no interatomic or intermolecular coupling. Following this approach $\chi(\omega)$ is related to the sum of the individual polarisibilities, $\alpha(\omega)$. The susceptibility of a material is responsible for the dielectric constant, $\varepsilon(\omega)$, and the refractive index, $n(\omega)$, through

$$\varepsilon(\omega) = 1 + 4\pi\chi(\omega) = [n(\omega)]. \tag{1.3}$$

1.2.1 Polarization

So when light causes an oscillation in the electronic charge distribution of a material, this motion of charge will re-emit radiation at the frequency of oscillation. For linear polarisation, this emitted
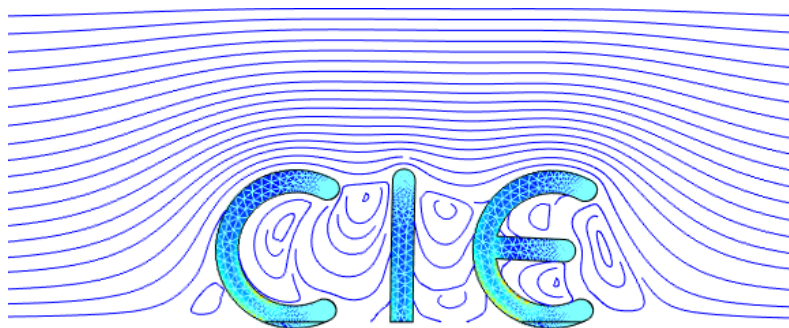
FIGURE 1.1: Optical polarisation as a function of field intensity in a non-centrosymmetric non-linear media. The polarisation response is linear only at low field intensities.

radiation will have the same frequency as the incident light. However this polarisation causes a change in the velocity of light, which is measured by the refractive index. So we see how the velocity of light in a material is dependent on the electron density within the material, in turn ultimately dictated by the molecular and solid state structure. The assumption that the induced polarisation of a molecule is a linear function of applied field is only an approximation. In fact, the induced polarisation generates an internal field that can interact and modify the applied field, and hence subsequent polarisation effects. In a majority of cases this interaction is minimal, and the linear approximation model discussed is sufficient. However, this is not true when more intense electromagnetic fields are present, such as those produced by a laser output, and nonlinear polarisation now occurs, Figure 1.1. Just as linear polarisation produces linear optical effects such as refraction, nonlinear polarisation leads to nonlinear effects. The nonlinear optical phenomena arises from the breakdown of equation (1.1) at sufficiently high field strengths. Equation (1.1) can be expressed as a power series in electric field to explain the non-linearity of the molecules' response, *i.e.*,

$$\mu = \mu_0 + \alpha \mathbf{E} + \beta \mathbf{E}^2 + \gamma \mathbf{E}^3 + \dots \tag{1.4}$$

where μ_0 = the intrinsic dipole of the molecule, β = the first molecular hyperpolarisibility, γ = the second molecular hyperpolarisibility etc. Similarly equation (1.2) can be modified to account for such nonlinear effects in the bulk material:

$$\mathbf{P} = \mathbf{P}_0 + \chi^{(1)} \mathbf{E} + \chi^{(2)} \mathbf{E}^2 + \chi^{(3)} \mathbf{E}^3 + \dots \tag{1.5}$$

where $\mathbf{P}_0$ = the bulk initial polarisation, $\chi^{(2)}$ = the second order susceptibility, $\chi^{(3)}$ = the third order susceptibility etc.

1.2.2 The Macroscopic $\chi^{(2)}$ Coefficient

The coefficient $\chi^{(2)}$ can only be non-zero for macroscopic structures lacking a centre of symmetry. Due to the present inability to predict how even simple organic molecules will pack in a crystal, the theoretical prediction of $\chi^{(2)}$ is not currently possible, but its magnitude may be measured experimentally. The most accurate determination is achieved by single crystal SHG studies[4] (*e.g.* for 2-methyl-4-nitroaniline), but $\chi^{(2)}$ may also be estimated by the Kurtz powder test. Methods of attempting to organise molecules in a non-centrosymmetric solid phase have been mentioned. As well as the crystal packing factors, a number of other important aspects will determine whether

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[4]Footnote 4

efficient bulk NLO properties (especially SHG) are displayed. Two major contributions are phase matching and absorption.

Phase Matching

Efficient SHG can only occur in a bifringent medium, that is one in which refractive index is directionally dependent. In practice this requires large biaxial (triclinic, monoclinc or orthorhombic) crystals so orientated that the fundamental frequency propagates as an o-ray (ordinary ray - refractive index independent of crystallographic direction) and the harmonic propagates as an e-ray (extraordinary ray - refractive index varies with crystallographic direction) or vice versa. The crystal orientation is adjusted so that both the e-ray and o-ray propagate at the same speed, *i.e.* their refractive indices are equal:

$$n_0^\omega = n_e^{2\omega} \tag{1.6}$$

Thus power is coupled from the fundamental to the harmonic as both rays propagate through the crystal. This condition is known as phase-matching (PM). If a large crystal displays PM then SHG will be detected at set angles between the fundamental beam, crystal and detector. The Kurtz test can detect the occurrence of PM by measuring the total second harmonic output as a function of crystallite size. As crystallite size is increased a saturation of output is observed for phase-matchable samples, while non-phase-matcheable samples exhibit a sharp decrease in output after a certain crystallite size is exceeded.

Absorption Effects

For the observation of NLO effects, the laser wavelengths used generally fall in the transparent region of the molecular absorption spectrum. This results in minimal light energy being removed from the incoming beam by electronic or vibrational excitation processes. The β coefficient is wavelength dependent, and it is found that its magnitude can be increased by using fundamental or harmonic wavelengths close to an absorption energy. This is called 'resonance enhancement' of the nonlinear response. However, due to the occurrence of photon absorption and possible thermal damage, this technique is rarely employed. This trade off between enhancement of β, and hence SHG efficiency against optical loss and sample degradation is another crucial factor in the exploitation of NLO materials.

1.3   Second Order NLO Effects In Molecular Materials

We have seen that the optimum second order NLO effects in molecules are enhanced by:

- Polarisable dipolar molecules

- Excited states close in energy to ground state

- Large oscillator strength for transition from ground to excited state

- Large difference between ground and excited state dipole moments

and for materials by:

- Non-zero $\chi^{(2)}$

- Non-centrosymmetric space group.

Current devices that exploit SHG effects are normally based on inorganic materials, typically binary and ternary metal oxides, such as quartz or certain perovskites, Table 1.1.

TABLE 1.1: SHG efficiencies of some inorganic materials relative to quartz and urea.

	SHG efficiency relative to quartz, Ξ_q	SHG efficiency relative to urea, Ξ_u
Quartz (α-SiO$_2$)	1	2.5×10^{-3}
NH$_4$H$_2$PO$_4$ (ADP)	15	37.5×10^{-3}
KH$_2$PO$_4$ (KDP)	16	0.04
LiNbO$_3$	600	1.5
Ag$_2$HgI$_4$	1500	3.75
PbTiO$_3$	2400	6
Urea [CO(NH$_2$)$_2$]	400	1

1.3.1 The Kurtz Powder Test

The Kurtz powder test[5] was devised in 1968 and is a convenient method to rapidly screen large numbers of powdered materials for second order NLO activity. By studying the variations of grain size and wavelength, it is possible to detect the occurrence of phase-matching (see later) and SHG efficiencies and derive estimates of $\chi^{(2)}$ values. The output of a laser, commonly a Nd:YAG at 1.06 μm (which is often Raman shifted to give a 1.91 μm fundamental) is split. One beam passes through the sample, while the other passes through a similarly mounted reference of known SHG efficiency. Filters behind the samples are used to remove the fundamental and leave only the second harmonic signals. The second harmonics are detected with photomultipliers, and the ratio of sample to reference signal is then produced and measured. This technique is crude in that it detects the sum of all the tensor components of $\chi^{(2)}$. The powder SHG observed for any given sample will vary with a number of parameters, including laser wavelength, bandwidth, particle size, temperature, crystallisation solvent and sample preparation, amongst others. Thus the results obtained by a Kurtz powder test are at best semi-quantitative, for instance a powder SHG difference of a factor of two should not generally be regarded as significant. The real power in this method lies in its ability to screen a large number of samples in order to pick out any which display significant NLO activity. These promising candidates can then be subjected to more precise studies. Lorem ipsum dolor sit amet, consectetur adipiscing elit. Donec sit amet enim lectus. Etiam quis facilisis libero. Sed interdum cursus aliquet. Sed volutpat interdum velit, facilisis tincidunt neque tempor eget. Donec id ultrices lorem. Nunc enim enim, auctor et vestibulum nec, malesuada sollicitudin libero. Phasellus malesuada leo a tortor scelerisque luctus. Sed sagittis blandit porttitor [1], [2] and [3]. Ut lobortis lacinia ante, vel mollis ante commodo sed. Integer quis orci nisl. Curabitur ornare diam ac eros sodales auctor. Integer vel neque nec elit ultrices cursus eget non est. Praesent a odio ac elit euismod scelerisque. Fusce eleifend turpis vel tortor elementum dignissim. In dictum rhoncus dolor at pellentesque. Nunc quis venenatis nunc. Cras tristique, velit quis placerat vehicula, nulla dui vestibulum ipsum, et convallis sapien lectus sit amet orci. Suspendisse adipiscing sapien ut nulla accumsan porta. Aenean porttitor mauris neque, eu tempus lectus. In hac habitasse platea dictumst. Pellentesque congue, nunc sit amet vehicula cursus, quam nunc scelerisque lectus, quis ultrices lorem ipsum eget neque. Nullam quis lorem diam.

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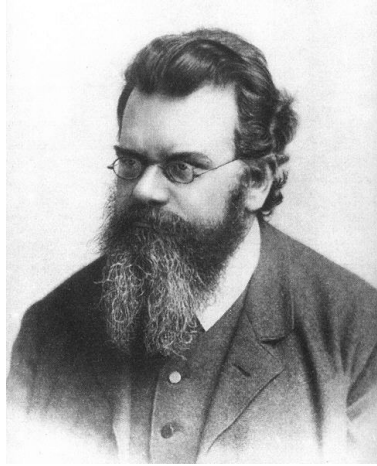
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[5]Footnote 5

FIGURE 1.2:   Ludwig Eduard Boltzmann (1844-1906)

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